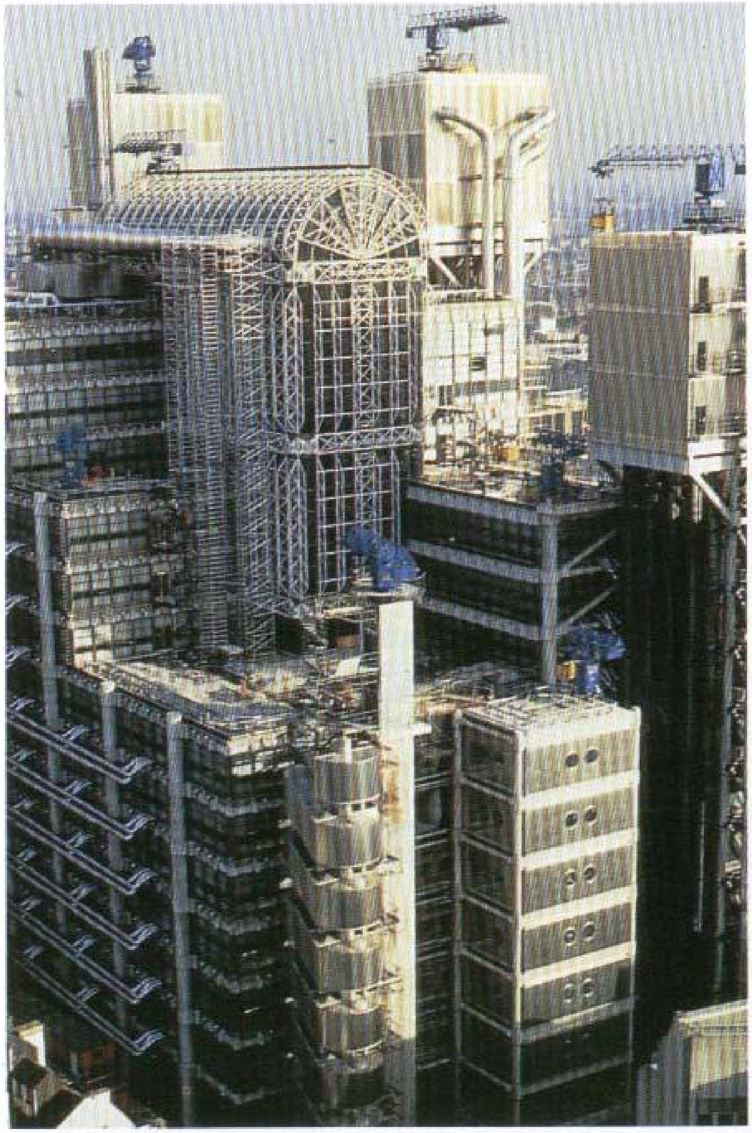
THE SHELL BITUMEN INDUSTRIAL HANDBOOK

Shell
Bitumen

Published by Shell Bitumen
Riversdell House
Guildford Street
Chertsey, Surrey
KT16 9AU

Designed and produced by
Design and Print Partnership Ltd
Guildford, Surrey

ISBN-0-95 16625-1-1



Lloyds Bank Building, London, with built up roofing (reproduced by kind permission of D. Anderson & Son Ltd).

Acknowledgements

We are indebted to colleagues both within Shell and from the bitumen industry for their valuable comments and advice. The content of the Industrial Handbook draws heavily on research and development work from all the major Shell laboratories but particularly those at Amsterdam, Hamburg, Chester and Grand Couronne. In producing this book published work on industrial uses of bitumen in the open literature has been quoted extensively. We have endeavoured to acknowledge all our sources in the references but if there are any sources not listed we hope the individual concerned will accept our apologies.

By way of special acknowledgement we would like to thank Terry Hoban (formerly Technical Manager Shell Bitumen) and Ian Menzies (Imprimatur Ltd) for their encouragement, help and advice during the planning and preparation of the book, We would also thank the following for their helpful comments:

Ray Allsop	Cambridge Asphalt Ltd
Ian Dussek	Wells (Trinidad Lake Asphalt) Ltd
Bryan Hayton	Longroyd Associates Ltd
Gerard Heimerikx	Shell Research Amsterdam
Len Prince	Callenders Ltd
John De Rosa	UK Water Research Centre
Mike Southern	Shell Bitumen
Willem Vonk	Shell Research Amsterdam
David Whiteoak	Shell Bitumen
Leslie Woolf	Corrosion consultant
Peter Yin	Shell Singapore

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R G Morgan

Foreword

Bitumen as a naturally occurring material has been used for building and civil engineering since the dawn of time and, from the advent of the petroleum refining industry at the turn of the 20th Century, has proved to be an inexpensive, durable and reliable material for a diverse range of applications. The utilisation of bitumen in industrialised society has increased manyfold during this century, the improvements in road transport infrastructure and the building and waterproofing of commercial property going hand in hand with increased bitumen usage. Despite the very large market for bitumen worldwide, about 75 million tonnes in 1994, there are few modern treaties on bitumen and its various end uses because bitumen is not covered to any great extent in chemistry, physics or engineering courses at schools or universities and the knowledge of the product tends to be held by a relatively few specialists. In consequence, for many applications the utilisation of bitumen is more of a black art than a science.

Since the early days of crude oil refining, Shell has conducted extensive research on bitumen. Indeed, the first Shell research and development laboratory was located on its present site in Amsterdam in 1914 and bitumen was one of the first refinery products to be investigated. As with all materials, bitumen is subject to the laws of nature and Shell scientists very quickly established relationships describing the behaviour of bitumen. In 1950 Shell published "The Properties of Asphaltic Bitumen" by J.Ph. Pfeiffer which laid the foundations for much of our understanding of the properties and behaviour of bitumen. Since then, there have been many contributions to the store of knowledge in this area by Shell companies around the world, the most recent being the "Shell Bitumen Handbook" which was published in 1990 and covers the use of bitumen in road construction.

The Shell Bitumen Industrial Handbook attempts to pull together in one volume a summary of the uses of bitumen in non-roads applications, otherwise known as "Industrial Uses". Industrial uses of bitumen account for only some twenty per cent of bitumen consumption. The Asphalt Institute in the USA lists over 200 end uses making this sector the most diverse and interesting market to service. Given the great diversity to be found in this area of technology, it would be impossible to cover all the myriad of applications in great detail. The authors have attempted to steer a course through the maze of interesting, sometimes esoteric, applications to produce a volume which is at once readable but which also captures the essential technology.

Developments in the bitumen industry are moving at an increasingly fast pace. Today's innovation is tomorrow's standard and, with the improvements in information technology and communications, the results of trials and new applications are flashed around the world in an instant. For the bitumen technologist an understanding of the basic fundamentals of the material is essential if he is to take full advantage of the many and varied innovations such as polymer modification and emulsification. The Shell Bitumen Industrial Handbook provides the technologist with this background.

Dr Lawrie J. Austin
Head of Marketing, Branding & Product Development
Shell International Petroleum Company

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Photograph 1.1 — An Egyptian mummy of the Ptolemaic period (about first century BC), showing black bitumen deposits (photograph reproduced by kind permission of Manchester Museum — University of Manchester, UK)

Chapter 1 - Introduction

Before discussing any of the myriad 'industrial' uses of bitumen it is necessary to define what we mean by the term industrial bitumen. Approximately 85 per cent of all bitumen is used in airfield and road construction or maintenance. Such uses call almost exclusively for penetration grade bitumens within the range 35-300 pen. The remaining 15 per cent is made up mainly of oxidised bitumen but includes penetration grades and hard grades for applications such as roofing, paints, carpet tiles etc. and is now termed, for convenience, industrial bitumen. The term 'industrial uses' was coined by the American Society for Testing and Materials when it established the ASTM committee D8 on Bituminous Materials for Roofing, Waterproofing and Related Building or Industrial Uses which has been in existence since 1905. Although smaller in market size, the industrial sector is far more diverse than the roads sector. This book shows some of the applications in which bitumens are used in the industrial sector.

Reference is made in the text to the relevant British Standards and, where appropriate, to other standards governing the properties of bitumen and its end products. At the time of writing the European Standards Committee (CEN) is in the process of standardising specifications across Europe. Once this process is complete it is recognised that the 'Euro'-specifications will replace national specifications for the same products. However, with an industry as conservative as the construction industry, it is likely that reference will be made to the relevant national standards for some time to come.

Bitumen is the oldest known engineering material and has been used from the earliest times as an adhesive, sealant and waterproofing agent(1). It is known that as long ago as 6000 BC there was a thriving shipbuilding industry in Sumeria that produced and used natural bitumen. The nomenclature for bituminous materials has been handed down from antiquity and the derivation of the modern terms asphalt and bitumen is difficult to determine with certainty. Ancient writings often consist of vague descriptions of materials as, for example, asphalt, pitch or bituminous earth, and lacked the essential technical detail such as the form or composition of the materials which would aid in identifying the types of materials used. This is essentially because of a lack of practical knowledge by the classical writers(2).

It is widely believed that the term 'bitumen' originated in Sanskrit, where the words 'jatu' meaning pitch and 'jatu-krit' meaning pitch-creating, referred to the pitch produced by some resinous trees. The Latin equivalent is claimed by some to be originally 'gwitu-men' (pertaining to pitch) and by others, 'pixtu-men' (bubbling pitch), which was subsequently shortened to 'bitumen' then passed via French into English.

There are several references to bitumen made in the bible, although the terminology used can be rather confusing. In Genesis reference is made to Noah's waterproofing of the ark, which was "pitched within and without with pitch", and to Moses' juvenile adventure in "an ark of bulrushes, daubed with slime and with pitch". Even more confusing are the descriptions of the building of the Tower of Babel. The Authorised Version of the bible says "they had brick for stone, and slime had they for mortar", the New International Version states that "they used bricks instead of stone and tar instead of mortar", Moffat's 1935 translation says "they had bricks for stone and asphalt for mortar", but the New English Bible states that "they used bricks for stone and bitumen for mortar". Even now it is not unknown for the terms bitumen, tar, asphalt and pitch to be used interchangeably.

Photograph 1.2 — Bas relief: "The spinner" (Susa, Persia, about 700 BC, reproduced by kind permission of Musée du Louvre and Réunion des Musées Nationaux, France)

1.1 The earliest uses of bituminous binders

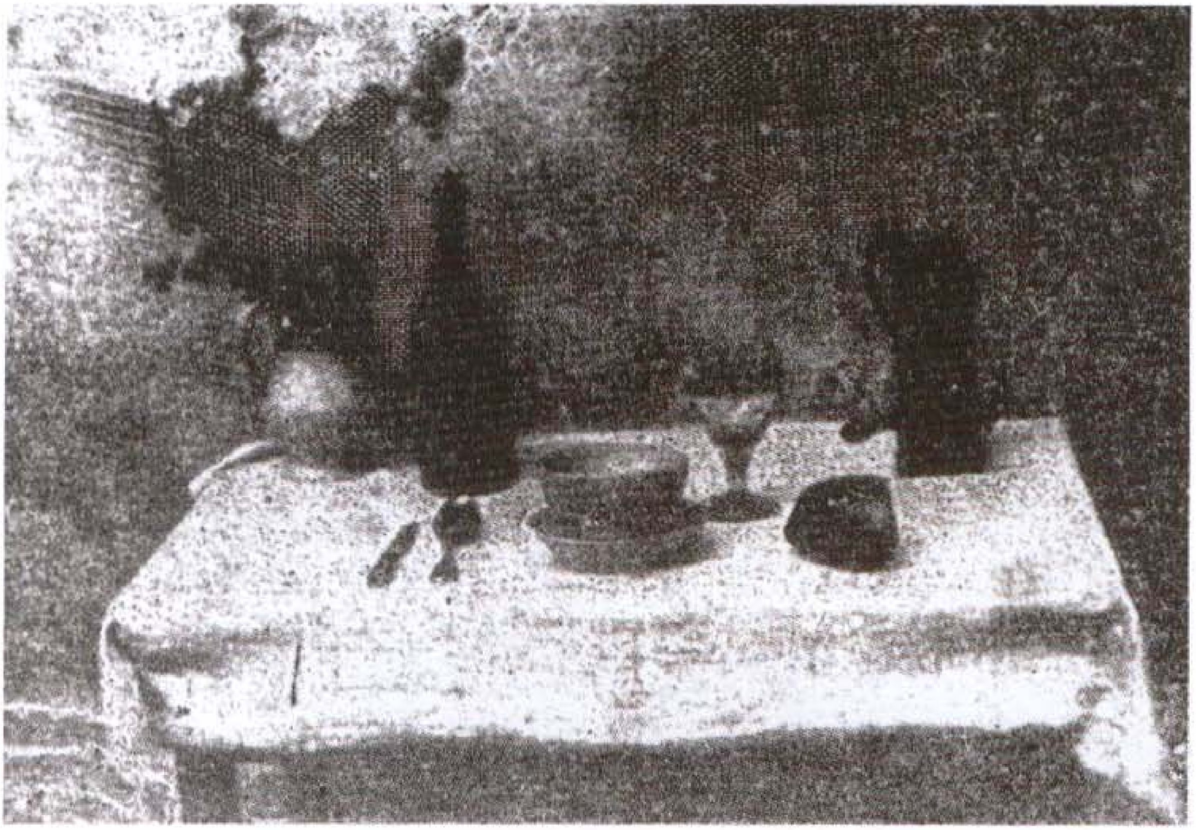
In the vicinity of subterranean crude oil deposits surface seepages occur at geological faults. The amount and nature of this naturally occurring material depends on a number of natural processes which modify the properties of the material. This product may be considered to be a 'natural' bitumen, usually being accompanied by mineral matter, the amount and nature of which will depend upon the circumstances which caused such an admixture to occur. These deposits may be found as soft, easily workable mortars such as those found in the Trinidad Lakes on the island of Trinidad, the Bermudez Lake in Venezuela, and the so-called Tar Sands of Canada. Alternatively, they may be hard, friable materials found in rock formations such as Gilsonite from the USA and Manjak from Barbados.

There are, of course, extensive crude oil deposits in the Middle East and for thousands of years there have been corresponding surface seepages of 'natural' bitumen. The ancient inhabitants of these parts were not slow to appreciate the excellent waterproofing, adhesive and preservative properties of the material placed so readily available at their disposal. At Mohenjo Daro in the Indus valley there is a particularly well preserved water tank which dates back to around 3,000 BC. In the walls of this tank, not only are the stone blocks bonded

Photograph 1.3 — The raft of the Medusa by Théodore Géricault, 1816 (Photograph reproduced by kind permission of the Musée du Louvre and Réunion des Musées Nationaux, France)

with a 'natural' bitumen, but there is also a vertical bituminous core in the centre of the wall. This same principle is used today in modern dam design. It is believed that Nebuchadnezzar was an able exponent of the use of bitumen because there is evidence that he used the product for waterproofing the masonry of his palace and as a grout for stone roads.

The process of mummification used by the ancient Egyptians also testifies to the preservative qualities of bitumen. Recent analysis of the preservative used in mummification has shown conclusively that bitumen was used in the mummification process(3) as long ago as 1200 BC during the Ptolemaic period, see photograph 1.1. Not only was bitumen identified as the preservative, but the principal sources of the bitumen were also determined by the identification of the geo-chemical "fossils" called steranes and terpanes(4). The bitumen is believed to have derived from the Dead Sea, where it occurred in floating blocks, and from Hit-Abu Jin in Iraq, from where the bitumen was exported to Babylon for use as a mortar in brick walls. This latest work has discredited the previous belief that mummies were preserved in resin which subsequently turned black with age. This discovery is supported by the fact that the word mummy is derived from the Persian 'mumia' meaning bitumen or pitch(5). The Mummy Mountain in Persia was famed for its production of a black, bituminous ooze which was said to have medicinal properties.



Photograph 1.4 — The first positive photographic image produced by Niepce in 1822 (Photograph reproduced by kind permission of Collection de la Société Française de Photographie, France)

Since its discovery in antiquity and subsequent development, bitumen has been used for a great variety of end uses many, surprisingly, in the field of art. There are numerous examples of ancient artefacts utilising a bituminous glue to attach gold-leaf decoration to statues or to act as an adhesive to bond wood, stone or metal, see photograph 1.2. Perhaps of interest to the casual reader would be two somewhat esoteric uses for bitumen in the more recent past. In 1816, Théodore Géricault (1791-1822), one of France's foremost artists, utilised natural bitumen in his pigments when he painted his controversial masterpiece 'The Raft of the Medusa', see photograph 1.3. This great painting, about eight metres long by six metres high, hangs in the Louvre in Paris and represents the surviving crew of the French frigate 'Medusa'. It has now darkened with age and is considered too fragile to move. At around the same time as Géricault was creating 'The Raft' another Frenchman, Joseph Nicephore Niepce (1765-1833) was experimenting with natural bitumen from the Dead Sea as a component in a photographic process. A dark room, a plaque of polished silver and some bitumen were all that was required to make the first positive photographic image produced by Niepce in 1822, see photograph 1.4.

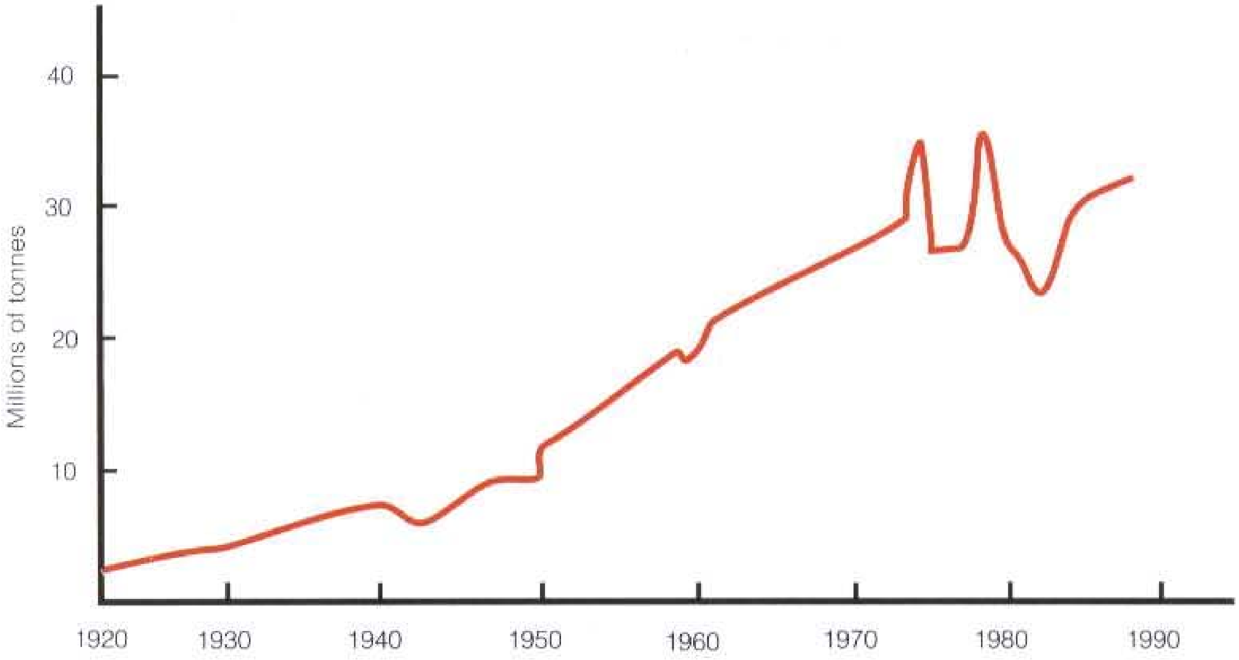


Figure 1.1 — Annual sales of asphalt products to domestic consumers in USA

1.2 The growth of bitumen consumption

The ancient uses of 'natural' bitumens no doubt persisted in those inhabited parts of the world where these deposits were readily available. However, there seems to have been little development of the art elsewhere and in the UK it was not until the nineteenth century that any of the present major uses of bitumen were introduced. However, there would appear to have been some knowledge of alternative binders in the interim period as it is on record that Sir Walter Raleigh, in 1595, proclaimed the lake asphalt he found in Trinidad to be "most excellent good" for ships' caulking. He further remarked that it was better than Norway pitch as it did not become soft in the sun. It is clear that throughout the Middle Ages naturally occurring bitumens from the many deposits throughout Europe were in common use for ships' caulking. In the middle of the nineteenth century attempts were made to utilise rock asphalt from European deposits for road surfacing and from this there was a slow development of the use of natural products for this purpose. By 1860 there was a thriving industry using coal tar and fluxed Trinidad Lake Asphalt (TLA) to make roofing and waterproofing membranes.

In the early 1900s in the USA the first refining of crude petroleum took place, resulting in the production of refined bitumen. The advent of cheap, inexhaustible supplies of bitumen, coupled with the invention of the motor car, created an expanding industry. By 1902, bitumen production in the USA was about 18,000 tonnes and has continued to increase to the present day consumption of more than 30 million tonnes, see figure 1.1.

Bitumen was imported into the UK on a small scale early in this century, but it was not until 1920, when Shell Haven refinery opened, that major bitumen production began outside North America. Development was then rapid and, with the facilities for bulk distribution, the basis was laid for the adoption of bitumen in a wide range of applications, see table 1.1.

Table 1.1 — The varied uses of bitumen (based on The Asphalt Institute's Asphalt handbook, MS4)

AGRICULTURE
(Also see Buildings, Hydraulics and Paving)
Cattle sprays
Dampproofing and waterproofing buildings, structures
Disinfectants
Fence post coating
Mulches
Mulching paper
Paved barn floors, barnyards, feed platforms, etc.
Protecting tanks, vats, etc.
Protection for concrete structures
Tree paints
Water and moisture barriers (above and below ground)
Wind and water erosion control
Weather modification areas

BUILDINGS
(Also see Industrial, Paving)

Floors
Dampproofing and waterproofing
Floor compositions, tiles, coverings
Insulating fabrics, papers
Step treads

Roofing
Building papers
Built-up roof adhesives, felts, primers
Caulking compounds
Cement waterproofing compounds
Cleats for roofing
Glass wool compositions
Insulating fabrics, felts, papers
Joint filler compounds
Laminated roofing, shingles
Liquid roof coatings
Plastic cements
Shingles

Walls, Siding, Ceilings
Acoustical blocks, compositions, felts
Architectural decoration
Bricks
Brick siding
Building blocks, papers
Dampproofing coatings, compositions
Insulating board, fabrics, felts, paper
Joint filler compounds
Masonry coatings
Plaster boards
Putty
Siding compositions
Soundproofing
Stucco base
Wallboard

Miscellaneous
Air drying paints, varnishes
Artificial timber
Ebonised timber
Insulating paints
Plumbing, pipes
Treated awnings

HYDRAULICS AND EROSION CONTROL
Canal linings, sealants
Catchment areas, basins
Dam groutings
Dam linings, protection
Dike protection
Ditch linings
Drainage gutters, structures
Embankment protection
Groynes
Jetties
Levee protection
Mattresses for levee and bank protection
Membrane linings, waterproofing
Ore leaching pads
Reservoir linings
Revetments
Sand dune stabilisation
Sewage lagoons, oxidation ponds
Swimming pools
Waste ponds
Water barriers

INDUSTRIAL
Aluminum foil compositions
Backed felts
Conduit insulation, lamination
Insulating boards
Paint compositions
Papers
Pipe wrapping
Roofing, shingles

Automotive
Acoustical compositions, felts
Brake linings
Clutch facings
Floor sound deadeners
Friction elements
Insulating felts
Panel boards
Shim strips
Tacking strips
Underseal

Electrical
Armature carbons, windings
Battery boxes, carbons
Electrical insulating compounds, papers, tapes, wire coatings
Junction box compound
Moulded conduits
Electrodes

INDUSTRIAL (cont)

Compositions

Black grease
Buffing compounds
Cable splicing compound
Embalming
Etching compositions
Extenders, rubber, etc
Explosives
Fire extinguisher compounds
Joint fillers
Lap cement
Lubricating grease
Pipe coatings, dips, joint seals
Plastic cements
Plasticisers
Preservatives
Printing inks
Well drilling fluid
Coffin liners

Impregnated, treated materials

Armoured bituminised fabrics
Burlap impregnation
Canvas treating
Carpet tiles
Deck cloth impregnation
Fabrics, felts
Mildew prevention
Packing papers
Pipes and pipe wrapping
Planks
Rugs, asphalt base
Saw dust, cork, asphalt composition
Textiles, waterproofing
Tiles
Treated leather
Wrapping papers

Paints, varnishes, et.

Acid-proof enamels, mastics, varnishes
Acid-resistant coatings
Air-drying paints, varnishes
Anti-corrosive and anti-fouling paints
Anti-oxidants and solvents
Base for solvent compostions
Baking and heat resistant enamels
Boat deck sealing compound
Lacquers, japans
Marine enamels
Wood stain

Miscellaneous

Belting
Blasting fuses
Briquette binders
Burial vaults
Casting moulds
Clay articles
Clay pigeons
Depilatory
Expansion joints
Flower pots
Foundry cores
Friction tape
Fuel
Gaskets
Gramophone records
Imitation leather
Mirror backing
Rubber, moulded compositions
Shoe fillers, soles
Table tops
Vacuum sealant

PAVING

Also see Hydraulics, Agriculture, Railroad, Recreaction)

Airport runways, taxiways, aprons, etc.
Asphalt blocks
Brick fillers
Bridge deck surfacing
Crack fillers
Curbs, gutters, drainage ditches
Floors for buildings, warehouses, garages, etc
Highways, roads, streets, shoulders
Parking areas, driveways
Portland cement concrete underseal
Roof-deck parking
Sidewalk, footpaths
Soil stabilisation

RAILWAYS

Ballast-treatment
Curve lubricant
Dust laying
Paved ballast, sub-ballast
Paved crossings, freight yards,
Station platforms
Rail fillers
Railway sleepers
Sleeper impregnating, stabilization

RECREATION

Paved surfaces for:

Dance halls
Drive-in movies
Gymnasiums, sports arenas
Playgrounds, school yards
Race tracks
Running tracks
Skating rinks
Swimming and wading pools
Tennis courts, handball courts

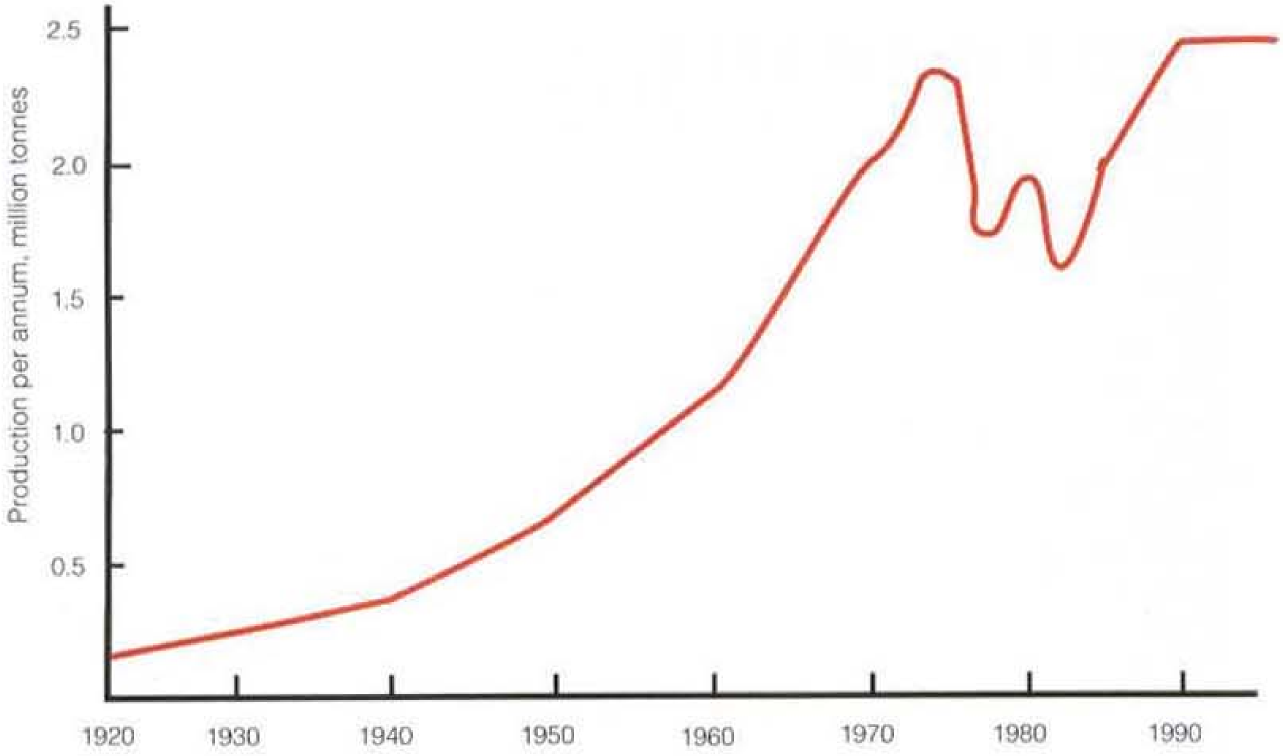


Figure 1.2 — UK bitumen production 1920-1990

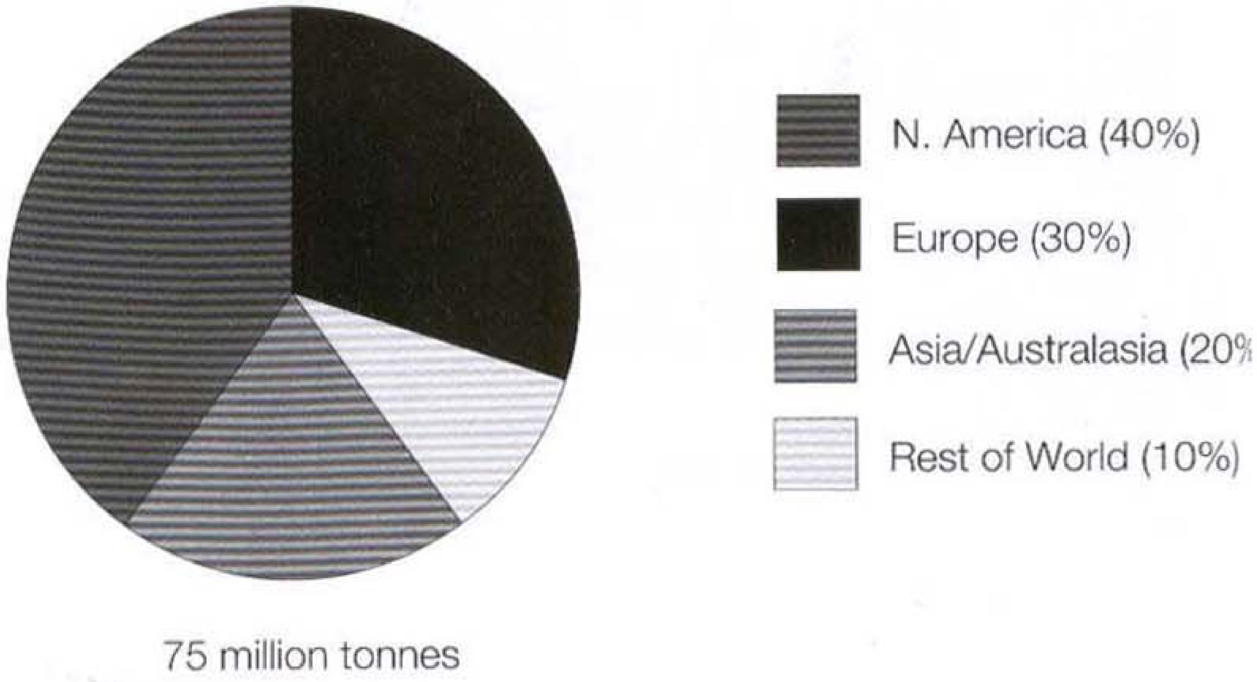


Figure 1.3 — World bitumen demand, 1994

In the early 1920s bitumen consumption in the UK was about 200,000 tonnes per annum. The demand increased rapidly, reaching 1 million tonnes per annum by 1960 and with the start of the motorway building programme in the early 1960s the demand for bitumen soared to 2 million tonnes per annum by 1970, reaching a peak of 2.4 million tonnes in 1973, see figure 1.2.

The first blowing of bitumen on a commercial scale was done by Byerly in the USA who obtained a patent on his process in 1894. His product was sold under the name Byerlyte and the Byerlyte Corporation is still a major producer of bitumen products in the Ohio area today.

It is not known when the first oxidised bitumens were made in the UK although it is believed to have been during the 1930s. By the 1940s oxidised production was well established.

World consumption of bitumen has risen to some 75 million tonnes in 1994, the greater part of which is used in the USA, see figure 1.3. The developed world (USA/Europe) consumes the greater part of this total although Asia/Australasia is expanding its use of bitumen very rapidly as major infrastructure development accompanies industrial growth.

1.3 Types of binders

As stated earlier, much confusion still exists in differentiating between binding agents produced from coal (coal tars, pitches, etc) and those produced from crude oil. A detailed review of the differences between bitumens and coal tar products is given by Puzinauskas and Corbett.(6)

Another semantic confusion arises from the difference in meaning of the world 'asphalt' in Europe and North America. In Europe asphalt always means a mixture of bitumen and mineral aggregate, eg rolled asphalt, mastic asphalt, Gussasphalt, etc. However, in North America, 'asphalt' means bitumen, 'asphalt concrete' means asphalt road surface and 'asphalt cement' refers to bitumen binder. The following brief description of the origin and manufacture of various binders should clarify the situation.

1.3.1 Bitumen

Bitumen is manufactured from crude oil. It is generally agreed that crude oil originates from the remains of marine organisms and vegetable matter deposited with mud and fragments of rock on the ocean bed. Over millions of years, organic material and mud accumulated into layers hundreds of metres thick, the immense weight of the upper layers compressing the lower layers into sedimentary rock. Conversion of the organisms and vegetable matter into the hydrocarbons of crude oil is thought to be the result of the application of heat from within the earth's crust, pressure applied by the upper layers of sediments, possibly aided by the effects of bacterial action and radio-active bombardment. As further layers of sediment were deposited on the sedimentary rock where the oil had formed, the additional pressure squeezed the oil sideways and upwards through porous rock. Where porous rock extended to the earth's surface, oil seeped through, resulting in the surface seepages described earlier. Fortunately, the majority of oil and gas was trapped in porous rock which was overlain by impermeable rock forming gas and oil reservoirs. Here the oil remained until it was recovered by drilling through the impermeable rock.

The four main oil producing areas in the world are the United States, the Middle East, the Caribbean and the countries of the former Soviet Union. Although the North Sea is important in European terms, it is a relatively small oil-producing area on a global scale. North Sea crudes are generally light with very low bitumen yields. Whilst they can be used to make good quality bitumen, they generally require special processing to achieve suitable properties.

Crude oils differ in both physical and chemical properties. Physically they vary from viscous black liquids to free-flowing straw coloured liquids. Chemically they may be predominately paraffinic, naphthenic or aromatic, with combinations of the first two being common.

There are nearly 1500 different crude oils produced world-wide. Based on the yield and the quality of the product produced, only a few of these are considered suitable for the manufacture of bitumen. In the UK, bitumens are principally manufactured using either Middle Eastern or South American crudes.

British Standard 3690 : Part 2 : 1989(7) defines bitumen as "A viscous liquid, or a solid, consisting essentially of hydrocarbons and their derivatives, which is soluble in trichloroethylene and is substantially non-volatile and softens gradually when heated. It is black or brown in colour and possesses waterproofing and adhesive properties. It is obtained by refinery processes from petroleum, and is also found as a natural deposit or as a component of naturally occurring asphalt in which it is associated with mineral matter."

1.3.2 Lake asphalt

This is the most extensively used and best known form of 'natural' asphalt. It is found in well defined surface deposits, the most important of which is located in Trinidad. It is generally believed that this deposit was discovered in 1595 by Sir Walter Raleigh. However, it is now known that the Portuguese and possibly the Spaniards knew of the existence of the deposit before this date. The first definite reference in the literature refers to Sir Walter Raleigh's cousin Robert Dudley, who visited Trinidad and 'discovered' the asphalt deposit just three months before Raleigh's arrival. It is doubtful if either Raleigh or Dudley saw the 'Pitch Lake' on their first visits, they probably only found the overflow material on the sea-shore approximately one kilometre north of the lake itself, as the intervening country was dense and virtually impenetrable jungle.

There are a number of small deposits of asphalt on the island of Trinidad, but it is the 'Pitch Lake', which is located in the southern part of the island one kilometre from the sea, which constitutes one of the largest deposits in the world. The lake is approximately 100 acres (35 ha) in area and is estimated to be about 90 m deep, containing between 10 to 15 million tonnes of material. The surface of the lake is sufficiently hard to take the weight of crawler tractors and dumper trucks which transport excavated material from the surface of the lake to railway trucks which run along the edge of the lake.

Several theories have been suggested to explain the origin of the pitch lake; however, it is generally considered(8) to have originated as a surface seepage of a viscous bitumen in the late Miocene times. Lowering of the earth's surface led to an incursion of the sea and as a result deposited silt and clay over the bitumen. Part of the silt and clay penetrated the bitumen, forming a plastic mixture of silt, clay, water and bitumen. Subsequently the land was elevated above sea level, lateral pressure deforming the material into its present shape of

Photograph 1.5 — Aerial view of the Trinidad lake (Photograph reproduced by kind permission of Wells (Trinidad Lake Asphalt) Ltd)

a pseudo-laccolite (a bulging dome). Erosion removed the silt and clay covering, exposing the surface of the lake.

The enormous mass of the lake appears to be in constant, very slow, circulatory movement, from the centre outwards at the surface and it is assumed to return to the centre in the body of the lake. The level of the lake falls much less than expected from the quantity of material removed. Holes dug in the surface slowly fill up and usually disappear within 24 hours.

The as-dug material is refined by heating to 160°C, vapourising any entrapped water. The molten material is passed through fine screens to remove the coarse foreign and vegetable matter. This 'refined product' is termed Trinidad Epuré and typically has the composition shown in table 1.2.

Component	% by mass
Binder	54
Mineral matter	36
Organic matter	10

Table 1.2 —Typical composition of Trinidad Epuré

The Epuré is too hard to be used as produced (it has a penetration of about 2 and a softening point of about 95°C) and is generally used in a blend with bitumen.

In the 1950s and 1960s Trinidad Epuré/bitumen blends were used extensively in roads because the addition of the Trinidad Epuré improved the durability of the asphalt surface. However, changes in bitumen manufacturing techniques have improved the "weathering" characteristics of refined bitumen. This, coupled with the fact that Trinidad Epuré/bitumen blends required several hours' heated blending before use, led to the rapid decline of Trinidad Epuré usage in the mid 1970s.

1.3.3 Rock asphalt

Rock asphalt is formed by the impregnation of calcareous rocks such as limestone or sandstone with seepages of natural bitumen. This product can be mined or quarried and contains up to 12 per cent by mass of bitumen. The principal sources of these deposits are the Gard district in France, Neuchâtel in the Val de Travers region Switzerland and at Ragusa in Italy.

There are numerous deposits of rock asphalt throughout Europe although their exact uses in the past are not known. It is clear from literature that towards the end of the 18th century there was great interest in rock asphalts and coal tar pitch for caulking ships and barges and for waterproofing roofs.

Today there is only minor usage of such natural asphalts in road paving or industrial applications. In nearly all cases it is combined with a flux-oil or soft bitumen.

1.3.4 Tar

'Tar' is a generic word for the liquid obtained when natural organic materials such as coal or wood are carbonised or destructively distilled in the absence of air(1). It is customary to preface the word tar with the name of the material from which it is derived: the products of this initial carbonisation process are referred to as crude coal tar, crude wood tar, etc.

Bitumen, derived from crude oil, and tar, produced during the manufacture of coke or smokeless solid fuel, are often considered synonymously. The reasons for this are two-fold. Firstly, to the naked eye, both materials appear to be very similar: black thermoplastic materials, having relatively high viscosities at ambient temperatures. Secondly, the two materials are used for similar applications - road construction, roofing and as protective coatings. However, there the similarity ends, since they are dissimilar, not only in their origin, but also in chemical constitution. Physical and chemical differences result in differences in behaviour and gaseous/vapour emissions during application and subsequent performance in service.

Two types of crude coal tar are produced as a by-product of the carbonisation of coal:

- *Coke oven tar*

  This material is produced at high temperatures (about 1200°C) in coke ovens during the manufacture of metallurgical or domestic coke. These coal tars have a high aromatic hydrocarbon content and a pitch content of around 50 per cent by mass.

- *Low temperature tar*

  This material is produced at comparatively low temperatures (600°C to 700°C) during the manufacture of smokeless solid fuel. This type of coal tar is less viscous than the high temperature coke oven tar, is paraffinic in nature and has a pitch content of about 35 per cent by mass.

Liquid by-products are produced by coal carbonisation. By cooling the hot gases and vapours from the oven or retort, aqueous liquor and crude tar are condensed and, since they are substantially immiscible, are separated by decantation. By scrubbing the cooled gas with a suitable solvent, a light hydrocarbon mixture is extracted.

The crude tar is refined by fractional distillation which separates it into a number of distillate oil fractions and a residue. The residue is termed 'pitch'. 'Refined tar' is produced by blending the pitch with distillate oil fractions. British Standard 76(9) includes eight grades of road tar from 30°C EVT to 58°C EVT in 4°C increments. The EVT (equi-viscous temperature) is the temperature at which 50 ml of the tar has a flow time of fifty seconds through the standard 10 mm orifice in the standard tar viscometer (see photograph 5.7). Thus the higher the EVT, the more viscous the tar.

In the last twenty years dramatic changes have occurred in the supply of crude coal tar in the UK. In the mid 1960s over two million tonnes of crude coal tar were produced per annum, of which 50 per cent was manufactured using carbonisation ovens used to produce town gas. However, the introduction of North Sea gas in the late 1960s rapidly diminished the output from carbonisation ovens and by 1975 tar from this source had totally disappeared.

Now the greatest proportion of crude coal tar available for distillation is produced by high temperature carbonisation ovens in the iron and steel industries. Although the demand for these products is difficult to predict, it seems likely that the availability of crude coal tar from this source will remain stable at between 0.3 to 0.4 million tonnes per annum into the next decade. On the continent of Europe, although widely available, tar is banned in some countries because of its toxicity and the problems of disposal and it is believed that its use will rapidly decline within Europe in the future.

Refined tar is more temperature susceptible than bitumen; as a result at high service temperatures, say 60°C, it is softer than the equivalent grade of bitumen. At low service temperatures tar is stiffer than bitumen and is therefore more susceptible to brittle fracture.

1.4 References

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Chapter 2 - Health, safety and environmental aspects of bitumen

Throughout industry in recent years there has been increasing general awareness of the need to improve health and safety procedures in the workplace. This applies also in the construction industry where the majority of bitumen is used.

Based on practical experience over a number of years and specific field studies there is no indication that bitumen presents an occupational health risk to workers who handle it regularly, nor does it present an environmental health problem to those who come into contact with bitumen during its manufacture and application(1). Thus bitumen presents a low order of potential hazard provided that good handling practices are observed(2,3). These are described in detail in the Institute of Petroleum Model Code of Safe Practice, Part 11, Bitumen Safety Code(4) and in Shell Bitumen material safety data sheets (MSDS) which are frequently revised to contain the most up-to-date information.

The following highlights some of the potential hazards associated with the handling of bitumen. However, this is not intended to be used as a substitute for health and safety information given by individual suppliers or the Institute of Petroleum Model Code of Safe Practice.

2.1 Recommended precautions for personnel

2.1.1 Protective clothing

The main hazard from handling hot bitumen is the heat burn. Thus it is essential to wear clothing which provides adequate protection commensurate with the hazard:

heat-resistant gloves with close-fitting cuffs;

eye and face protection;

an all-cotton oversuit with close-fitting cuffs and overlapping at the boots and gloves;

heat-resistant, non-sparking boots with reinforced toes, close-fitting at the top;

head covering with neck flap over collar (see photograph 2.1).

Garments soiled with bitumen should be either replaced or dry cleaned to avoid penetration to the underclothing.

Soiled rags or tools should not be placed in the pockets of overalls as contamination of the lining of the pocket will result.

2.1.2 Personal hygiene

Personnel handling bitumen and bituminous materials should be provided with <u>and use</u> barrier creams to protect exposed skin, particularly hands and fingers. Skin should be thoroughly washed after any contamination and always before going to the toilet, eating or drinking.

Photograph 2.1 — Protective clothing worn during a bulk delivery of bitumen

The application of barrier creams, prior to handling bitumen, assists in subsequent cleaning should accidental contact occur. However, barrier creams are not substitutes for gloves or other impermeable clothing and therefore they should not be used as the sole form of protection. Solvents such as petrol, diesel oil, white spirit, etc, should not be used for removing bitumen from the skin and may spread the contamination. Use an approved skin cleanser and warm water.

Tools may be cleaned by warming gently until the bitumen is molten and wiping with rags or by soaking in kerosene.

2.2 Potential hazards during the handling of bitumen(4,5)

As bitumen is normally handled at temperatures well in excess of 100°C the major hazard is heat burn on skin in direct contact with the hot bitumen. However, low temperature skin contact of some grades of bitumen and inhalation of fumes from bitumen also create potential health hazards, particularly as substances which may be toxic can be present from materials associated with bitumen, eg hydrogen sulphide, or added to bitumen, eg cutback diluents, emulsifying agents, adhesion agents, coal tar products, etc.

Users of bitumen should refer to the latest Shell Bitumen material safety data sheets (MSDS) as these will contain the most up-to-date information.

Source	g/1000 m^3 of air
asphalt mixing plant	13
power station , gas	100
power station, coal	300
diesel engine	5000
refuse burning	11,000
coke oven volatiles	35,000
domestic boiler, coal	100,000

Table 2.1 — Benzo(a)pyrene emissions from various sources(6)

Water/foodstuff	Benzo(a)pyrene content, ppm
bitumen (see table 2.3)	0.1 - 27
groundwater	< 5
garden water	ca 90
woodland water	60 - 1300
sunflower oil	ca 10
lettuce	ca 13
cabbage	12 - 25
tea extract	ca 20
grilled steak	< 50
grilled sausage	< 85
grilled pork	< 140

Table 2.2 — Benzo(a)pyrene content of water and foodstuffs(6)

2.2.1 Toxicity of bitumen(1)

Bitumens are complex hydrocarbon materials containing components of many chemical forms, the majority of which are of high molecular weight including polycyclic aromatic hydrocarbons (PCAs). The toxicity of these components needs to be considered in view of their known carcinogenicity. In experimental studies polycyclic aromatics with 3 to 7 (usually 4 to 6) fused rings with molecular weights in the range 200 to 450 have been shown to be biologically active carcinogens. In particular benzo(a)pyrene and benz(a)anthracene are considered to be powerful carcinogens. However, the concentrations of these carcinogens(6) in bitumen are extremely low, as indicated by the data for benzo(a)pyrene in tables 2.1 and 2.2.

Bitumen and coal tar are often erroneously associated with each other because of their similar superficial appearance and former parallel applications. Consequently there is some confusion regarding the toxicity of these two products. Numerous animal studies have been carried out to evaluate the cancerous effects of prolonged contact with bitumen and coal tar. A study carried out by Wallcave(7) showed that contact with coal tar pitch induced a high incidence (over 90 per cent) of epidermal carcinomas and papillomas on the skin of mice, whereas less than 0.5 per cent of the mice in contact with bitumen developed epidermal carcinomas and only 2 per cent developed papillomas. These results reflect the level of carcinogens in the two materials. The benzo(a)pyrene content of coal tar pitch is between 8,400 ppm and 12,500 ppm, whereas that of bitumen is between 0.1 ppm and 27 ppm, see table 2.3.

		Bitumens from various sources								Two examples of coal tar pitch	
PCAs*, ppm	Formula	A	B	C	D	E	F	G	H	A	B
Anthracene	$C_{14}H_{10}$	-	-	-	-	-	-	-	-	8 600	10 000
Phenanthrene	$C_{14}H_{10}$	2.3	0.4	3.5	1.3	0.6	35	1.1	2.3	31 000	29 000
Pyrene	$C_{16}H_{10}$	0.6	1.8	4.0	8.3	0.9	38	0.3	0.08	20 000	29 000
Fluoranthene	$C_{16}H_{10}$	+	+	2.0	+	+	5	-	-	40 000	43 000
Benzofluorenes	$C_{17}H_{12}$	+	+	+	+	+	+	+	-	7 300	5 100
Benz (a) anthracene	$C_{18}H_{12}$	0.15	2.1	1.1	0.7	0.9	35	0.2	-	8 900	12 500
Triphenylene	$C_{18}H_{12}$	0.25	6.1	3.1	3.4	3.8	7.6	1.0	0.3	1 500	1 100
Chrysene	$C_{18}H_{12}$	0.2	8.9	2.3	3.9	3.2	34	0.7	0.04	7 400	10 000
Benzo (a) pyrene	$C_{20}H_{12}$	0.5	1.7	1.3	2.5	1.6	27	0.1	-	8 400	12 500
Benzo (e) pyrene	$C_{20}H_{12}$	3.8	13	2.9	3.2	6.5	52	1.6	0.03	5 400	7 000
Benzo (k) fluoranthene	$C_{20}H_{12}$	+	-	+	+	+	-	-	-	7 100	9 000
Perylene	$C_{20}H_{12}$	-	39	2.2	6.1	2.9	3.0	0.1	-	2 000	3 300
Anthanthrene	—	-	Tr	Tr	Tr	+	1.8	-	-	1 300	2 100
Benzo (ghi) perylene	$C_{22}H_{12}$	2.1	4.6	1.0	1.7	2.7	15	0.6	Tr	3 200	3 300
Indeno (1,2,3-cd) pyrene	$C_{22}H_{12}$	Tr	-	Tr	Tr	Tr	1.0	-	-	7 300	9 300
Picene	$C_{22}H_{14}$	+	+	+	+	+	1.0	+	-	NE	2 000
Coronene	$C_{24}H_{12}$	1.9	0.8	0.5	0.2	0.9	2.8	0.9	-	700	700

* PNA is equivalent to PCA

Tr	Trace
NE	Not estimated but present in substantial amounts
+	Not estimated but present in small amounts
-	Not detected

Table 2.3 — Polycyclic aromatics (PCAs) in different bitumens and coal-tar pitches(6)

The presence of small amounts of these compounds in bitumen does not necessarily constitute a risk to health in practice but the information is necessary to enable appropriate precautions to be taken by personnel handling the product.

2.2.2 Skin contact

Other than heat burns, the hazards associated with skin contact of most bitumens are negligible. Studies by the International Agency for Research on Cancer (IARC)(8), part of the World Health Organisation, conclude that bitumens have been widely used for many years and there was no direct evidence to associate them with long-term skin disorders in man. However, they do contain polycyclic aromatic compounds some of which have been shown to have carcinogenic properties. Therefore it is prudent to avoid intimate and prolonged skin contact with bitumen.

Cutback bitumens and bitumen emulsions are handled at lower temperatures; therefore the likelihood of skin contact is increased (see chapter 6). If personal hygiene is poor, regular skin contact may occur, and if prolonged over many years there is a slight risk of skin cancer. However, good personal hygiene would eliminate this risk, see section 2.1.2. Bitumen emulsions cause irritation to the skin and eyes and allergic responses in some individuals. These effects are almost certainly caused not by the bitumen but by the emulsifier systems which, by their very nature, contain highly active chemical groups.

Although bitumen contains carcinogens, where skin contact occurs they are normally retained in the bitumen and do not migrate into the skin. However, materials are sometimes added to bitumen which decrease its viscosity and therefore increase bioavailability. Some of these materials will be more hazardous than bitumen and suitable extra precautions must be taken.

2.2.3 Inhalation/fume exposure(1)

Generally, when bitumens are heated in bulk or mixed with hot aggregate, fumes are emitted. The fumes contain particulate matter, hydrocarbon vapour and very small amounts of hydrogen sulphide.

The Asphalt Institute have measured fumes emitted from hot asphalt immediately after discharge from the pug mill(9,10). The concentration of bitumen fumes ranged from 0.2 to 5.4 mg/m^3 with an average of 1.6 mg/m^3. The level of known carcinogenic polycyclic aromatic hydrocarbons in all cases was very low. A similar study on fume emission during paving(11) showed that for paver operators particulate emission levels varied from 0.15 to 5.6 mg/m^3 and for other operators the levels varied from 0.25 to 3.5 mg/m^3 with mean levels of 0.9 mg/m^3.

Another study by the Asphalt Institute measured the fumes emitted from a roofing kettle(12). The concentration of bitumen fume may occasionally exceed 5 mg/m^3 depending on the bitumen used, the temperature of the kettle and the distance from the kettle. Workers' exposure to PCAs or to carcinogenic PCAs is extremely low and is estimated to be less than 0.003 mg/m^3 which is far lower than the 0.2 mg/m^3 limit proposed by the Occupational Safety and Health Administration of the USA.

The UK occupational exposure limits for bitumen fumes in the working atmosphere are(13):

- Long-term exposure limit (8 h time weighted average) = 5 mg/m^3
- Short-term exposure limit (10 min time weighted average) = 10 mg/m^3

Thus the measured concentrations of total particulate matter only occasionally exceeded the long-term UK exposure limit and never exceeded the short-term limit.

When working with hot bitumen in the open air, hydrogen sulphide does not present a hazard as the concentration is too low to be a significant risk to health. However, it is possible for hydrogen sulphide to accumulate to dangerous levels above hot bitumen in the vapour space of bulk storage tanks. The familiar odour of 'bad eggs' cannot be relied upon to warn operatives of the presence of hydrogen sulphide because the gas deadens the sense of smell at concentrations greater than 200 ppm. Where storage tanks are enclosed it is essential that adequate ventilation is maintained.

The UK occupational exposure limits for hydrogen sulphide in the working atmosphere are(13)

- Long-term exposure limit (8 h time weighted average) = 10 ppm (14 mg/m^3)
- Short-term exposure limit (10 min time weighted average) = 15 ppm (21 mg/m^3)

In all cases unnecessary exposure to bitumen fumes should be avoided and where there is <u>any</u> doubt, tests to determine the concentration of bitumen fume or hydrogen sulphide in the working atmosphere should be carried out, eg Draegar tube analysis.

2.3 First aid

2.3.1 Skin burns

Skin burns from accidental contact with hot bitumen should immediately be thoroughly drenched under cold running water and held there for at least ten minutes, or until completely cold. No attempt should be made to remove firmly adhering bitumen from the skin. Once the bitumen has cooled, it will do no further harm and in fact provides a sterile covering over a burnt area. Where a large splash completely encircles a limb it is generally believed that the bitumen can shrink on cooling and form a tourniquet which may restrict blood flow around the burn. If this is considered to be a likely possibility, the bitumen layer should be snipped through with scissors under a liberal application of medicinal paraffin. As healing takes place the bitumen plaque will detach itself, usually after a few days. When it is absolutely necessary to remove adhering bitumen from the skin, because of the site and size of contact or the nature of the material, eg cutback bitumen, liberal amounts of warm medicinal paraffin can be used. If solvent treatment is required, it should be followed by washing with soap and water, and then the application of a proprietary refatting agent or skin cleansing cream.

2.3.2 Inhalation of bitumen fumes

Persons affected by inhalation of bitumen fumes should be removed to fresh air as soon as possible. If the symptoms are severe or persistent, medical help should be sought without delay.

2.4 Fire prevention and fire fighting

The adoption of safe handling procedures will substantially reduce the risk of fire. However, if a fire occurs, it is essential that personnel are properly trained and well equipped to extinguish the fire, thereby ensuring that risk of injury to personnel and damage to plant is minimised. Detailed advice on fire prevention and fire fighting is given in the Institute of Petroleum Bitumen Safety Code(4).

Small bitumen fires can be put out using dry chemical powder, foam, vaporising liquid or inert gas extinguishers, fog nozzle spray hoses or steam lances. Direct water jets should be avoided because frothing may occur which tends to spread the hot bitumen and, therefore, the fire.

Internal tank fires where the roof of the tank is largely intact can be extinguished by injection of steam or a 'fog' of water into the vapour space. However, this method should be used only by trained operatives because water vaporises instantly on contact with hot bitumen. This initiates foaming which may result in the tank overflowing, creating an additional hazard. Alternatively foam extinguishers may be used. The foam ensures that the water is well dispersed, thereby reducing the risk of froth-over. The disadvantage with this type of extinguisher is that the foam breaks down rapidly when applied to hot bitumen.

Portable aqueous film-forming foam extinguishers and dry chemical powder extinguishers are suitable for 'first attack' of small bitumen fires. These should be placed at strategic locations which are permanent and conspicuous around bitumen handling areas. The type and location of 'main attack' equipment should be discussed with the local fire brigade before installation.

2.4.1 Toxicity of combustion products

Like all hydrocarbons, bitumen will burn fiercely if its temperature is raised sufficiently. The main products of combustion are carbon dioxide and water but there will also be smaller amounts of carbon monoxide and other minor components. The main hazard from combustion is the soot and smoke which, because of the nature of bitumen, are produced in large quantities.

2.5 Environmental aspects

2.5.1 The Environmental Protection Act

Nobody can be unaware these days of the need to protect the environment in which we live. The UK government, reflecting strong public opinion and European Commission moves, passed the Environmental Protection Act in 1990 which placed responsibilities on producers and users alike.

2.5.2 Fume production

As discussed in section 2.2.3, all hydrocarbons give off fumes when they are heated and all hydrocarbon fumes are potentially damaging to the environment. The production of fumes cannot be eliminated totally but can be minimised by careful temperature control and storage of hot materials. Although no figures are available for the total amount of fumes produced, studies show the amounts to be small.

2.5.3 Odour

Odour from fumes is probably the major problem associated with bitumen use. It is not that the fumes are damaging to the environment but that residents living near the boundary of plants and factories using bitumen can smell the fumes. This may be the case during delivery where 20 tonnes of bitumen will quickly displace 20 cubic metres of fumes in the storage tank. Once the public become aware of the odour, they become sensitive, possibly because of fear of damage to their health and the unpleasantness of a smelly environment and there may be mounting pressure from the local authority.

One way of alleviating the odour, which is a nuisance rather than a hazard, is to use countervaillants. These are essentially industrial deodorants. A spray of perfume is emitted at the same point as the odour so that neighbours smell, eg roses or strawberries, instead of bitumen.

2.5.4 *Spillages*

Of all the hydrocarbon materials which could be spilled, bitumen is the most 'environmentally friendly'. On cooling it becomes virtually solid and poses no hazard whatsoever. It is waterproof and does not leak, it is chemically inert and because of its viscosity does not migrate through the ground. It does not contaminate water courses and indeed is used throughout the world to line canals, reservoirs and potable water pipes.

Spillages on water are extremely easy to deal with. On contact with water hot bitumen will immediately cool and become to all intents and purposes solid. Since its density is very close to that of water it will either float (usually in salt water) or sink (in fresh water). It can be retrieved in lumps or, in deep water, left on the sea bed where it will remain virtually inert.

2.5.4.1 Spillages during delivery

When discharge of bitumen into a customer's tanks is complete, it is normal practice to blow air through the flexible hose to clear the hose and customer lines of molten bitumen. The reasons for this are to leave the customer line clear for subsequent deliveries, to ensure that the vehicle lines and valves are clear for future cargoes and to minimise risk to the driver when he disconnects the hose. Clearly there will always be some residual bitumen remaining in the hose, the amount depending almost entirely on the length of the customer lines.

In the past the hose has been drained either into a container such as an oil drum cut in half or onto the floor which has been spread with sand or paper. On cooling, the solid bitumen is gathered up and dumped along with other industrial refuse. This practice is likely to change in the future with environmental legislation. To meet this challenge there is now available a 'no-spill' system from a major manufacturer. The system is essentially a small heated reservoir fitted between the vehicle hose and the customer tank which collects all drainings at the end of the delivery. The drainings remain in the heated reservoir until they are displaced by the next cargo.

2.6 References

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Chapter 3 - The manufacture, storage and handling of bitumen

3.1 The manufacture of bitumen

Crude oil is a complex mixture of hydrocarbons varying in molecular weight and consequently in boiling range. Before it can be used, crude oil has to be separated, purified, blended, and sometimes chemically or physically changed into components suitable for different uses.

Of the approximately 1500 known crudes a somewhat smaller number, perhaps a few hundred, would be available for purchase by a refinery. Whereas most petroleum products can be produced from any crude, only a handful of crudes would produce bitumen suitable for the UK market although that is not to say that other crudes could not make perfectly acceptable bitumens for countries with different climatic conditions. A large, complex refinery may use twenty crudes for its mainstream products but only one or two of these would be used for its bitumen. A bitumen-only refinery would probably use the same one or maybe two crudes all the time.

3.1.1 Fractional distillation of crude oil

The first process in the refining of crude oil is fractional distillation which is carried out in a tall steel tower known as a fractionating or distillation column. The inside of the column is divided at intervals by horizontal steel trays with holes to allow vapour to rise up the column. Over the holes are small domes called bubble caps which deflect the vapour downwards so that it bubbles through liquid condensed on the tray, thus improving the efficiency with which the individual components are separated and reducing the necessary height of the column.

On entering the distillation plant, crude oil is heated in a furnace to temperatures between 300°C and 350°C before being passed into the lower part of a column operating at slightly above atmospheric pressure. The material entering the column is a mixture of liquid and vapour; the liquid comprises the higher boiling point fractions of the crude and the vapour the lower boiling point fractions. The vapours rise up the column through the holes in the trays, losing heat as they rise. When each fraction reaches the tray where the temperature is just below its own boiling point, it condenses back into a liquid. As the fractions condense on the trays they are continuously drawn-off via pipes.

The lightest fractions of the crude remain as a vapour and are taken from the top of the distillation column; heavier fractions are taken off the column as side-streams; the heaviest fractions remain as a liquid and therefore leave at the base of the column. The lightest fractions produced by the crude distillation process include propane and butane which are gases under atmospheric conditions. Moving down the column, a slightly heavier product, naphtha, is produced which is a feedstock for gasoline production and the chemical industry. Then there is kerosene, which is used primarily for aviation fuel and to a lesser extent for domestic fuel. Heavier again is gas oil, which is used as a fuel for diesel engines and domestic heating. The heaviest fraction taken from the crude oil distillation process is long residue, a complex mixture of high molecular weight hydrocarbons, which requires further processing before it can be used as a feedstock for the manufacture of bitumen. The long residue is further distilled in a vacuum distillation column. This is carried out under a vacuum of 10 to 100 mm Hg (absolute pressure) at 350 to 400°C to produce gas oil, distillates and

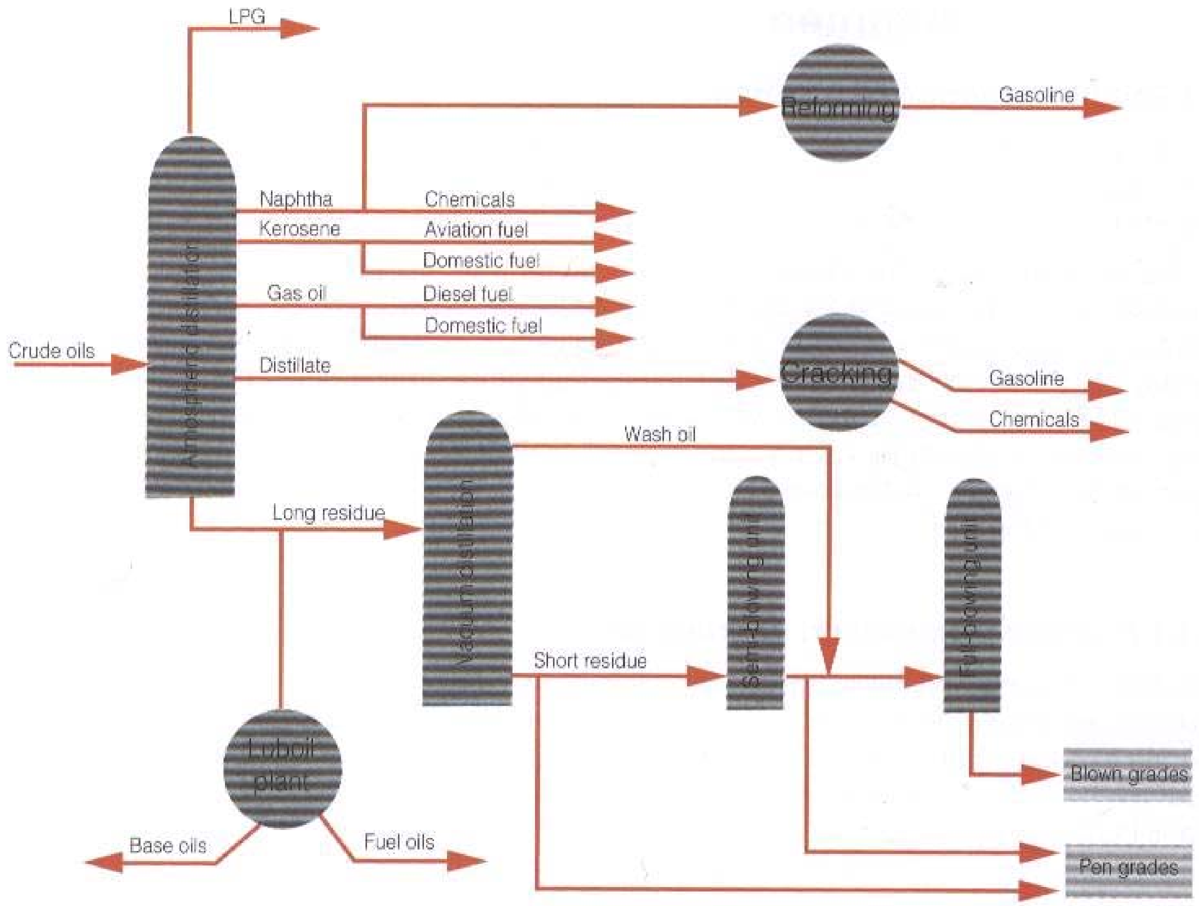


Fig 3.1 — Schematic diagram of the manufacture of bitumen

short residue. If this second distillation were carried out by increasing the temperature of the process, cracking or thermal decomposition of the long residue would occur.

The short residue is the feedstock used for the manufacture of over 20 different grades of bitumen. The viscosity of the short residue is a function of both the origin of the crude oil and the temperature and pressure in the vacuum column during processing. Depending on the origin of the crude oil, the conditions in the column are adjusted to produce a short residue with a penetration in the desired range which is normally 100 to 300 dmm.

Some crudes, most notably South American, can be used to produce short residues with a penetration of 50 dmm or even harder. Bitumens produced in this way are known as straight run or steam distilled bitumens even though these terms do not describe the manufacturing route.

Figure 3.1 shows a schematic representation of the distillation process and its relationship with other fundamental refining processes, such as reforming and cracking for the

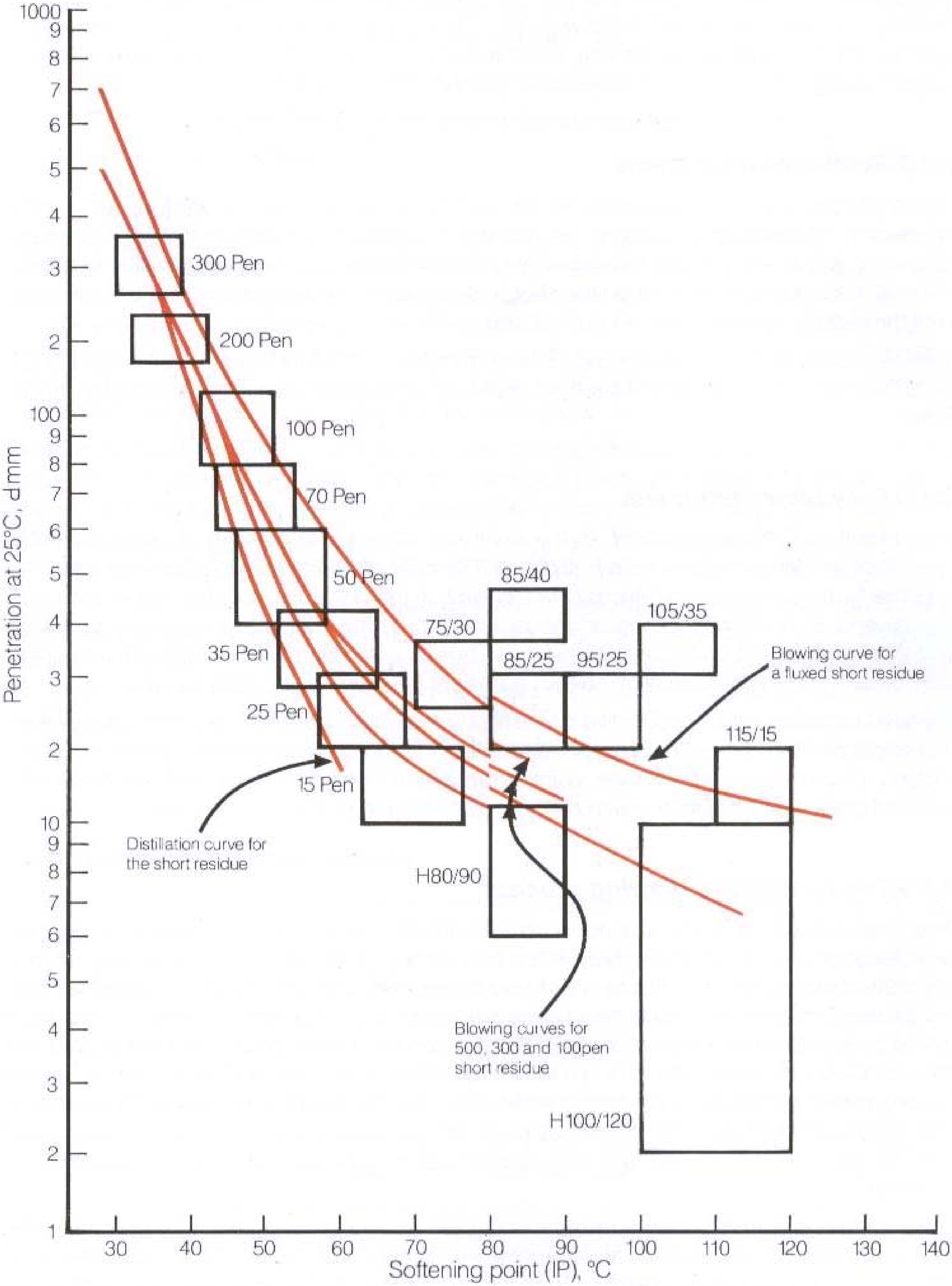


Figure 3.2 — Distillation and blowing curves for a bitumen feedstock

Note:: The discontinuity at 80°C is an artefact of the test method for softening point manufacture of motor gasoline and lubricating oils, waxes, etc. Figure 3.1 shows a semi-blowing unit and a separate full blowing unit. This is done for the sake of clarity although in practice the two units would be one and the same. A manufacturer would normally have a single blowing unit which is run under varying conditions.

3.1.2 Semi-blown bitumens

Some crudes give short residues which can be used as bitumen without any further processing whereas others require 'air-blowing' to produce penetration grades. Such air-blowing is very limited and carried out under mild conditions. It is an oxidation process which involves the blowing of air through the short residue, either on a batch or a continuous basis, with the short residue at a temperature of 240 to 320°C.

This process is termed semi-blowing or air-rectification. Used judiciously, semi-blowing can be applied to reduce the temperature susceptibility of the bitumen, ie increase its penetration index.

3.1.3 Fully blown bitumens

Fully blown or oxidised bitumens are produced by vigorous air-blowing of short residue or short residue blended with a heavy distillate. The position of the blowing curve on figure 3.2 is primarily dependent on the viscosity of the feed, ie the softer the feed the higher the curve. The severity of blowing depends on the temperature in the column, typically 250 to 300°C, and to a lesser extent on the residence time. Thus by controlling the viscosity of the feed and the conditions in the column all the blown grades of bitumen can be manufactured.

Oxidised bitumens have a distinctive consistency at room temperature which is different from that of penetration or hard grades. As well as being slightly brittle, oxidised bitumens have a rubbery property and will recover visibly from applied strains. Shell Bitumen Mexphalte oxidised grades are designated with an R (eg R85/40), the R standing for rubbery.

3.1.4 The continuous blowing process

After preheating, the short residue is introduced into the blowing column just below the normal liquid level. Air is blown through the bitumen by means of an air distributor located at the bottom of the column. The air is not only the reactant but also serves to agitate and mix the bitumen, thereby increasing the surface area and rate of reaction. Oxygen is consumed by the bitumen as the air ascends through the material. Steam and water are sprayed into the vapour space above the bitumen level, the former to suppress foaming and dilute the oxygen content of waste gases and the latter to cool the vapours to prevent after-burning. The 'blown' product flows from the bottom of the blowing column into a surge drum via an external draw-off line. In this way the minimum level of product in the blowing column is controlled.

From the surge drum the blown product is passed through heat exchangers to achieve the desired 'rundown' temperatures and to provide an economical means of preheating the short residue, before pumping the product to storage. The penetration and softening point of the blown bitumen are affected by:

- the viscosity of the feedstock;
- the temperature in the blowing column;
- the residence time in the blowing column;
- the origin of the crude oil used to manufacture the feedstock;
- the air-to-feed ratio.

Figure 3.2 shows distillation and blowing 'curves' for a Middle East feedstock. In both the distillation and blowing processes the softening point increases and the penetration falls. However, in the distillation process the temperature susceptibility (or penetration index) of the material is effectively unchanged. Thus the distillation line on the figure is virtually a straight line, whereas the curves for the blown bitumen flatten substantially as the softening point of the bitumen increases, showing that the temperature susceptibility of the material is substantially reduced, ie the penetration index is increased.

The blowing and distillation lines are shown as smooth curves whereas in practice a discontinuity is observed at 80°C. The discontinuity is purely an artefact of the test method and is due to the fact that the softening point of bitumen must be determined in water if the softening point is below 80°C and in glycerine if it is greater than 80°C; as glycerine possesses different thermal characteristics to water it produces a higher softening point.

The blowing process dehydrogenates the short residue, resulting in oxidation and subsequent polycondensation. It is not oxidation in the inorganic sense of the word as the actual oxygen uptake by the bitumen is negligible. The reaction increases the overall molecular size of the asphaltenes already present in the feed and forms additional asphaltenes from the maltene phase, see chapter 4, section 4.1. The exothermic reaction requires close temperature control which is achieved by regulating the air-to-short residue ratio in the reaction vessel (blowing column).

3.1.5 The batch-blowing process

Many industrial users of bitumen require a variety of grades on an intermittent basis. Where their demand cannot be met economically by a local refinery or where the method of supply is expensive or cumbersome, eg in drums, a number of users have constructed their own blowing facility. This is particularly the case in the USA but is also not uncommon in the UK and on the continent of Europe. The technique involves charging the reaction vessel with a batch of feedstock, usually 15-50 tonnes, and raising it to the required temperature. Air is blown through the mixture and an exothermic reaction begins at about 200°C. The temperature must be controlled to avoid the risk of fire and/or damage to the product.

Compared to continuous blowing, where very sophisticated and expensive control mechanisms are required batch, plants have the following advantages:-

- economic when throughput is small;
- cheap to construct and run (air pressures as low as 1 bar are adequate);
- extremely flexible and can produce a variety of grades tailored to the operator's specific requirement;
- simple process control;
- blowing is complete within a single shift.

3.1.6 Catalytic blowing

The first patents describing the process appeared around the turn of the century in the USA. As the name implies, a catalyst is added during the blowing process to speed up the rate of conversion. Possible catalysts include:

- — ferric chloride,
- — sulphuric acid,
- — phosphoric acid,
- — nitric acid,
- — aluminium chloride,
- — oxides of Fe, V, Cr, Zn, Mn, Cu,
- — alkali metal carbonates.

Catalytic blowing has not been taken up very widely in Europe because of the availability of a wide variety of standard grades of oxidised bitumen and the relative ease of transport from refinery to customer. However, where non standard grades of oxidised bitumen are required or delivery from a refinery is difficult due to the distances involved, locally operated catalytic blowing plants have been successfully used. In the main, catalytic oxidised bitumen plants may be commonly found in the USA and Australia.

Catalytic oxidation plants suffer greater attack by corrosion than conventional continuous oxidation plants due to the fact that many of the catalysts are corrosive and can attack parts of the blowing plant. Furthermore, the products that are produced by this process can behave in a different way from the conventionally oxidised bitumens, particularly in respect of softening point "fall-back" on overheating. This phenomenon results in the softening point of the bitumen decreasing by as much as 20°C if the bitumen is heated above 250°C. In the roofing industry, bitumen adhesive grades are commonly overheated to temperatures well in excess of this with the result that the bitumen may fail to perform as expected.

3.1.7 Chemistry of the blowing process

The aim of the blowing process is to encourage the formation of asphaltenes in the bitumen. Penetration grades of bitumen typically contain about 8 to 15 per cent of asphaltenes while the blown grades contain about 20 to 30 per cent. Three reaction phenomena can be identified in the process:-

- reactions during which molecular size increases; formation of esters is particularly important; they not only account for about 60 per cent of the oxygen in blown bitumen but also link up two different molecules and thus contribute to the formation of material of higher molecular weight; this mechanism results in an increase in the asphaltene content and a change in the colloid-chemical constitution and rheological properties of the bitumen;
- reactions during which molecular size is unchanged; formation of cyclic hydrocarbons by means of dehydrogenation with water as a side product;

- reactions during which molecular size decreases; separation of side branches from the molecules with blown distillate produced as a side product.

The blowing of bitumen is a chemical reaction and must be treated with great care. The reaction temperature and composition of the waste gases must be closely controlled both to protect the product and to prevent thermal runaway, autoignition, explosion and fire.

3.1.8 Bitumens produced by blending

3.1.8.1 Penetration grades

Most refineries produce a range of penetration grades by blending a soft penetration grade eg 100, 200 or 300 pen with a hard penetration grade such as 25, 35 or 50 pen, that is, the short residue with the semi-blown component. For most crudes the differences in properties of bitumens produced in this way, compared with the same grades produced by direct distillation or direct semi-blowing, are negligible. However for some crudes this is not the case and bitumen manufacturers need to evaluate fully any proposed changes to their production methods.

Grades softer than the short residue, ie 450 pen and 300 pen can be produced by direct distillation but are usually made by adding 'flux', which is a general term for a heavy distillate, to the short residue. For bitumen the flux used is usually wash oil which comes directly from the vacuum distillation column during bitumen manufacture.

3.1.8.2 Oxidised grades

While many refineries still manufacture each oxidised grade of bitumen individually, some now produce intermediate oxidised grades by blending hard and soft components. This enables a reduction in tankage from, say, six down to three or four.

3.1.8.3 Cutback grades

In the UK cutback bitumens are made by mixing kerosene, or another fraction with a similar volatility, and penetration bitumen, typically 100 or 200 pen. Blending is usually carried out in-line with kerosene injected in a continuous stream at around 5 to 15 per cent depending on the grade of cutback required, see chapter 6.

3.2 Storage and handling temperatures of bitumens(1,2)

When handled properly, bitumens can be reheated or maintained at elevated temperatures for a considerable time without adversely affecting their properties. However, maltreatment of bitumen by overheating or by using conditions which promote oxidation, can adversely affect bitumen properties and could influence the long-term performance of materials made with it. The degree of hardening (or, under certain circumstances, softening) produced as a result of mishandling is a function of a number of parameters such as temperature, the presence of air, the surface-to-volume ratio of the bitumen, method of heating and the duration of exposure to these conditions.

3.2.1 Bitumen tanks[3]

All bitumens should be stored in tanks specifically designed for the purpose. To minimise the possible hardening of the bitumen during storage certain aspects of the design of the tank should be considered:

- to minimise the risk of overheating the bitumen, the tank should be fitted with accurate temperature sensors and readout devices; these should be positioned in the region of the heaters and preferably be removable so that regular cleaning and maintenance can be easily carried out;
- oxidation and loss of volatiles from bitumen are both related to the exposed surface-to-volume ratio of the storage tank, which for a vertical cylindrical vessel equals the reciprocal height of the filled part of the tank:

$$\frac{\text{surface}}{\text{volume}} = \frac{\pi\ r^2}{\pi\ r^2 h} = \frac{1}{h}$$

where h = height of bitumen
r = radius of the tank;

- this relationship holds true for any parallel-sided flat-topped tank but does not take any account of the increase in surface area caused by the internal tank framework. Thus, the dimensions of the bulk storage tank should aim to minimise the surface-to-volume ratio and therefore storage tanks with a high h-to-r ratio are preferable to horizontal tanks.

- it is common practice for bitumen in bulk storage tanks to be recirculated around a ring main to heat the pipework delivering the bitumen to the processing point; return lines in a recirculation system should re-enter the storage tank below the bitumen surface to prevent hot bitumen cascading through the air; often the bitumen is returned to the bulk storage tank through a pipe fitted into the upper part of the tank flush with the side, roof or protruding just into the airspace at the top of the tank; if the bitumen enters the tank above the liquid level all the factors which promote oxidation are present:

    - high temperature;
    - access to oxygen;
    - high exposed surface-to-volume ratio.

Grade	Minimum pumping temperature	Typical application temperature		Maximum safe handling temperature
		Mixing/coating	Spraying	
Penetration grades				
450	90	130	160	190
300	95	135	165	190
200	100	140	175	190
100	105	155	190	200
70	110	160	—	200
50	115	165	—	200
40 HD	125	175	—	200
35	125	175	—	220
25	135	185	—	220
15	140	190	—	220
Oxidised grades				
75/30	150	195	—	230
85/25	165	210	—	230
85/40	165	210	—	230
95/25	175	220	—	230
105/35	195	220	—	230
115/15	205	230	—	230
Hard grades				
H 80/90	160	200	—	230
H 100/120	190	230	—	230
Cutback grades				
50 secs	65	105	150	160
100 secs	70	110	160	170
200 secs	80	120	170	180

Maximum pumping viscosity	2 Pa.s (2000 cSt)
Mixing/coating viscosity	0.2 Pa.s (200 cSt)
Spraying viscosity	
Penetration grades	0.06 Pa.s (60 cSt)
Cutback grades	0.03 Pa.s (30 cSt)

Note - Bitumen should always be stored and handled at the lowest temperature possible consistent with its efficient use

Table 3.1 — Recommended handling temperatures, °C(1, 2, 3)

Fortunately, the residence time of bitumen in the tank is usually sufficiently low for any hardening to be insignificant. However, if material is stored for a prolonged period, re-circulation should be used only intermittently and the bitumen should be tested before use to ensure its continued suitability for the application.

In preference to manual dipping, tanks should be fitted with automatic level indicators with low and high level alarms, the former to prevent exposure of hot heater tubes and thereby creating a fire/explosion risk and the latter to avoid overfilling the tank. Manual dipping should be carried out only to check the accuracy of automatic devices. Whether or not a high level alarm is fitted, a maximum safe working level for the tank should be predetermined. This should allow a margin for thermal expansion of the product in the tank and for the expansion which might result from accidental ingress of a small amount of water.

Before intake of additional product, a check should be made to ensure that there is sufficient ullage in the tank for the quantity to be taken in, without exceeding the maximum safe working level. Every tank should be clearly labelled with the grade of bitumen it contains. When the grade of bitumen in a tank is changed it is important to ensure that the tank is empty and relabelled before the new grade is delivered.

3.2.1.1 Skin formation

When bitumen is stored hot a skin can form at the surface. 'Skinning', as it is termed, is caused both by evaporative loss from the bitumen and oxidation of the bitumen surface. The degree of skinning is a result of a number of factors which include storage temperature, bitumen grade, tank geometry and construction, heater type, product throughput and the amount of ventilation. Given a standard set of severe conditions, all bitumens will produce a skin, which will not redissolve, in as little as a few hours. The blown grades of bitumen, particularly the very highly blown grades such as R 115/15, tend to be more susceptible to skin formation than the penetration grades. As a general rule harder bitumens tend to skin more readily than softer grades and blown bitumens form skin more readily than penetration grades. Cutback grades are not normally susceptible to skin formation. Once formed at the surface, the skin will protect the bitumen from further oxidation as long as it remains unbroken. Unfortunately most tanks are fitted with internal bracing and as the bitumen level falls through use the skin ruptures and breaks, exposing fresh surfaces. Bits of skin may adhere to the bracing or may sink to the bottom of the tank. Either way, if it remains in the tank, skin will eventually form a hard coke.

Skinning can be minimised by gentle circulation of the bitumen so that a static surface is avoided and by minimising the degree of ventilation (both volatile outlet and air inlet) comensurate with safe operation. Although it is possible to 'blanket' the surface with an inert atmosphere, this process brings with it other hazards and hence its use is not recommended.

3.2.2 Storage and pumping temperatures

Bitumen should always be stored and handled at the lowest temperature possible, consistent with efficient use. As a guide, working temperatures for specific operations are given in table 3.1(1,2,3). These temperatures have been calculated on the basis of viscosity measurements and are supported by operational experience. For normal operations, ie the blending and transferring of liquid bitumen, temperatures of 10°C to 50°C above the minimum pumping temperature are recommended, but to minimise the risk of autoignition of the bitumen 230°C should not be exceeded.

The residence time of bitumen resides in a storage tank at elevated temperature and undercirculation should be minimised to prevent hardening of the bitumen. If bitumen must be stored for an extended period, ie say for more than one week without addition of fresh material, the temperature should be reduced to approximately 20 to 25°C above the softening point of the bitumen and, where possible, recirculation stopped.

When bitumen is being reheated in bulk storage, care must be taken to heat the bitumen intermittently over an extended period to prevent localised overheating of the product around the heating pipes or coils. This is particularly important where direct flame tube heating is used because surface temperatures in excess of 300°C can be reached. In such instances initially only a limited amount of heat should be applied, sufficient to raise the temperature of the product to just above its softening point. This will allow the material to soften and then the heat can be reapplied to bring the temperature of the product to the required working temperature. This technique is beneficial because when the bitumen is a fluid, albeit a viscous fluid, convection currents are more able to dissipate the heat throughout the bulk and therefore localised overheating is less of a problem. Circulation of the tank contents should begin as soon as the product is sufficiently fluid, thereby further reducing the likelihood of local overheating. If prolonged direct flame heating is used, cracking of the bitumen may result. With hot oil, steam or properly designed electric heaters, reheating from cold should not cause these problems.

3.2.3 Sampling

Sampling of bitumen is hazardous because of the risk of heat burns from spills and splashes of the material. It is therefore essential that protective clothing is always worn when sampling bitumen.

3.2.3.1 Dip Sampling

A sample of bitumen may be obtained by dipping a weighted can or 'thief' on the end of a rope or rod through the manlid into bitumen stored in a bulk tank. The sample is then transferred to a suitable permanent container. The method is simple but is appropriate only for small samples. Dip sampling from cutback tanks should be avoided because of the presence of flammable atmospheres in tank vapour spaces. Safe access to and from the sample point should be provided. Gantry access should be provided where dip samples are required from vehicle tanks. Dip sampling should be undertaken only where it is impractical to provide safer means.

3.2.3.2 Sample valves

Properly designed sample valves are preferable for sampling from pipelines or from tanks. Their design should ensure that they are kept hot by the product in the pipeline or tank to avoid blockage when in the closed position.

Sample valves should preferably be the screw driven, plunger type. When closed, the plunger of this type of valve extends into the fresh product, so that when the valve is opened a representative sample of product is obtained without 'fore-runnings'. With ball and plug type valves fore-runnings have to be collected and disposed of before a representative sample can be obtained.

3.3 References

(1) Refined Bitumen Association : *Safe handling of petroleum bitumens.* Technical Bulletin No 5, 1981.

(2) Refined Bitumen Association : *Recommendations to users for the storage and handling of Bitumen.* Technical Bulletin No 7, 1988.

(3) Institute of Petroleum : *Model code of safe practice in the petroleum industry.* Part 11, Bitumen Safety Code, 1990.

Chapter 4 - Bitumen constitution, structure and rheology

The rheology of a bitumen at a given temperature is determined by both the constitution (chemical composition) and structure (physical arrangement) of the predominantly hydrocarbon molecular structures in the material. Changes to either the constitution, structure or both will result in a change in the rheology. Thus to understand changes in bitumen rheology, it is essential to understand how the structure and constitution of a bitumen interact to influence rheology.

4.1 Bitumen constitution

Bitumen is a complex mixture of molecules of a predominantly hydrocarbon nature with a minor amount of structurally analogous heterocyclic species and functional groups containing sulphur, nitrogen and oxygen atoms(1,2,3). Bitumen also contains trace quantities of metals such as vanadium, nickel, iron, magnesium and calcium which occur in the form of inorganic salts and oxides or in porphyrin structures. Elementary analysis of bitumens manufactured from a variety of crude oils show that the composition of most bitumens falls within the range shown in table 4.1.

Element	Concentration % by mass
Carbon	82 - 88
Hydrogen	8 - 11
Sulphur	0 - 6
Oxygen	0 - 1.5
Nitrogen	0 - 1

Table 4.1 — Chemical composition of bitumen

In addition, trace amounts of metals may be found in bitumens in the form of inorganic salts and oxides or in porphyrinic structures. Organic functional groups such as C=O (carbonyl), S=O (sulphonyl), N-H (amide) and COOR (alkyl carboxylate) can be detected by infra-red analysis.

The precise composition varies according to the source of the crude oil from which the bitumen originates, the modification induced by semi-blowing and blowing during manufacture and subsequent ageing in service.

The chemical composition of bitumen is extremely complex; thus, a complete analysis of bitumen (if possible) would be extremely laborious and would produce such a large amount of data that correlation with the rheological properties would be impossible. However it is possible to separate bitumen into four broad chemical types called saturates, aromatics, resins and asphaltenes. The four groups are not exact entities but are a function of the techniques used and inevitably some overlap between the groups occurs. However, it does enable bitumen rheology to be compared with broad chemical composition.

The methods available for separating bitumens into fractions can be classified as follows:

- solvent extraction;
- adsorption by finely divided solids and removal of unadsorbed solution by filtration;
- chromatography;
- molecular distillation used in conjuction with one of the above techniques.

Solvent extraction is attractive because it is a relatively rapid technique(4), but the separation obtained is generally poorer than when using chromatography where a solvent effect is combined with selective adsorption. Similarly, simple adsorption methods(5) are not as effective as column chromatography in which the eluting solution is constantly re-exposed to fresh adsorbent and different equilibrium conditions as it progresses down the column. Molecular distillation is lengthy and has limitations in terms of how far separation and distillation of high molecular weight components of bitumen can be effected.

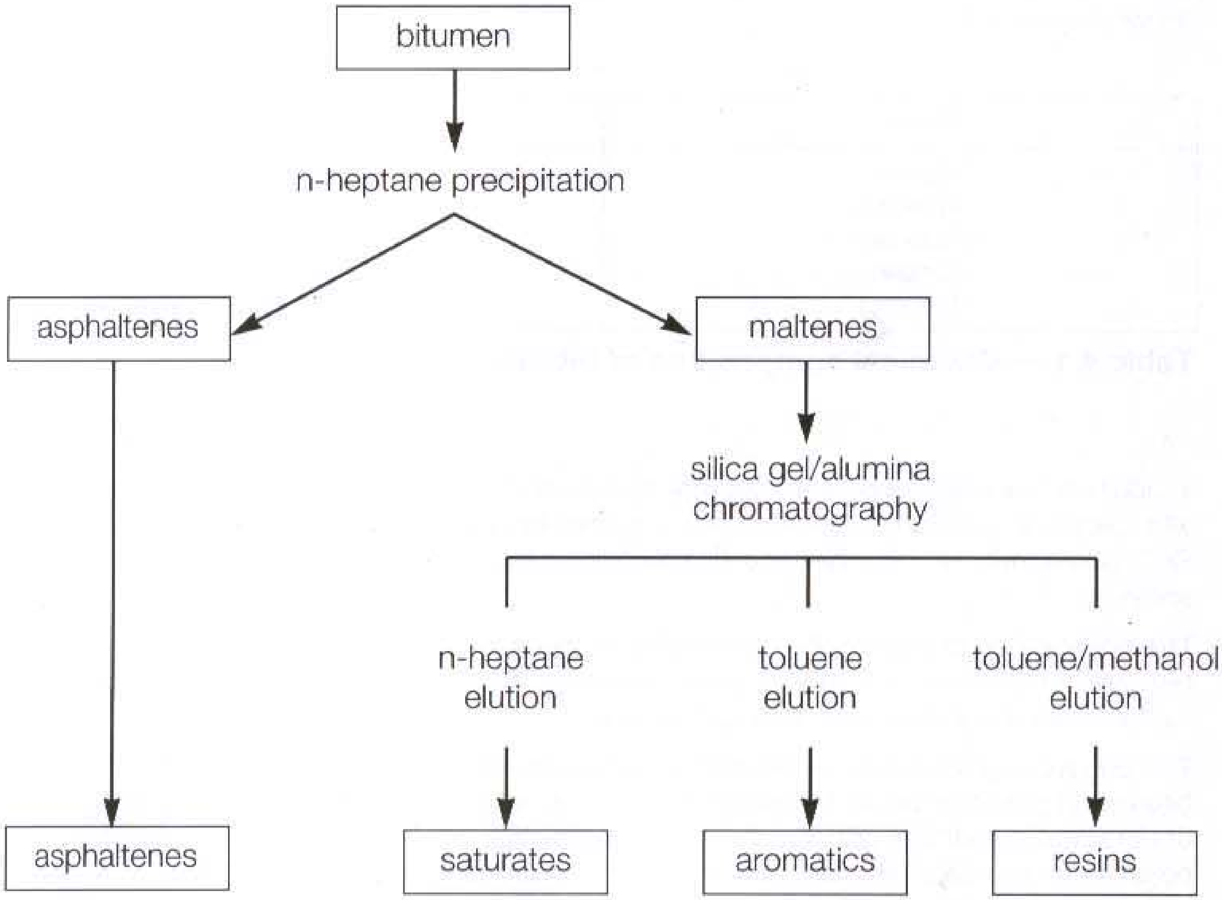


Figure 4.1 — Schematic for the separation of chemical constituents in bitumen

Chromatographic techniques(6,7,8) have, therefore, been most widely used to define bitumen constitution. The basis of the method is to initially precipitate asphaltenes using n-heptane followed by chromatographic separation of the remaining 'maltene' phase. Figure 4.1 shows a schematic representation of the chromatographic method.

The main characteristics of these four broad component groups are as follows:

4.1.1 Asphaltenes

These are n-heptane insoluble black or brown amorphous solids containing, in addition to carbon and hydrogen, some nitrogen, sulphur and oxygen. Asphaltenes are generally considered as highly polar and complex aromatic materials of fairly high molecular weight. Different methods of determining molecular weights have led to different values ranging widely from 600 to 300,000 depending on the separation technique employed. However, the majority of test data indicates that the molecular weights of asphaltenes range from 1,000 to 100,000. They are believed to form micelles with a hydrogen/carbon (H/C) atomic ratio of about 1.1 and a particle size of 5 nm to 30 nm which is equivalent to molecular weights of approximately 20,000 to over 1,000,000. The asphaltenes content has a large effect on the rheological characteristics of a bitumen. Increasing the asphaltenes content produces a harder, more viscous bitumen with a lower penetration, higher softening point and consequently higher viscosity. Asphaltenes constitute 5 to 25 per cent of the bitumen. Figure 4.2a shows a typical chemical structure of an asphaltene.

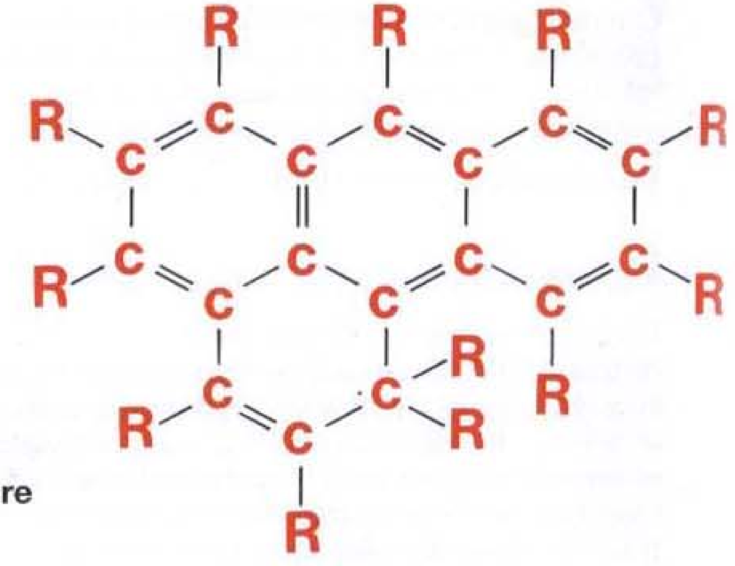
It is perhaps important to note here that the structure of the asphaltenes is not fixed. The gel structure is destroyed on heating and reforms on cooling. On stronger and more prolonged heating the asphaltene micelles may break down. Hence if two bitumens of equal asphaltenes content are blended together it is not unusual for the resultant blend to be higher or lower in asphaltenes than either starting material.

4.1.2 Resins

Resins are soluble in n-heptane; like asphaltenes they are largely composed of hydrogen and carbon, and contain small amounts of oxygen, sulphur and nitrogen. They are dark brown in colour, solid or semi-solid, and very polar in nature. This particular characteristic makes them strongly adhesive. They are dispersing agents or peptisers for the asphaltenes and the proportion of resins to asphaltenes governs to a degree the solution (Sol) or gelatinous (Gel) type character of the bitumen. Resins separated from bitumens are found to have molecular weights ranging from 500 to 50,000, a particle size of 1 nm to 5 nm and an H/C atomic ratio of 1.3 to 1.4.

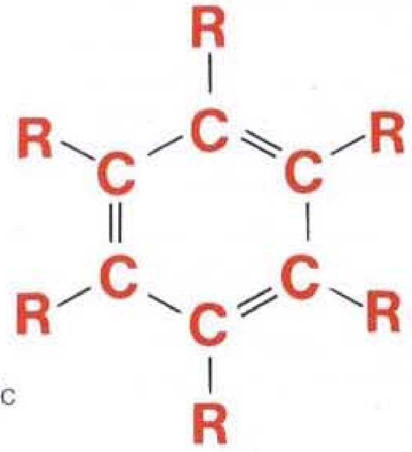
4.1.3 Aromatics

Aromatics comprise the lowest molecular weight naphthenic aromatic compounds in the bitumen and represent the major proportion of the dispersion medium for the peptised asphaltenes. They constitute 40 to 65 per cent of the total bitumen and are dark brown viscous liquids. The average molecular weight range is in the region of 300 to 2,000, they consist of non-polar carbon chains in which the unsaturated ring systems (aromatics) dominate, and they have a high dissolving ability for other high molecular weight hydrocarbons (see figure 4.2b).



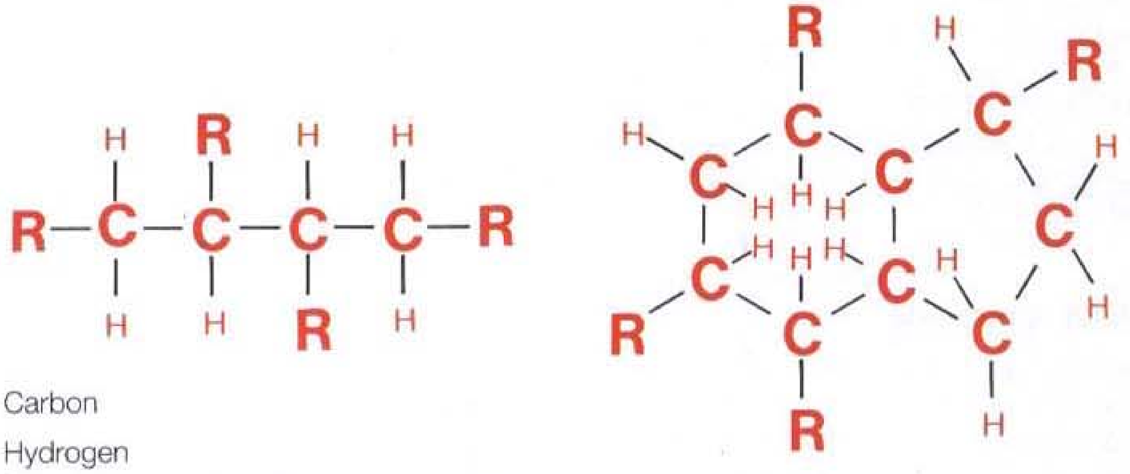
R — Aliphatic naphthenic or aromatic carbon chains

Figure 4.2 a — Asphaltene structure



R — Aromatic and/or naphthenic carbon chains

Figure 4.2 b — Aromatic structure



C — Carbon

H — Hydrogen

R — Aliphatic and/or naphthenic carbon chains

Figure 4.2 c — Saturate structure

4.1.4 Saturates

Saturates comprise straight and branch-chain aliphatic hydrocarbons, together with alkyl-naphthenes and some alkyl-aromatics. They are non-polar viscous oils which are straw or white in colour. The average molecular weight range is similar to that of aromatics and the components include both waxy and non-waxy saturates. This fraction forms 5 to 20 per cent of the bitumen. Figure 4.2c shows a saturate structure.

An elemental analysis of the above four groups from a 100 pen bitumen is detailed in table 4.2(9).

	Yield on bitumen % mass	Carbon % mass	Hydrogen % mass	Nitrogen % mass	Sulphur % mass	Oxygen % mass	Atomic ratio H/C	Molecular weight
Asphaltenes (n-heptane)	5.7	82.0	7.3	1.0	7.8	0.8	1.1	11 300
Resins	19.8	81.6	9.1	1.0	5.2	—	1.4	1 270
Aromatics	62.4	83.3	10.4	0.1	5.6	—	1.5	870
Saturates	9.6	85.6	13.2	0.05	0.3	—	1.8	835

Table 4.2 — Typical elemental analysis of the four groups of a 100 pen bitumen(9)

4.1.5 Metallic constituents of bitumen

That bitumens contain metalloporphyrins was known in the 1930s(10) from analytical work which identified iron and vanadium and consequently established the link between marine plant chlorophyll and petroleum genesis. Ash from fuel oil on examination by UV emission spectrography has been shown to contain the following metallic elements(11).

Silver
Barium
Chromium
Iron
Potassium
Magnesium
Molybdenum
Nickel
Strontium
Vanadium
Zinc
Silicon
Aluminium
Calcium
Copper
Gallium
Lanthanum
Manganese
Sodium
Lead
Tin
Tantalum
Zirconium
Uranium

These elements occur principally in the heavier or involatile components of the oils, some as inorganic contaminants, possibly in colloidal form, but also as salts (eg of carboxylic acids), transition metal complexes and porphyrin type complexes. An analysis of a Boscan crude gave the elemental analysis shown in table 4.3.

The predominant metals present in most fuel oils are sodium, vanadium, iron, nickel and chromium with most of the sodium present as sodium chloride. Vanadium and nickel are largely present as porphyrin structures, which also represent large numbers of different molecules depending upon ring substituents and structural isomerism. Bitumen and fuel oil are related products and Crump(11) surmises that similar elements will be present in bituminous compounds.

Element	Concentration, µg/g
Nickel	109
Vanadium	1110
Cobalt	0.2
Mercury	0.03
Iron	4.8
Zinc	0.7
Chromium	0.4
Arsenic	0.3
Antimony	0.3
Sodium	20

Table 4.3 — Analysis of a Boscan crude

4.2 Bitumen structure

Bitumen is traditionally regarded as a colloidal system(12) consisting of high molecular weight asphaltene micelles dispersed or dissolved in a lower molecular weight oily medium (maltenes). The micelles are considered to be asphaltene clusters together with an absorbed layer of high molecular weight aromatic resins which act as a stabilising solvating medium. Away from the centre of the micelle there is a gradual transition to less polar aromatic resin layers which extend outwards to the less aromatic oily dispersion medium.

In the presence of sufficient quantities of resins and aromatics of adequate solvating power the asphaltenes are fully peptised, and the resulting micelles have good mobility within the bitumen. These are known as 'Sol' type bitumens, figure 4.3a. If the aromatic/resin fraction is not present in sufficient quantities to peptise the micelles, or has insufficient solvating power, the asphaltenes can associate further. This can lead to an irregular open packed structure of linked micelles, in which the internal voids are filled with an intermicellar fluid of mixed constitution. These bitumens are known as 'Gel' types, figure 4.3b, the best examples being the blown or oxidised grades used for roofing purposes. In practice most bitumens are of intermediate character.

The colloidal behaviour of the asphaltenes in bitumens results from aggregation and solvation. The degree to which they are peptised will considerably influence the resultant viscosity of the system. Such effects decrease with temperature and the Gel character of certain bitumens may be lost when they are heated to high temperatures. The viscosities of the saturates, aromatics, and resins depend on the molecular weight distributions. The higher the molecular weight the higher the viscosity. The viscosity of the continuous phase, ie the maltenes, imparts an inherent viscosity to the bitumen which is increased by the presence of the dispersed phase, ie the asphaltenes. The saturates fraction decreases the ability of the maltenes to solvate the asphaltenes, because high saturates contents can lead to marked agglomeration of the asphaltenes. Increase in Gel character and a lower temperature dependence for bitumens therefore not only results from the asphaltenes content but also from the saturates content.

⬢ Asphaltenes

⬡ High molecular weight aromatic hydrocarbon

⬡ Low molecular weight aromatic hydrocarbon

○ Aromatic/naphthenic hydrocarbons

∿ Naphthenic/aliphatic hydrocarbons

— Saturated hydrocarbons

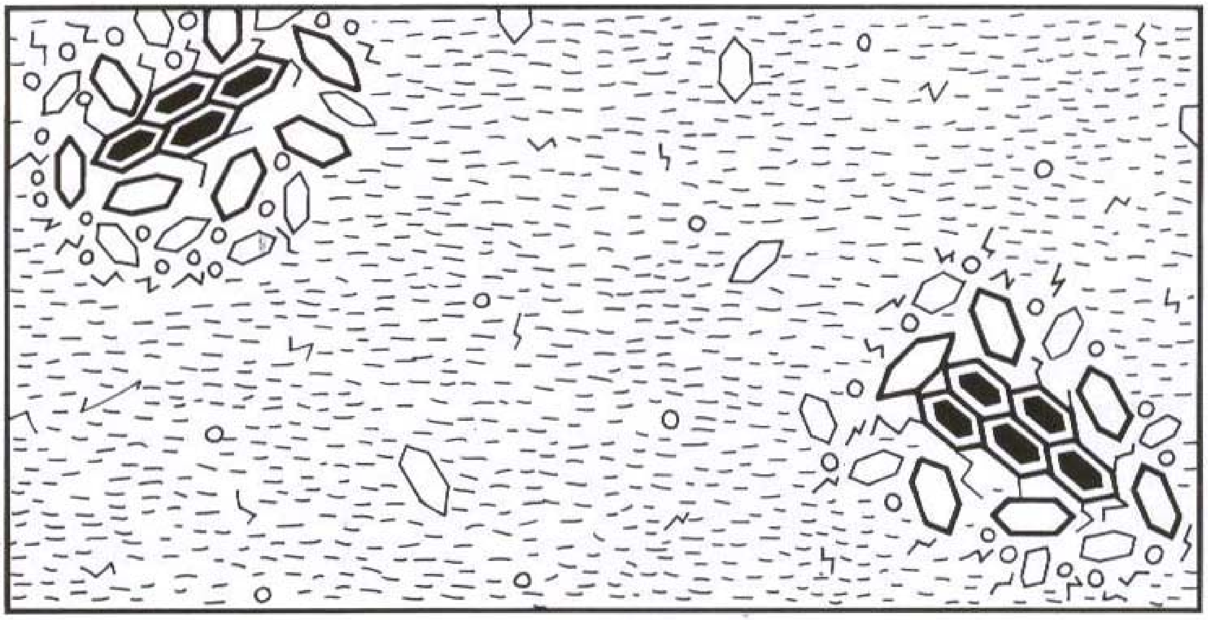


Figure 4.3a — Schematic representation of a 'SOL' type bitumen

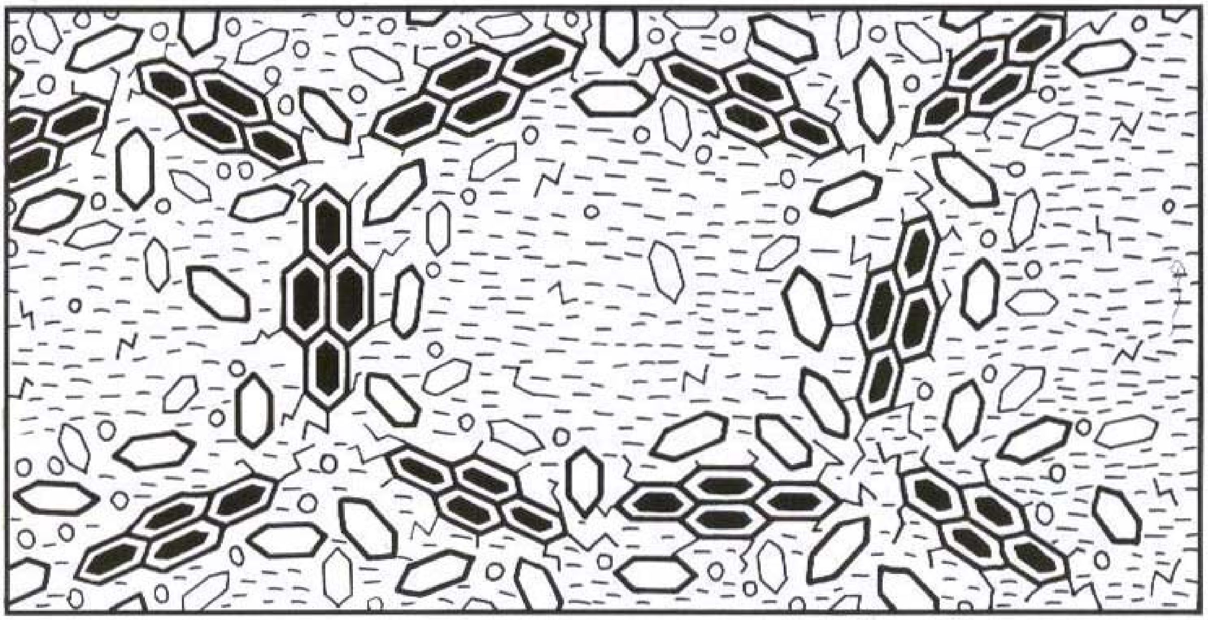


Figure 4.3b — Schematic representation of a 'GEL' type bitumen

4.3 The relationship between constitution and rheology

Systematic blending of saturates, aromatics, resins and asphaltene fractions separated from bitumen has demonstrated the dependence of rheology on constitution(13,14,15,16,17). By holding the asphaltene content constant, and varying the concentration of the other three fractions, it has been demonstrated that:

- increasing the aromatics content at a constant saturate to resins ratio has little effect on rheology, other than a marginal reduction in shear susceptibility;
- maintaining a constant ratio of resins to aromatics and increasing the saturates content softens the bitumen;
- the addition of resins hardens the bitumen, reduces the penetration index and shear susceptibility but increases the viscosity.

It has also been shown that the rheological properties of bitumens depend strongly on the asphaltenes content. At constant temperature the viscosity of a bitumen increases as the concentration of the asphaltenes blended into the parent maltenes is increased. The increase in viscosity, however, is substantially greater than would be expected if the asphaltenes were spherical, non-solvated entities. This suggests that the asphaltenes can interact with each other and/or the solvating medium. Even in a dilute toluene solution the viscosity increase observed with asphaltenes corresponds to a concentration of non-solvated spheres some five times higher than the amount of asphaltenes used. Bitumen asphaltenes are believed to be stacks of plate-like sheets formed of aromatic/naphthenic ring structures. The viscosity of a solution, in particular a dilute solution, depends on the shape of the asphaltene particles. Size is important only if shape changes significantly as size increases. At high temperatures the hydrogen bonds holding the sheets/stacks together are broken, resulting in a change in both the size and shape of the asphaltenes. Dissociation of the asphaltene entities continues until the limiting moiety, the unit sheet of condensed aromatic and naphthenic rings, is reached. Consequently, viscosity falls as temperature increases. However, as a hot bitumen cools, associations between asphaltenes occur to produce extended sheets. These, in turn, interact with other chemical types present (aromatics and resins) as well as stacking together to form discrete asphaltene particles.

The marked increase in non-Newtonian behaviour as a bitumen cools is a consequence of the inter- and intra-molecular attractions between asphaltenes and other entities. Under shear these extended associations will deform or even dissociate, in a way not adequately described by classical Newtonian concepts. Consequently, at ambient and intermediate temperatures, it can be reasonably concluded that the rheology of bitumens is dominated by the degree of association of asphaltene particles and the relative amount of other species present in the system to stabilise these associations.

4.4 The relationship between broad chemical composition and physical properties

Atmospheric and vacuum distillation removes the lighter components from the bitumen feed stock. The loss of distillates leads to the preferential removal of saturates and concentration

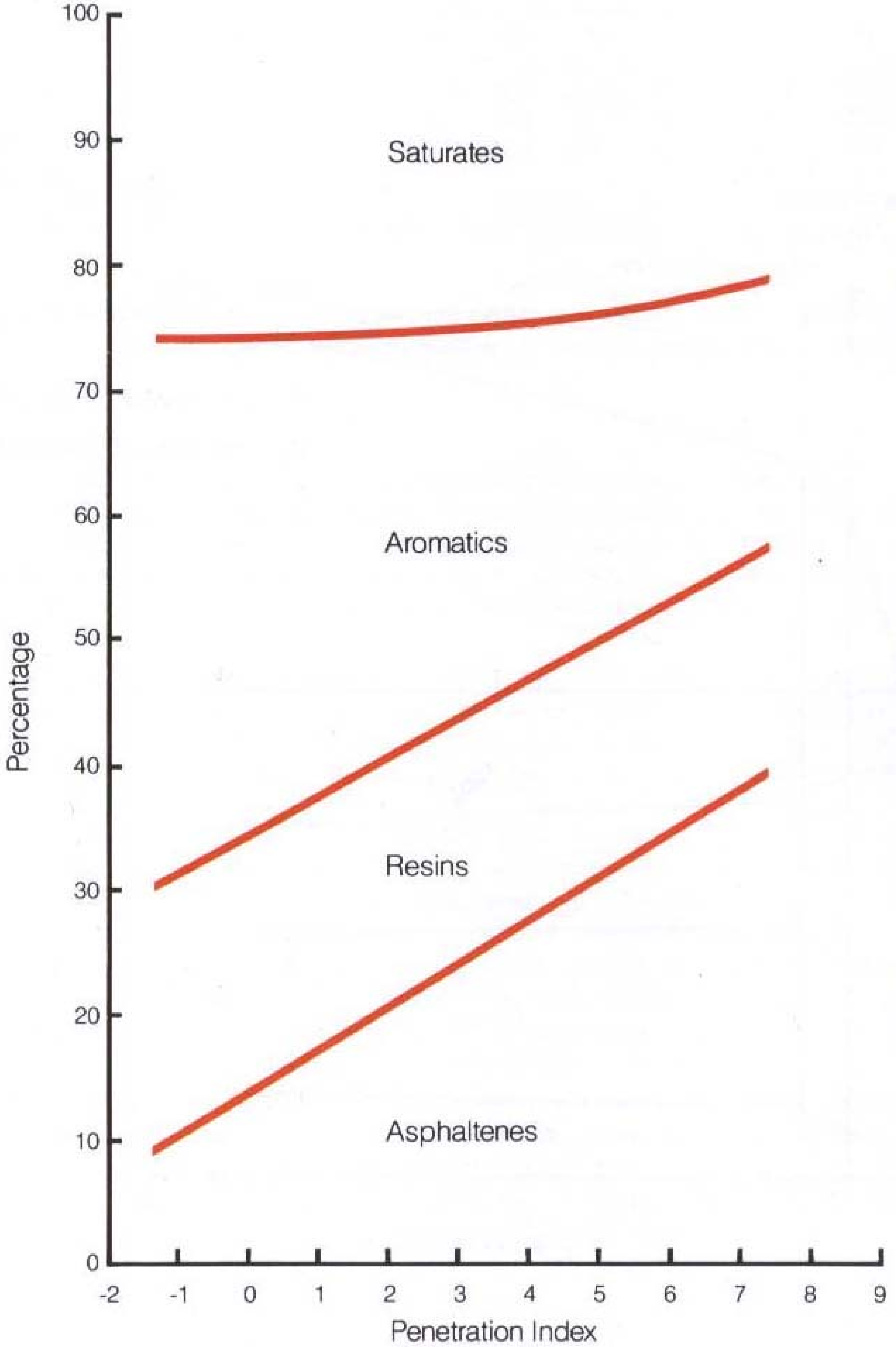


Figure 4.4 — Relationship between broad chemical composition and penetration index(18)

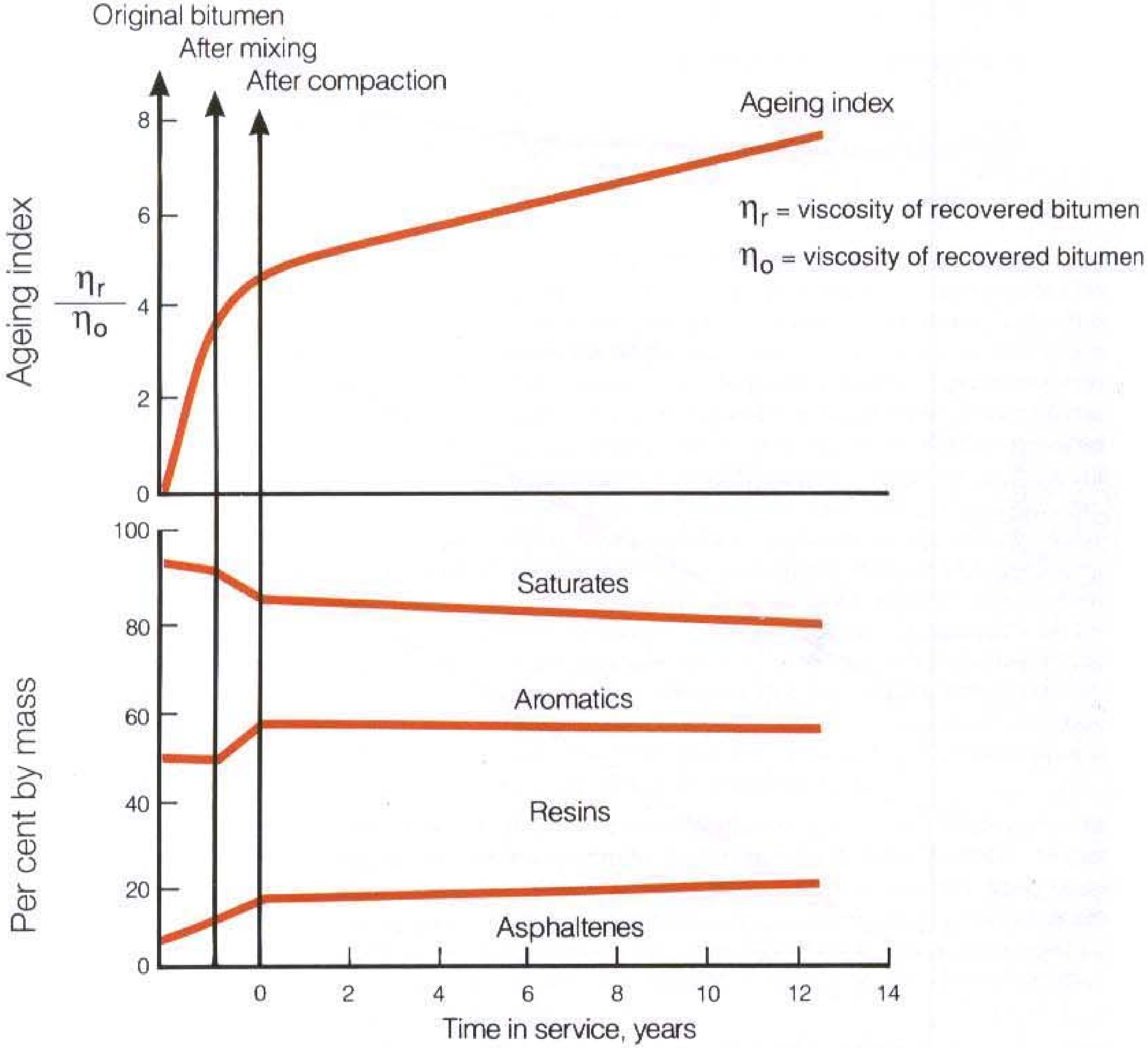


Figure 4.5 — Change in bitumen composition during asphalt manufacture and service(19)

		Vacuum residue	Distillation →				Blowing →		
Penetration at 25°C, dmm		285	185	99	44	12	84	46	9
Asphaltenes	% mass	9.1	9.9	10.5	11.3	12.5	15.2	17.3	22.9
Resins	% mass	18.6	16.7	18.2	17.7	21.3	21.0	22.1	21.5
Aromatics	% mass	51.2	53.0	52.4	58.4	53.8	47.6	45.0	40.5
Saturates	% mass	16.2	15.1	14.1	11.2	9.4	16.2	15.6	15.1

Note: The recovery of components is incomplete because of the techniques used.

Table 4.4 — Comparison of the broad chemical composition of distilled and blown bitumens manufactured from a single short residue(9)

of asphaltenes. Air blowing of bitumens from a given vacuum residue or fluxed vacuum residue considerably increases the asphaltenes content and decreases the aromatics content. Saturate and resin contents remain substantially of the same order as before commencing blowing; this is shown graphically in figure 4.4(18). In table 4.4(9) a comparison of the chemical compositions is given for bitumens derived by distillation or blowing of the same feed stock.

Although data on oxidised grades are scant, full-scale road trial studies have been undertaken on penetration grades to determine if the chemical composition of bitumen changes with time(19). The results of the studies are shown in figure 4.5 in terms of the ageing index (ratio of viscosity of recovered bitumen to viscosity of the original bitumen at 25°C) and also the chemical components. The major changes in viscosity are associated with the mixing and laying process. Changes in the viscosity of the binder are small with time. For the chemical composition, the asphaltenes content increases with mixing and shows a gradual increase with time. The resins and aromatics contents decrease with time. Although little change was expected in the saturates content, some increase has been noted probably due to oil spillage from vehicles on the road. Overall changes after mixing are very small even though the initial void contents of the mixes studied were relatively high (5 per cent to 8 per cent); recovered bitumen samples were obtained from the top 3 mm of cores extracted from the test sections and service temperatures were high.

Whilst chemical composition can be related to physical properties given specific components, it should be noted that bitumens of very different chemical compositions can have very similar physical properties, if derived from different crude oils(20). It is, therefore, impossible to describe bitumens generally in terms of chemical component concentrations and defining individual components, such as a minimum asphaltenes content, has little, if any, relevance.

4.5 References

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Chapter 5 - Specification, testing and properties of bitumen

Bitumen is a complex material with a complex response to stress. All bitumens show a more or less pronounced viso-elastic behaviour, their resistance to deformation being dependent on both the temperature and time during which a force is applied (see section 5.9.1). Only under extreme conditions can a bitumen behave either as a typical elastic solid (low temperature very short loading time) or as a viscous liquid (high temperature, long loading time). Under normal temperature conditions, both viscous and elastic behaviour play their part. Since both temperature and loading time are variable under the conditions of practice, the temperature and time susceptibilities of bitumen are important performance factors.

In order to characterise the numerous bitumen grades a number of test methods have been developed. Initially these tests aimed at measuring an arbitrary mechanical property which made it possible to discriminate between various bitumens. The limits between which such properties had to be were well known from practical experience. Examples of such methods of characterisation and their appropriate consistency are:-

Fraass breaking point - brittleness
Penetration - semi solid range
Softening point - beginning of fluidity
Viscosity - fluidity range
Penetration Index - temperature susceptibility

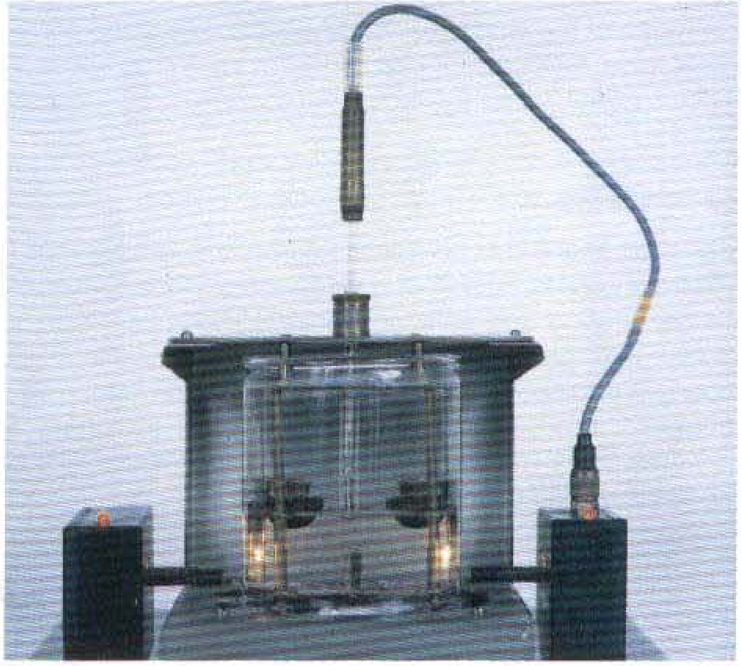
There are no universally accepted specifications for bitumen, cutback bitumen, or bitumen emulsions. The text here discusses specifications in relation to the relevant British Standards; however, other bitumen specifications are acknowledged to be equally valid, differing only in the specification tests detailed or the test ranges for the various different grades. In Europe, the national specifications for bitumen are in the process of being consolidated into a unified CEN specification, whilst in much of the world the ASTM specifications are commonly used. Most bitumen specifications have a degree of commonality centering around the use of penetration and softening point values, whilst the remaining specification properties vary.

5.1 Standard specification tests

As an almost infinite variety of bitumens can be manufactured, it is necessary to have tests which can characterise different grades. The two principal tests used most frequently to characterise bitumens are penetration and softening point. These two tests are used to specify different grades of bitumen. Although they are arbitrary empirical tests, it is possible to estimate from them important engineering properties, such as high temperature viscosity and low temperature stiffness. The use of the penetration test for characterising the consistency of bitumen dates from the late 19th century(1). Figure 5.1 shows how penetration and softening point is related to end-use.

As the penetration and softening point tests are empirically derived it is essential that they are always carried out under exactly the same conditions. The Institute of Petroleum (IP)(2), the American Society for Testing and Materials (ASTM)(3), and British Standards (BS)(4,5) publish standard methods for testing bitumen. In many cases the methods are identical and

Photograph 5.1 — The penetration test



Photograph 5.2 — The softening point test

therefore methods are published jointly. However, some methods differ in detail, for example the IP and ASTM softening point method, and in these cases a correction factor must be applied to relate test results obtained using these two test methods. The majority of the methods quote limits for assessing the acceptability of test results. Precision data for results obtained by a single operator (repeatability) and by different operators in different laboratories (reproducibility) are specified. Thus tolerance is given to allow for differences between operators and equipment at different locations.

5.1.1 Penetration bitumens

Penetration grades of bitumen are normally designated by the mid-point or limits of the permissible range of penetration values. For example, a bitumen with a penetration of 200 dmm may be known as a 200 pen bitumen, or may be known as a 180/220 pen bitumen if its penetration values lie between 180 and 200 pen. Both of these terms are equally valid in normal parlance. Penetration grade bitumens are specified by the penetration(4) and softening point(5) tests (see photographs 5.1 and 5.2 respectively), eg 100 pen bitumen has a penetration of 100 ± 20 and a softening point of 46 ± 5°C. The grades range from 15 pen through to 450 pen above which it is not possible to measure penetration using standard equipment. In addition to penetration and softening point, limits are given for solubility in trichlorethylene(6) and loss on heating(7). The loss on heating test ensures that there are no volatile components in the bitumen that could result in excessive hardening during storage, application or in service. The solubility content limits ensure that contaminants such as carbon (coke) and mineral matter are kept to negligible proportions. In BS 3690 : Part 1(8) there is a minimum permittivity requirement for several of the grades which are used in road construction. Apart from permittivity the requirements for penetration grades in Part 1(8) and Part 2(9) are the same, see table 5.1. In addition to these basic tests some countries have specifications which include other tests such as viscosity, Fraass breaking point, ductility etc.

5.1.2 Oxidised bitumens

Oxidised bitumens are used almost entirely for industrial applications, eg roofing, flooring, mastics, pipe coatings, paints, etc and are specified and designated by both softening point and penetration tests, eg 85/40 is an oxidised grade bitumen with a softening point of 85 ± 5°C and a penetration of 40 ± 5 dmm. Oxidised bitumens also have to comply with solubility and loss on heating criteria. Table 1 of BS 3690 : Part 2(9), details the specification requirements for the six UK oxidised grade bitumens and this has been reproduced here in table 5.2. The softening points of oxidised grades of bitumen are much higher than those of the corresponding penetration grade bitumen and therefore the temperature susceptibility is much lower and the penetration index is much higher, ranging from two to eight.

5.1.3 Hard bitumens

Hard bitumens are used entirely for industrial applications, eg coal briquetting, paints and mastic production etc. They are also specified by both softening point and penetration tests but are designated by a softening point range only, and a prefix H; eg H80/90 is a hard grade bitumen with a softening point between 80°C and 90°C. The penetration index varies from 0 to + 2. Table 4 of BS 3690 : Part 2 details the specification requirements of hard grade bitumens and has been reproduced here in table 5.3.

Property	Test method	Grade of bitumen								
	BS 2000:	15 pen	25 pen	35 pen	50 pen	70 pen	100 pen	200 pen	300 pen	450 pen
Penetration @ 25 °C dmm	Part 49	15±5	25±5	35±7	50±10	70±10	100±20	200±30	300±45	450±65
Softening point °C	Part 58	63-76	57-69	52-64	47-58	44-54	41-51	33-42	30-39	25-34
Loss on heating for 5 h at 163°C,										
Loss by mass % max	Part 45	0.1	0.2	0.2	0.2	0.2	0.5	0.5	1.0	1.0
drop in penetration % max		20	20	20	20	20	20	20	25	25
Solubility in trichloroethylene, by mass % min	Part 47	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5

Table 5.1 — BS 3690: Part 2 Specification for penetration grade bitumens[9]

Property		Test method	Grade of bitumen					
		BS 2000:	75/30	85/25	85/40	95/25	105/35	115/15
Softening point	°C	Part 58	75±5	85±5	85±5	95±5	105±5	115±5
Penetration @ 25 °C	dmm	Part 49	30±5	25±5	40±5	25±5	35±5	15±5
Loss on heating for 5 h at 163°C,	loss by mass % max	Part 45	0.2	0.2	0.5	0.2	0.5	0.2
Solubility in trichloroethylene,	by mass % min	Part 47	99.5	99.5	99.5	99.5	99.5	99.5

Table 5.2 — BS 3690: Part 2 Specification for oxidised grade bitumens[9]

Photograph 5.3 — Standard tar viscometer

5.1.4 Cutback bitumens

Cutback bitumens are manufactured by blending usually 100 pen or 200 pen bitumen with kerosene to comply with a viscosity specification. In the UK cutback bitumens are specified and designated by the flow time through a standard tar viscometer (STV)(10) as shown in photograph 5.3. Three grades are available, 50 seconds, 100 seconds and 200 seconds. The majority of cutback bitumen is used in road maintenance.

Table 2 of BS 3690 : Part 2 details the specification requirements of cutback bitumens and this table has been reproduced here in table 5.4. In addition to viscosity and solubility, cutback bitumens have to comply with a distillation specification(11) and a penetration requirement on the residual bitumen. This ensures that during application and in service the diluent will evaporate at a consistent and predictable rate and that the residual bitumen will have the appropriate properties.

The suffix X on the Shelphalt range of cutback bitumens indicates that they have been doped with a specially formulated heat stable passive adhesion agent. This additive assists 'wetting' of the substrate and resists stripping of the binder in the presence of water.

There is again a difference between the cutback specifications contained in Parts 1 and 2 of BS 3690. A third grade of cutback is specified for road use, ie 200 second grade, whereas only two are used for industrial purposes. Also, the viscosity specifications for 100 second grade are different in the two parts, ie 100 ± 20 s for road purposes compared to 100 ± 30 s for industrial uses.

5.1.5 The penetration test IP 49, ASTM D5, BS 2000 : Part 49

The penetration of a sharp object into a material is the usual criterion of consistency. This is the principle of the well known penetration test for bitumen which was originally published in 1889. In the form standardised by the ASTM it subsequently became the most frequently used test method. In this test a needle of specified dimensions is allowed to penetrate into a sample of bitumen, under a known load (100 g), at a fixed temperature (25°C), for a known time (5 seconds) (see photograph 5.1). The distance the needle penetrates, in units of decimillimetre, dmm (0.1 mm), is termed the penetration. Therefore the greater the penetration of the needle the softer the bitumen. Penetrations less than 2 and greater than 500 cannot be determined with accuracy and even within this range the specified procedure has to be followed closely to obtain reliable results. This test is the basis upon which penetration grade bitumens are classified into standard penetration ranges.

For each test three individual measurements of penetration are made. The average of the three values is recorded to the nearest whole unit. The recorded penetration is reported if the difference between the individual three measurements does not exceed a specified limit.

The acceptable repeatability and reproducibility quoted in IP 49 for the penetration test are as follows:

- *Repeatability*
  If the penetration is less than 50 - 1 dmm
  If the penetration is greater than 50 - 3% of the mean of the two results
- *Reproducibility*
  If the penetration is less than 50 - 4 dmm
  If the penetration is greater than 50 - 8% of the mean of the two results.

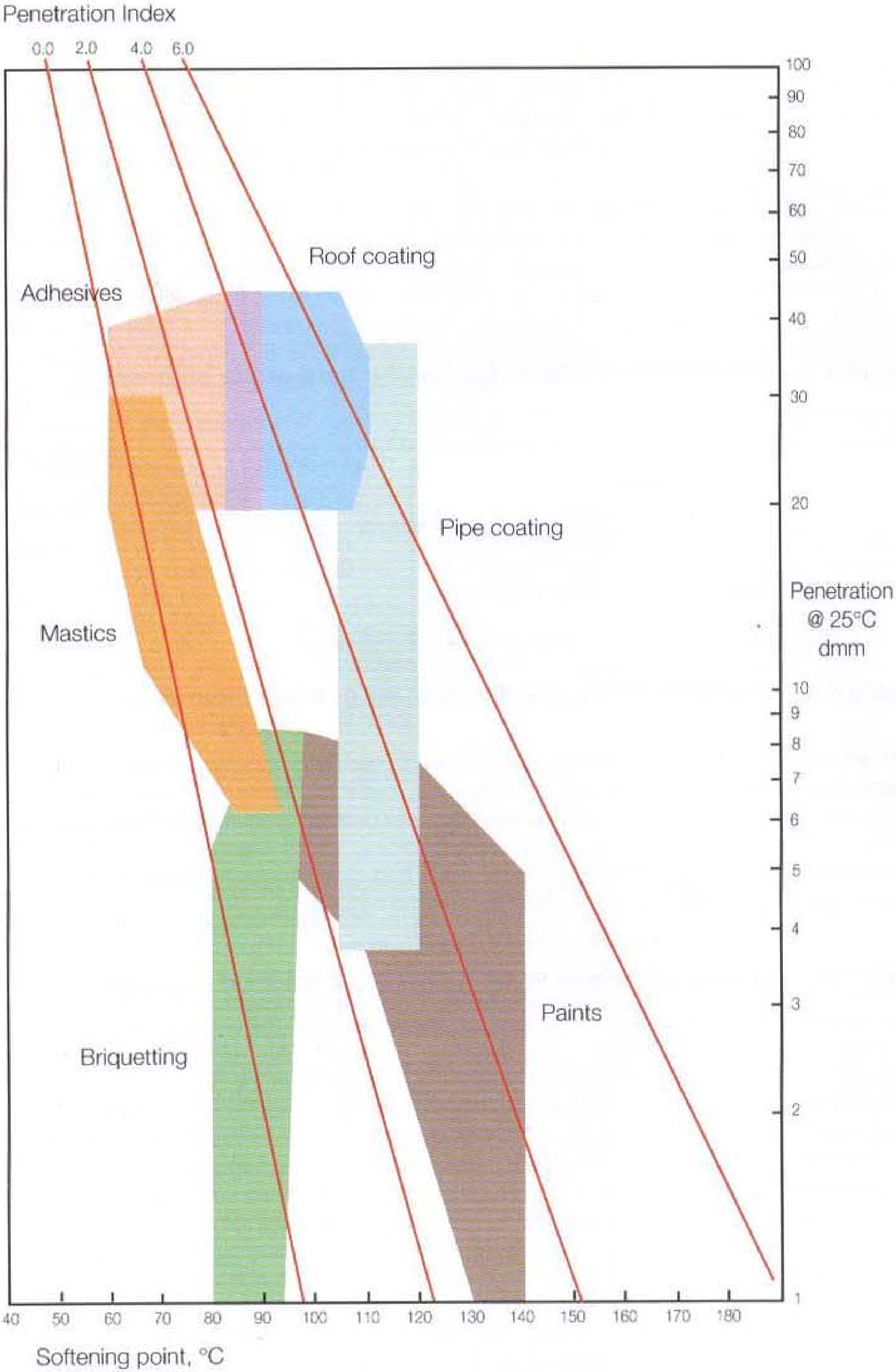


Figure 5.1 — Properties required for industrial applications of bitumen

Property		Test method	Grade of bitumen	
		BS 2000	H80/90	H100/120
Softening point,	0°C	Part 58	85 ± 5	110 ± 10
Penetration at 25°	dmm	Part 49	9 ± 3	6 ± 4
Loss on heating for 5 h at 163°C, loss by mass	% max	Part 45	0.05	0.05
Solubility in trichloroethylene, by mass	% min	Part 47	99.5	99.5

Table 5.3 — BS 3690: Part 2 Specification for hard grade bitumens(9)

Property		Test method	Grade of cutback	
		BS 2000	50 second	100 second
Viscosity (STV) at 40°C,	10mm cup, seconds	Part 72	50 ± 10	100 ± 30
Distillate to 225°C,	% by volume max	Part 27	1	1
to 360°C,	% by volume max		11 ± 3	9 ± 3
Penetration at 25°C of residue,	dmm	Part 49	100 to 350	100 to 350
Solubility in trichloroethylene,	by mass % min	Part 47	99.5	99.5

Table 5.4 — BS 3690: Part 2 Specification for cutback bitumens(9)

It is essential that the test methods are followed precisely, as even a slight variation can cause large differences in the result. The most common errors are: poor sampling and sample preparation; badly maintained apparatus and needles; and incorrect temperature and timing. Temperature control is critical, control to ± 0.1°C is essential. Needles must be checked regularly for straightness, correct profile and cleanliness. Automatic timing devices are needed for accuracy but these must be checked regularly.

5.1.6 The softening point test IP 58, ASTM D 36, BS 2000 : Part 58

The softening point of a bitumen is used as an indication of the temperature at which the bitumen begins to show fluidity. The softening point test determines the temperature at which a certain consistency is reached. Essentially the temperature of a sample is raised at a constant rate and read when the bitumen has undergone a specified deformation. The test most commonly used is the softening point (ring and ball) test. In this test a steel ball (3.5 g) is placed on a sample of bitumen contained in a brass ring which is suspended in a water or glycerine bath (see photograph 5.2). Water is used for bitumen with a softening point of 80°C or below, and glycerine is used for softening points greater than 80°C. The bath temperature is raised at 5°C per minute, the bitumen softens and eventually deforms slowly as the ball falls through the ring. At the moment the bitumen and steel ball touch a base plate 25 mm below the ring, the temperature of the water is recorded. The test is performed in duplicate and the mean of the two measured temperatures is reported, to the nearest 0.2°C for a penetration grade bitumen and 0.5°C for an oxidised bitumen. If the difference between the two results exceeds 1.0°C, the test must be repeated. The reported temperature is designated the softening point of the bitumen, and represents an equi-viscous temperature. In the ASTM version of the softening point test the bath is not stirred, whereas in the IP version the water or glycerine is stirred; hence the softening points determined by using these two methods differ. As a consequence the ASTM results are generally 1.5°C higher than for the IP or BS method(12).

As with the penetration test, the procedure for carrying out the softening point test must be followed precisely to obtain accurate results. Sample preparation, rate of heating, and accuracy of temperature measurement are critical. For example it has been shown(13) that varying the heating rate from 4.5°C to 5.5°C, the tolerance permitted by the IP 58 test method, can result in a difference of 1.6°C in the measured softening point. Automatic softening point machines are available which ensure close temperature control and which automatically record the result at the end of the test.

The acceptable repeatability and reproducibility quoted in IP 58 for the softening point test are as follows:

- *Repeatability*

		°C
For penetration grade bitumens		1.0
For oxidised bitumens:		
	Under 80	1.5
	Over 80 - 100	2.0
	Over 100 - 120	2.5
	Over 120 - 140	3.0

- *Reproducibility*

For penetration grade bitumens	2.5
For oxidised bitumens	5.5

The consistency of bitumen at the softening point temperature has been measured by Pfeiffer and Van Doormaal(14) in terms of penetration. Using a specifically prepared, extra-long penetration needle they found a value of 800 pen for many, but not all, bitumens. The exact value was found to vary with penetration index and wax content. It has also been demonstrated by direct measurement that the viscosity at the softening point temperature of the majority of bitumens is 1200 Pa.s (12,000 poise).

Three types of softening point test have been used. The temperature obtained is dependent upon the bitumen reaching a specific consistency which, expressed in terms of penetration value, is roughly as follows:

Krämer and Sarnow	200 dmm
ASTM (ring and ball)	800 dmm
Ubbelohde	3000 dmm

5.1.7 Viscosity, STV IP72

A metal cup is filled to a mark with cutback bitumen and brought to 40 ± 0.1°C for the required time. The cup has a ten millimetre orifice in its base which is covered by a smooth ball. When the temperature has equilibrated the ball is lifted and the sample allowed to flow through the orifice. The flow is timed for 50 cm^3 of sample and the result is the viscosity in seconds, see photograph 5.3.

Although this is a simple test, care is needed in sample preparation and temperature control for consistent results. This is reflected in the precision of the method where, for grades within BS 3690, reproducibility is given as ten per cent of the mean.

5.2 Specification tests relating to quality

In addition to the tests which describe the rheological properties of the bitumen, most specifications contain requirements which describe the 'purity' of the binder. Solubility in a powerful solvent ensures that coke particles, which gradually form in all storage tanks that hold bitumen, are kept to a minimum and also ensures that lake asphalt which contains finely dispersed mineral matter cannot be supplied as bitumen. Similarly the loss-on-heating (LOH) test measures the amount of volatile material present and gives safeguards with respect to bitumen performance during application and in service. It also ensures that manufacturers cannot incorporate volatile fractions into bitumen.

5.2.1 Solubility test IP47, ASTM D2042, DIN1995 U9

The solubility test is used primarily to restrict the amount of coke and/or mineral matter in bitumen. Because of the simplicity of the test, most methods are very similar and are to all intents directly comparable. Bitumen is defined(8,9) as being soluble in trichloroethylene. Previously it was defined as being soluble in carbon disulphide but because of the special precautions needed when using this solvent it is rarely used. The nature of the product requires the use of very aggressive solvents which have included:

carbon disulphide
benzene
dichloromethane
trichloroethane
trichloroethylene
toluene.

Trichloroethylene is in common usage at present but because of concern over the toxicity of halogenated hydrocarbons there is pressure to replace it with an aromatic hydrocarbon such as toluene or xylene.

The sample is dissolved in solvent and filtered through a layer of powdered glass in a sintered crucible. The insoluble material is washed, dried and weighed.

The solubility of modified bitumens may require the use of a modified method or the use of solvent mixtures to ensure the total dissolution of both bitumen and polymer additive.

5.2.2 Loss on heating test IP45, ASTMD6, DIN1995 U12

Bitumens are manufactured to meet certain specifications on delivery to the customer. Their performance, however, depends on their properties after processing and application which the user must take into account when selecting the grade for this process. For example, it is well known that in the asphalt manufacturing process, where the binder is exposed to massive contact with air, a penetration bitumen hardens by about 30 per cent of its penetration value. To avoid excessive hardening and increased brittleness, it is necessary to control the ageing properties of the bitumen as well as the properties on delivery.

The loss on heating test controls the volatility of a bitumen and determines the degree to which it may have been 'cut' by a low molecular weight flux. In addition, it was an early attempt to simulate the change in properties of a bitumen in an asphalt plant.

A fifty gram sample of bitumen in a film approximately 5 mm deep is heated in moving air for five hours at 163°C and the loss in weight is determined.

In an attempt to assess the susceptibility to hardening as well as loss of volatiles, the Thin Film Oven Test, TFOT, (ASTM D1754) was devised. In this test a three-millimetre bitumen film is heated in a similar oven at 163°C for five hours.

A third test has recently been introduced to assess the effect of heat and air on a moving film of bitumen (ASTM D2872), the Rolling Thin Film Oven Test, RTFOT. A sample of bitumen is placed into a glass container fitted with an internal rim. The container is placed on its side and rotated in an oven at 163°C for 75 minutes. An air blast is directed over the sample film once per revolution.

In all these tests the properties of the resultant bitumen compared with those of the original give a measure of the effect of the treatment. Penetration or viscosity changes can be measured. Of the three tests the first is used widely for specification purposes. The TFOT is popular on mainland Europe, whereas RTFOT is used in the UK, to assess the effects of the manufacturing process for road materials on penetration grade bitumens.

For oxidised bitumen no tests have been shown to adequately predict the effects of hardening. This is possibly due to the low temperatures of the tests and/or because of skin formation on the samples.

5.2.3 Distillation

Bitumens diluted with low-boiling hydrocarbons are known as cut-back bitumens or cutback. Typically they are diluted with 10 to 20 per cent, but maybe up to 50 per cent, of kerosine or white spirit. The diluent lowers the viscosity to the point that the product can easily be applied by spray or brush at moderate temperature. It is important that the viscosity at the surface temperature should be low enough for the cutback to wet, eg chippings, quickly but high enough for them to be held firmly. Once applied, the diluent evaporates leaving the base bitumen firmly holding the chippings. The rate of evaporation of the diluent depends upon the boiling range of diluent.

For rapid curing (ASTM designated RC) grades a boiling range of 140-200°C is required. For medium curing (MC) grades the preferred boiling range is 210-260°C. For some uses a high boiling kerosene with a range of 150-250°C may be used.

The main methods for testing of cutbacks are viscosity determinations by routine methods (ASTM D-88 D2170) and a distillation technique to check the nature of the diluent.

5.2.3.1 Distillation test IP27, BS 2000 : Part 27(11)

This test controls the quality of the volatile fraction in the cutback and, therefore, the rate of binder 'cure' once it is applied. As well as measuring the amount present it also controls volatility and ensures that the cutback will harden at a predictable rate and to a predictable final hardness. The properties of the bitumen after distillation are not necessarily characteristic of the base bitumen used as it is not possible to remove the volatile fraction completely.

Two hundred millilitres of sample are distilled at a controlled rate to a temperature of 260°C and the volumes of distillate obtained at specified temperatures are recorded. The residue from the distillation is subsequently tested for penetration.

5.3 Safety testing of bitumens

In common with all petroleum products safety testing is carried out on all bitumens for either transportation, storage or application purposes.

5.3.1 Flash point

There are many types of flash point depending on the properties of the test material. For bitumens both Pensky-Martens(15) and Cleveland(16) flash points are used.

5.3.1.1 Pensky-Martens closed cup(15) (PMCC), IP IP34, ASTM D93

Approximately 80 g of the product is placed into a brass cup and a close-fitting lid attached. The sample is stirred while the temperature is raised at 5°C per minute and tested every 2°C. A lever is turned which opens a window in the lid and lowers a small flame through. The flash point is the temperature at which vapour from the sample first ignites.

5.3.1.2 Cleveland open cup(16) (COC), IP36, ASTM D92

Approximately 80 g of product is placed into a brass cup and heated at the rate of 5°C per minute. Every 2°C a flame is moved across the top of the cup until the flash point is reached.

5.3.1.3 Modified Abel(17) IP113

This test is used for cutback bitumens. It is very similar in appearance to the PMCC but because of the lower flash points has flame-proofed construction.

5.3.1.4 Abel flash point(18), IP170

This test is used for low flash point materials such as petroleum spirits and kerosenes. Shelphalt Primer is tested using this procedure which involves heating the sample in a water jacket and stirring manually.

All flash points must be corrected for atmospheric pressure.

Open cup flash points, because the hot vapour is not confined, always give higher flash points than closed cup techniques. For bitumens this difference is around 40-100°C.

Grade	Flash point, COC (°C)
Penetration grades	
300 pen	250 - 300
200 pen	250 - 320
100 pen	270 - 310
50 pen	250 - 320
25 pen	240 - 300
Hard grades	
H100/120	280 - 340
H80/90	280 - 340
Oxidised grades	
R75/30	270 - 300
R85/25	280 - 300
R85/40	290 - 300
R95/25	290 - 300
R105/35	280 - 300
R115/15	270 - 310

Table 5.5 — Typical flash points for some bitumens

Typical flash points for a range of bitumens are given in table 5.5. In considering flash point it is important to understand the significance of the data. All flash point methods are completely arbitrary and provide no fundamental data from the test material. Flash point measures only the response of the sample to heat and flame under controlled laboratory conditions. It is a purely comparative method which is used almost exclusively for the purposes of transportation and safety regulations. In assessing the overall flammability hazard of a material, flash point is only one of a number of properties which must be considered. Flash point alone cannot be translated into real situations and it could be dangerous to attempt to do so.

5.3.2 Fire point

The fire point is the temperature at which the sample will support a flame for a period of at least five seconds. This test is carried out in an open cup flash point apparatus (either COC or Pensky-Martens Open Cup, PMOC) and is usually done on the same sample immediately following a flash point determination. Fire point is not included in any standards but is mentioned for completeness.

5.3.3 Autoignition temperature

Autoignition is defined as the temperature at which a substance will ignite in the absence of an external ignition source such as a flame or spark. It is subjective and is highly dependent on the test method used. Probably the best known test method is ASTM E659(19) in which a small sample is introduced into a preheated glass flask. The flask is observed in darkness for ten minutes and ignition is deemed to have occurred if a significant temperature rise or a flame is observed. The test conditions take into account the 'induction period' observed in many substances before auto ignition occurs.

Although there are few published data, the auto ignition temperature of bitumen is around 400°C(20,21). The temperature is largely independent of bitumen grade although the softer

Grade	Temperature (°C) at viscosity in Pa.s (0.1 P)					
	20	5	2	1	0.2	0.1
Penetration grades						
200 pen	70	85	97	108	138	156
100 pen	78	94	106	117	149	166
70 pen	85	101	113	123	155	172
50 pen	90	105	118	128	160	177
35 pen	95	111	124	135	168	185
25 pen	101	117	130	142	175	193
15 pen	111	128	141	153	186	205
Hard grades						
H80/90	133	150	163	172	206	224
H100/120	154	170	184	195	227	245
Oxidised grades						
R85/25	126	144	157	169	205	225
R85/40	127	144	157	168	201	220
R95/25	143	161	176	188	225	245
R115/15	166	186	202	216	(256)	—
R135/10	190	210	225	240	—	—

Table 5.6 — Typical equiviscous temperatures for some bitumen grades

grade temperatures are slightly lower. It has been known for autoignition temperatures to be exeeded in bitumen boilers during roofing operations: this practice is highly dangerous, as well as having a deleterious effect on the properties of the bitumen.

5.4 Performance-related tests on bitumen

Other tests which are sometimes specified fall broadly into the categories of either rheology or stability related. The most frequently used tests are described here.

5.4.1 Rheological test methods

5.4.1.1 Viscosity

As well as penetration and softening point which are used to characterise the grade of bitumen both high temperature and low temperature properties of oxidised grades are important. Many products which incorporate oxidised bitumen involve the application of a thin layer (approximately 0.5 - 5 mm thick) to a carrier sheet. The film thickness is governed by the consistency and rate of hardening of the bitumen. The rate of hardening is controlled, all other things being equal, by the Penetration Index (PI) which is in turn characterised largely by the choice of grade. Consistency is another term for viscosity and can vary to some extent within a grade. The bitumen manufacturer ensures that viscosity is constant at the required application temperatures in order that the user can operate his plant without the need for constant checking and adjustment.

Viscosity can be measured in a variety of ways. Whilst viscosity is normally expressed as x Poise at y°C, a more convenient and frequently used form is y°C at x Poise. This is termed the Equi-Viscous Temperature (EVT) and is usually quoted at 200, 20 and 2 Poise (20, 2 and 0.2 Pa.s). Typical EVTs for some grades are shown in table 5.6 and figure 5.2.

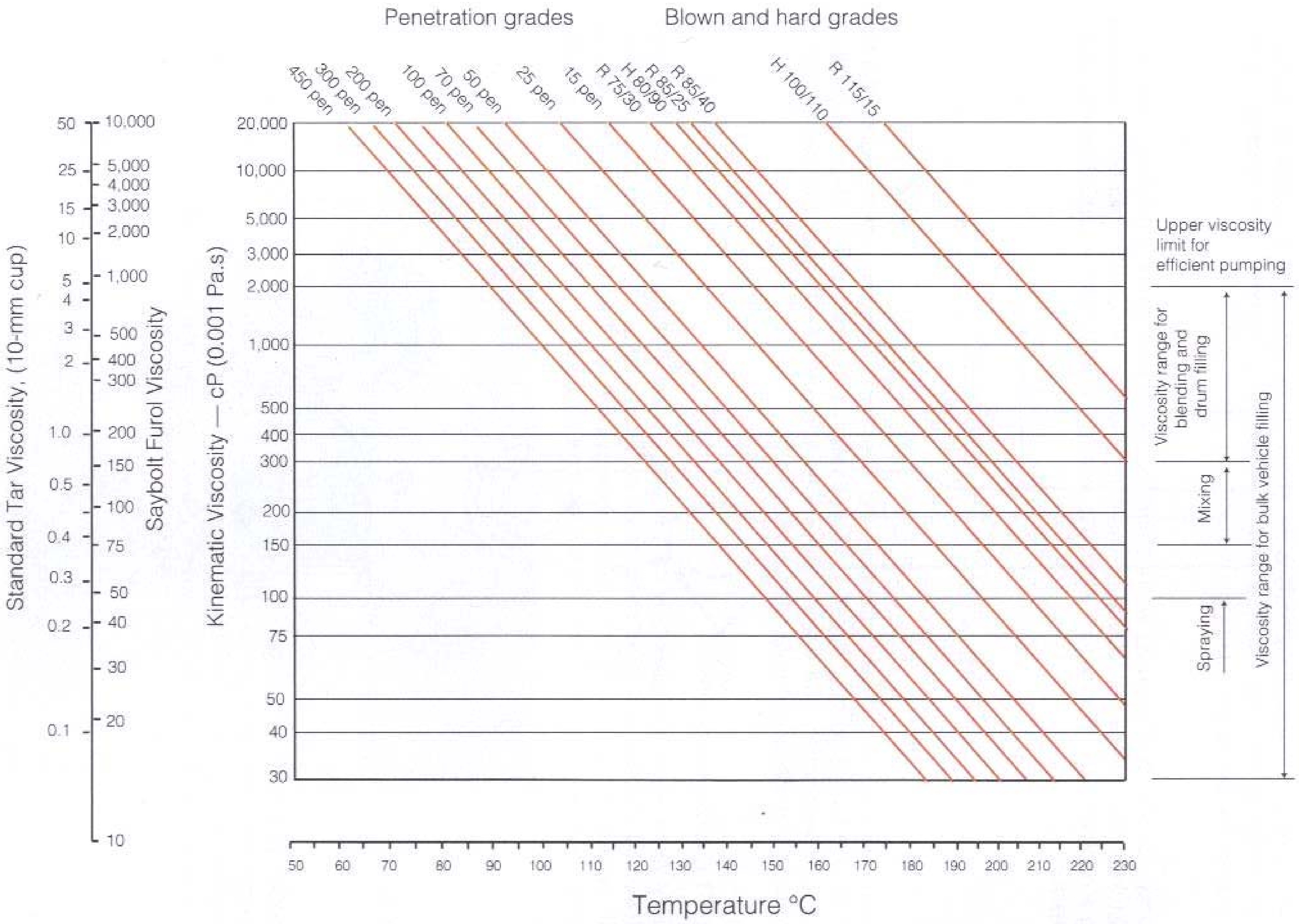


Figure 5.2 — Typical viscosity temperature chart for bitumens

The basic unit of viscosity is the Pascal second (Pa.s). The absolute or dynamic viscosity of a bitumen measured in Pascal seconds is the shear stress applied to a sample of bitumen in Pascals divided by the shear rate per second; 1 Pa.s = 10 P (poise). The absolute viscosity of a bitumen can be measured using a sliding plate viscometer(22).

Viscosity can also be measured in units of m^2/s, /or more commonly mm^2/s (1 mm^2/s = 1 centistoke (cSt)). These units relate to kinematic viscosity. Kinematic viscosity is measured using a capillary tube viscometer. Kinematic viscosity is related to dynamic viscosity by the expression:

$$\text{Kinematic viscosity} = \frac{\text{dynamic viscosity}}{\text{density}}$$

For many purposes it is usual to measure the viscosity of a bitumen by measuring the time required for a fixed quantity of material to flow through a standard orifice. These methods are useful for specification and comparative purposes and, if required, the results can be converted into more fundamental units of viscosity.

5.4.1.1.1 Capillary viscometers

Capillary viscometers are essentially narrow glass tubes through which the bitumen flows. The tube has narrower and wider parts and is provided with two or more marks to indicate a certain volume of flow (see figure 5.3 and photograph 5.4). The measurement of kinematic viscosity is made by timing the flow of bitumen through a glass capillary viscometer at a given

Photograph 5.4 — A capillary viscometer

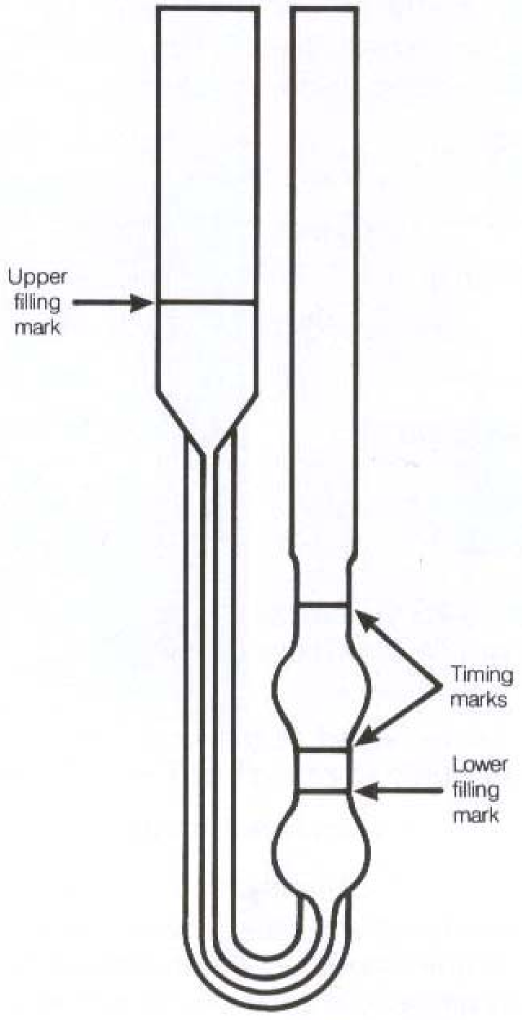


Figure 5.3 — U-tube reverse flow viscometer

temperature. Each viscometer is calibrated and the product of flow time and viscometer calibration factor gives the kinematic viscosity in mm^2/s. Temperature/viscosity curves are obtained by measuring kinematic viscosity at a number of different temperatures, and plotting the viscosity on a logarithmic scale against temperature on a linear scale (see figure 5.2).

5.4.1.1.2 Cup viscometers

Cutback bitumens and emulsions are both specified by viscosity. A cup viscometer is the simplest means of comparing the viscosity of similar bitumens in the range 0.01 to 100 Pa.s. Cutback bitumens are specified using the Standard Tar Viscometer(10) (STV) (see photograph 5.3). The viscosity of emulsions can be determined using either the Engler viscometer or the

Redwood II viscometer(23). In these tests a metal cup is filled with cutback bitumen or emulsion at a standard temperature, and the time is recorded in seconds for a standard volume of material to flow out through the orifice in the bottom of the cup.

There are several cup type viscometers available which differ mainly in the size of opening through which the bitumen is drained. Since the stress is provided by gravity, the absolute viscosity, η, in Pa.s is given by:

$$\eta = \text{flow time} \times \text{density} \times \text{constant}$$

where: the flow time is expressed in seconds

density in g/ml

the constant depends on the instrument used, viz:

viscometer	*constant*
Saybolt Universal	0.000218
Redwood	0.000247
Saybolt Furol	0.00218
Redwood II	0.00247
Engler	0.00758
Standard Tar Viscometer (4 mm)	0.0132
Standard Tar Viscometer (10 mm)	0.400

The test results may also be expressed as the kinematic viscosity, υ, in m^2s^{-1}, or more commonly mm^2s^{-1}, is defined as:

$$\upsilon = \text{flow time} \times \text{constant}$$

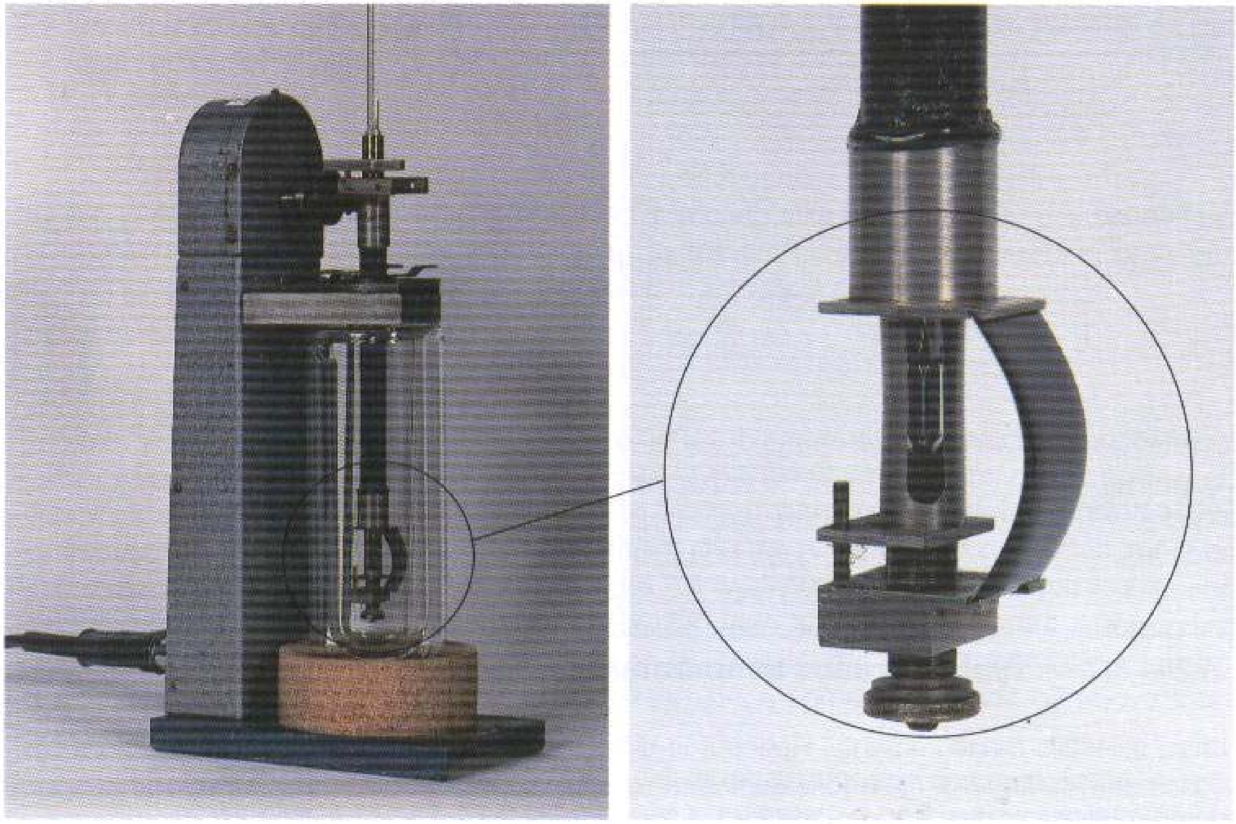
Table 12.2 in chapter twelve gives a number of conversion factors for comparison of viscosities measured by different methods. Some materials (including many bitumen emulsions) show non-Newtonian viscous behaviour, ie their apparent viscosity depends on shear rate. Since the shear rate is variable in all orifice viscometers, conversion factors can not be used with non-Newtonian materials.

5.4.1.2 Low temperature tests

5.4.1.2.1 The Fraass breaking point test IP80

Bitumen used for roofing has to withstand low temperatures both in service and during application. If the bitumen becomes too brittle and cracks under the strain caused by movement of the substrate or even unwinding a roll of felt, it may allow moisture into the building.

The Fraass breaking point test(24) (IP 80) is one of very few tests which can be used to describe the behaviour of bitumens at very low temperature (as low as -30°C). The test was developed by A Fraass(25) in 1937 and it is essentially a research method which determines the temperature at which the bitumen reaches a critical stiffness and cracks. However, a number of countries with very low winter temperatures, for example Canada, Finland, Norway and Sweden, have maximum allowable Fraass temperatures for individual grades of bitumen.



Photograph 5.5 — The Fraass breaking point test

In the Fraass test (see photograph 5.5) a steel plaque 41 mm x 20 mm coated with 0.5 mm of bitumen is slowly flexed and released. The temperature of the plaque is reduced at 1°C per minute until the bitumen reaches a critical stiffness and cracks. The temperature at which the sample cracks is termed the breaking point and represents an equi-viscous or equi-stiffness temperature. It has been shown(26) that at fracture the bitumen has a stiffness of 2.1 x 10^9 Pa(26) which is approaching the maximum stiffness of 2.7 x 10^9 Pa. For penetration grade bitumens the Fraass temperature can be predicted from penetration and softening point because it is equivalent to the temperature at which the bitumen has a penetration of 1.25 for a bitumen with a PI of zero.

Here again it is essential that the test method is followed exactly if large differences in results are to be avoided. The most common errors are: poor sampling and sample preparation and in particular overheating of the plaque, incorrect cooling rate, poor temperature control and uneven flexing of the test specimen.

Table 5.7 shows typical values for a range of bitumens.

5.4.1.2.2 Ductility test ASTM D113, IP32, DIN 1995 U7

The ductility test(27) is used to describe the ductile behaviour of a bitumen at, more or less, ambient temperature and is believed to reflect the homogeneity of the bitumen and its ability to flow. However, it is an empirical test whose result cannot be derived or calculated from

Grade	Fraass temperature (°C)
Penetration grades	
450 pen	-20 to -30
300 pen	-20 to -25
200 pen	-20 to -25
100 pen	-15 to -20
50 pen	-10 to -15
25 pen	-5 to -10
Hard grades	
H100/120	+10 to +20
H80/90	0 to +10
Oxidised grades	
R75/30	-10 to -15
R85/25	-10 to -15
R85/40	-15 to -20
R105/35	-15 to -25
R115/15	0 to -10

Table 5.7 — Typical Fraass temperatures for standard bitumen grades

basic scientific measurement. Hence it is difficult to appreciate the significance of the test. This is particularly the case for penetration grades softer than 50 pen which invariably give ductility results of over 100cm and for oxidised grades which give results typically of less than ten cm. Nevertheless, many countries and/or customers include ductility in their specifications for both penetration and oxidised grades.

A dumbell-shaped sample is placed in a water bath and allowed to equilibrate. The sample is stretched at 50 mm/min until it breaks and the distance of rupture is reported as the ductility in centimetres. It is usually carried out at 25°C and 50 mm/min. If other conditions are used these must be specified along with the result.

5.4.1.2.3 Cold bending test(28) DIN 52123

A strip of bitumen approximately three millimetres thick is bent through 180 degrees over a mandrel of 30 mm diameter within five seconds. If it cracks or breaks then a fail is reported along with the test temperature. The sample is cooled and the test repeated every 5°C until failure.

The practical significance of this test is doubtful and the reproducibility very poor. Nevertheless it is popular with roofing felt manufacturers in some European countries.

5.4.2 Stability-related tests

In the early days, most of the methods used to produce the saturant grades for roofing felt and coating were developed by the ever popular trial and error method. Various natural asphalts were heated and mixed with fractions of petroleum oil to make the required consistency. At times, vegetable and animal oils were used in place of petroleum oils, and resin was mixed with soft bitumen to make coating grades. Many of the mixtures were unstable and exuded oils into the mineral aggregate surface, producing dark stains.

The following tests are all related to the chemical constitution and chemical 'balance' of the individual components within the bitumen.

5.4.2.1 Staining tests

Staining is a phenomenon sometimes observed in roofing felts and shingles. It is caused by oily components within the bitumen migrating to the felt surface and absorbing onto the mineral coating causing it to darken (see section 8.1.3.11.2).

5.4.2.1.1 Stain index test(29) ASTM D1328-86

The stain index test measures the tendency of a hot bitumen to stain through successive layers of paper. 30 discs are cut from a sheet of paper and held tightly, one on top of another, in a metal holder. The papers are in contact with the bitumen at 99°C for the required period after which the holder is dismantled and the papers checked. The number of papers which are marked is called the stain index. A weakness of this test is that it does not give any requirements for the type of paper to be used and hence different laboratories obtain very different values. Also, no guidance is given to the acceptability of materials. Clearly, results will depend upon the grade tested since some grades will be above their softening points while others are below.

Although still used by some laboratories, this method was withdrawn in 1992 and has been replaced by ASTM D2746.

5.4.2.1.2 Stain index test(30) ASTM D2746

A brass softening point ring is filled with bitumen. The sample is placed on a filter paper and stored at 79.4°C for 120 hours. The diameter of the resulting stain ring is measured. The stain index is the difference between the ring diameter and the stain diameter measured in 64ths of an inch.

5.4.2.2 Oliensis test

This is probably one of the most confused tests in the bitumen industry. Oliensis was a chemist interested in bitumen constitution. There are two tests which bear his name; the compatibility test described below and the 'spot' test described in section 5.5.4.

5.4.2.2.1 Oliensis compatibility test(31) ASTM D1370-84

For coating saturated felts, it is necessary that the coating and the saturant bitumens are compatible. That is, troubles such as delamination, strike-through, exudation from pinholes and edges, etc., should not be experienced in practice. It is known that when some combinations of penetration and blown grades of bitumens are placed in contact, an oily phase can separate at the interface. This arises from the different constitutions of the two grades and in general increases with increasing difference in PI and hardness between the grades. It is found for instance that using conventional saturating grades (Mexphalte 100 or 200) compatibility problems are rarely found with Mexphaltes R85/25 or R115/15 but may be experienced with Mexphaltes R85/40 or R105/35 as coating.

The most widely used test for compatibility is the Oliensis test. In this test, the surface of a sample of the coating grade bitumen is covered with talc and a spot of the saturating grade bitumen is placed on the talc. The spot is observed after storage for a given time at a controlled temperature and the width of the stain ring (if any) in the talc is measured. The greater the width of the ring, the greater the exudation and therefore the incompatibility between the two bitumens. The test can be carried out at different storage temperatures for different times, and as the ring width depends on both time and temperature (increasing with both), these variables must be specified for the results to be meaningful. Three days at 43°C is often taken as a standard test condition. (Other test variables which must be controlled to get consistent comparable results are the amount, grading and dryness of the talc).

It is generally agreed that there is quite a good relationship between the results of the Oliensis test and the occurrence of incompatibility in the roofing felt. This is certainly so in the sense that if the ring in the Oliensis test (standard conditions as above) is negligible or non-existent, then incompatibility will not cause problems in practice. It is not possible, however, to lay down a precise value of the ring width outside of which problems will always arise. Some roofing felt manufacturers specify a ring width of one millimetre/two millimetres maximum, but rings up to 2 mm will usually be satisfactory in practice and bitumens giving wider rings (three to four millimetres) have been used successfully in cases where the manufacturing technique is good, such as when good quality felt is used and the saturant is well squeezed out before coating.

5.4.2.3 Thermal stability

Because of their higher viscosities oxidised bitumens are handled at higher temperatures than penetration grades, typically within the range 180 to 220°C and for some applications they may be held at even higher temperatures for extended periods. Although very tolerant of mishandling, bitumens can oxidise and harden at high temperatures and, in extreme cases, can 'crack' and soften. Thermal cracking is a normal refinery process used to produce lighter fractions from heavy crudes. In the process molecules are 'cracked' and broken in two, the net result being a volatile, light fraction and a heavy residue. This can also happen to bitumen if it is overheated excessively.

Some catalytically blown bitumens are susceptible to the effects of high temperature which causes the softening point to fall back sometimes by as much as 15 to 29°C. In order to ascertain the susceptibility to fall back, the bitumen may be heated up to 300°C for several hours, followed by penetration and softening point determinations.

In the laboratory the tendency for a bitumen to be thermally unstable is checked by storage at two temperatures. If penetration and softening point measured before and after storage are found to change by more than a few points the bitumen is judged to be unstable and hence unsuitable.

5.5 Constitutional analysis

Chemical constitution within a bitumen is particulary important in a number of specialised areas of application which include the manufacture of emulsions, the production of bitumen/polymer compositions and in mastic asphalt formulations. It is well known that asphaltene and aromatic contents play an important role in stabilising bitumen/SBS polymer systems, see section 7.2.3.3, and the bitumen acid value has a profound effect on the

Grade	Saturates %	Aromatics %	Resins %	Asphaltenes %
Penetration grades				
200 pen	9	59	23	9
100 pen	8	58	23	11
70 pen	8	57	23	12
Oxidised grades				
105/35	23	32	26	19
85/25	11	38	30	21

* By chromatographic separation and gravimetry.
Note that constitution is heavily dependent on the extraction method used.

Table 5.8 — Typical constitutional analysis* of some bitumens

stability of some bitumen emulsions. There are no standards covering constitution and few published test methods although many customers and suppliers use their own in-house procedures.

5.5.1 SARA (saturate, aromatic, resin, asphaltene) analysis

There are a number of variants of this test, eg ASTM D4124, but all are based on solvent extraction and chromatography. A small sample is dissolved in n-heptane and filtered to remove the insoluble asphaltenes. The solution is then passed through a chromatographic column and eluted with successive solvents to release the various fractions - saturates, aromatics and resins. As an alternative technique, thin layer chromatography can be used; however, the overall principle is the same. Some methods measure only the three fractions and assume the difference to be asphaltenes. This assumption may be erroneous as more than 90 to 95 per cent of bitumen is rarely recovered in this type of analysis. For in-house purposes this may be adequate, but problems may arise when comparing results between laboratories. A typical constitutional analysis is shown in table 5.8.

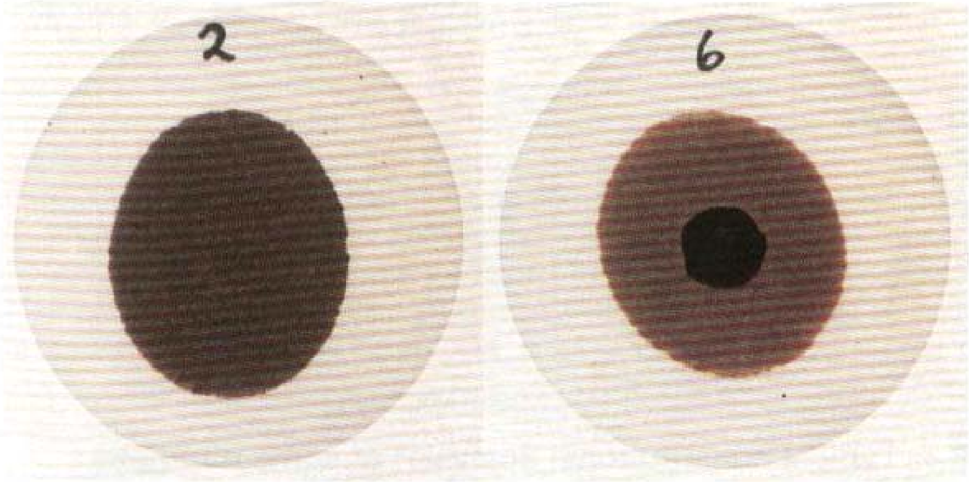
5.5.2 Asphaltene determination(32), IP143, ASTM D3279

For the determination of asphaltene content test method IP 143 has been developed and the use of n-heptane has been internationally accepted, although many literature references quote data using n-pentane.

The sample is dissolved in n-heptane and the insoluble material, consisting of asphaltenes and wax, is filtered out. The waxy material is removed by reflux with hot n-heptane and the asphaltenes isolated by reflux with toluene.

5.5.2.1 Flocculation ratio, AASHTO T102(33)

The flocculation ratio measures the apparent 'stability' of a bitumen in an increasingly paraffinic solvent mixture. The ratio of heptane to xylene is increased until precipitation of asphaltenes is observed. The test result is a function of the peptising ability of the bitumen maltene phase as well as the level of asphaltenes in the sample. As no firm correlation has been established with bitumen behaviour in practice, the test is not very useful, except perhaps for research purposes.



Photograph 5.6 — The Oliensis spot test

5.5.3 *Wax content measurement(34,35) DIN 52015, NF T66-015*

Most bitumens contain a small percentage of waxy constituents, the amount, chemical constitution and consistency of which varies with the origin of the crude oil and the processing route used. The wax content is specified in a number of countries, especially for penetration grades of bitumen used in road construction. The presence of wax in the bitumen changes its rheology as described in section 5.7.3. Wax is never added to a bitumen by the refiner but may be added as a viscosity modifier by an industrial product manufacturer.

There are several methods for determining wax contents, but they are generally based on the same principle. A sample of bitumen is dissolved in a suitable solvent mixture, eg alcohol/ether mixture. The mixture is cooled to, say, -20°C whereupon the paraffinic components become insoluble and precipitate out of solution. The precipitate is filtered and weighed.

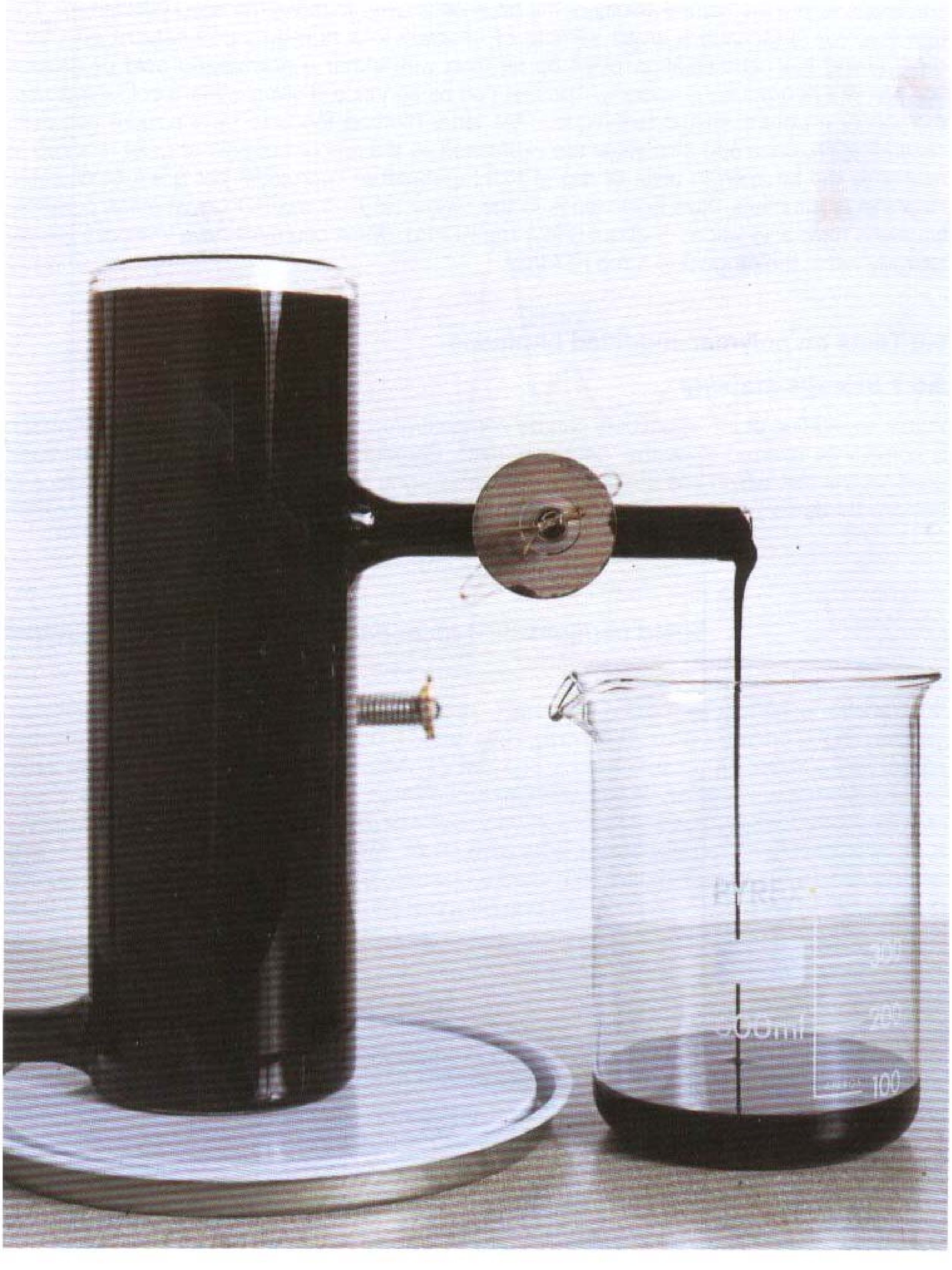
5.5.4 *Oliensis spot test(31)*

A spot of bitumen is placed on a filter paper and several drops of a special solvent are washed over the sample. After a short time the solvent is seen to form a brown ring around the bitumen drop. If a black ring develops within the brown ring the test is deemed to be positive, otherwise it is negative.

This test was developed to detect cracked petroleum residues in bitumen formed during excessive heating of the bitumen. However, it is now known that some crudes produce bitumens which give positive results in this test.

5.5.5 *Acid value, base value, neutralisation value IP 213, BS 2000 : Pt 213, IP 177, ASTM D664, IP 139, BS 2000 : Pt 139, ASTM D974*

The neutralisation value of a bitumen may be of interest, particularly when manufacturing certain types of roofing emulsions which require the use of low acid value bitumens or anionic



Photograph 5.7 — Hot storage test

emulsions where the natural acidity of the bitumen is used to make the soap (emulsifier). The test involves dissolving a small sample of bitumen in a non-aqueous solvent and then determining the neutralisation point by titrating with either a normalised acid or alkaline solution in a non-aqueous solvent. The test can be conducted using either a colour indicator method or a potentiometric technique. The latter method tends to be the more accurate. Neutralisation, base and acid value are expressed as the amount of acid or base required to neutralise the bitumen in units of mg of KOH (potassium hydroxide) per gram of bitumen. Naphthenic bitumens have acid values in the range 1.5 to 5 mg KOH/g whereas paraffinic bitumens have acid values of about 0 to 1 mg KOH/g. Most bitumens have low base values, typically within the range 0 to 1 mg KOH/g.

5.6 Tests on polymer-modified bitumens

5.6.1 Storage stability

Phase separation or incompatibility can be demonstrated by a simple hot storage test, which is sometimes referred to as the 'beer-can' test. Photograph 5.7 shows one storage vessel used for the test which has three discharge arms along its length to enable top, middle and bottom thirds to be obtained separately. Tests are carried out on the top and bottom

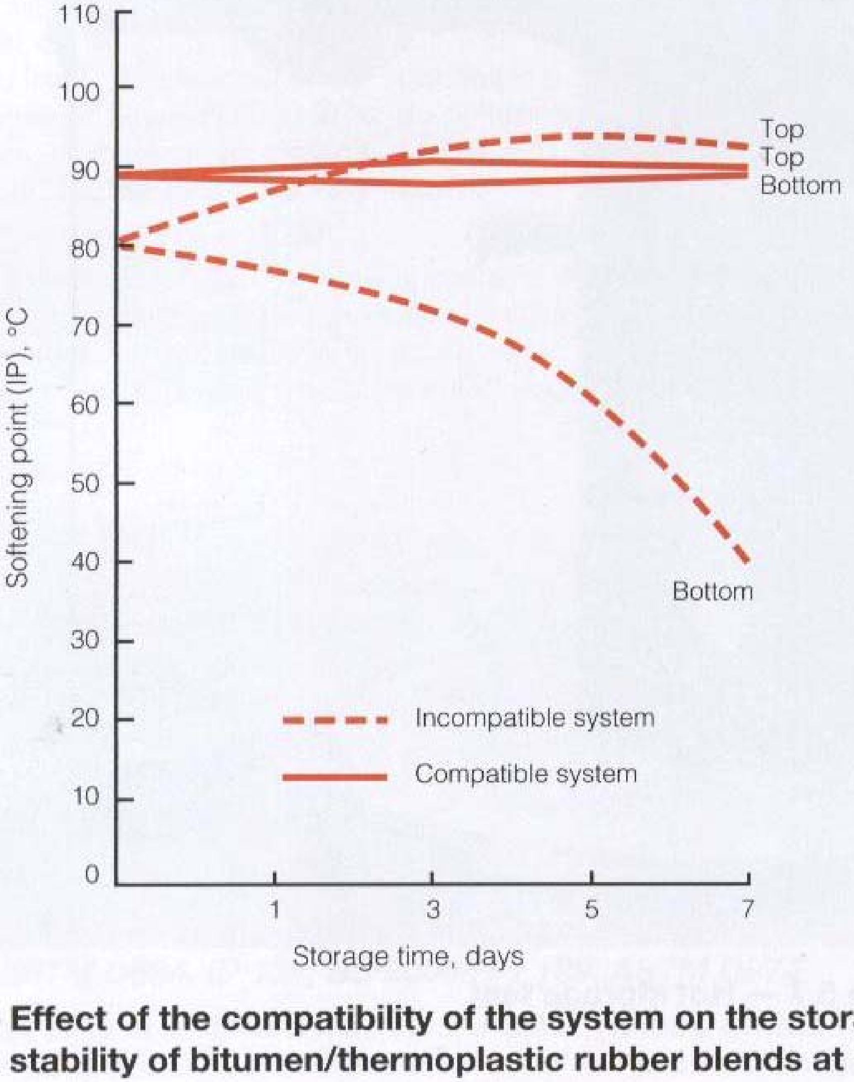


Figure 5.4 — Effect of the compatibility of the system on the storage stability of bitumen/thermoplastic rubber blends at 160°C

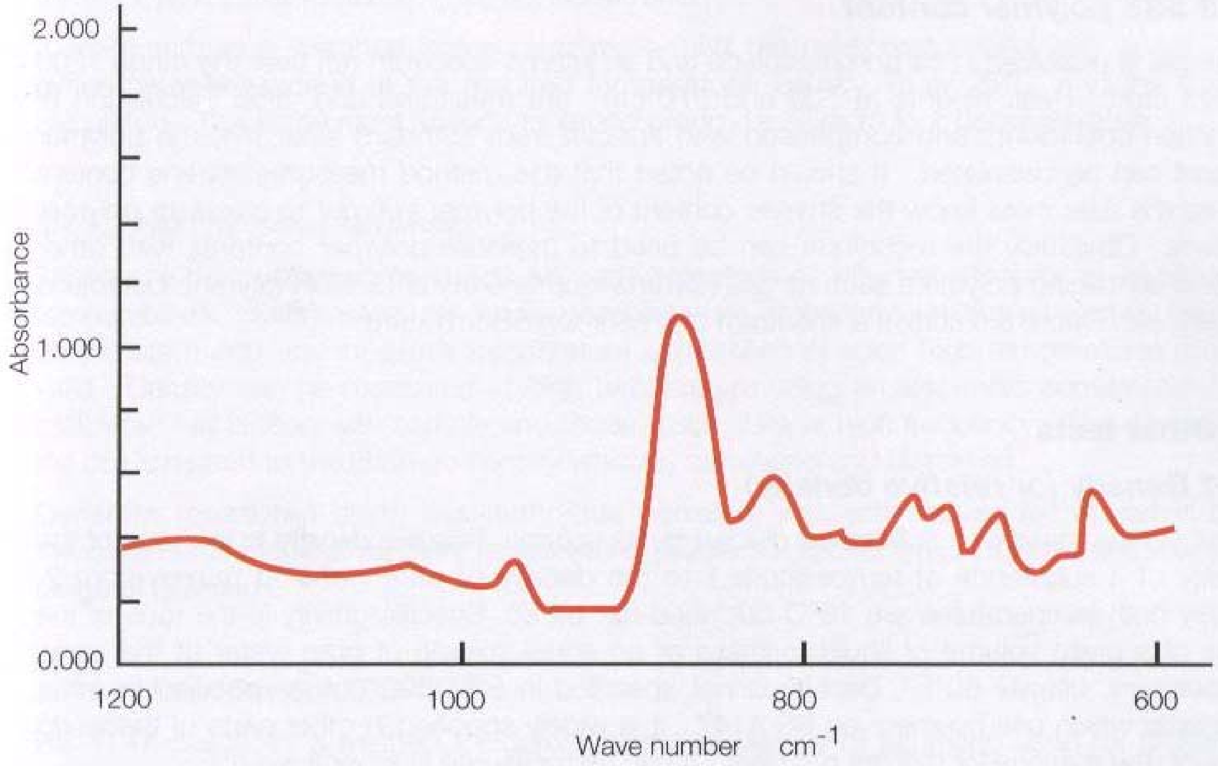


Figure 5.5 — Infrared spectrum of an SBS/bitumen blend

samples whilst the middle sample is discarded. Figure 5.4 shows the numerical difference in softening point of the top and bottom samples of two bitumens containing 7 per cent by mass of SBS thermoplastic rubber after 1, 3, 5 and 7 days storage at 160°C. The results clearly show that the compatible system is extremely stable, whereas the incompatible system has separated dramatically with virtually no polymer remaining in the bottom sample after 7 days. A variation of this is the 'toothpaste tube' test which has been proposed as a European 'CEN' method. A metal toothpaste tube is filled with binder and the end crimped shut. After storage in an oven the tube is cooled and peeled open. The solid binder is cut in half and the top and bottom halves tested.

5.6.2 Microscopic dispersion

Microscopic dispersion is used to assess the completeness of blending and the compatibility of SBS/bitumen blends. Blending in a high-shear mixer normally takes 1 to 4 hours depending on a number of factors, see section 7.3.3.2. To monitor progress operatives take a periodic sample and spread it into a thin film. As well as giving a rough measure of consistency (viscosity) during spreading, the thin film shows any lumps of polymer remaining. On completion of processing a sample can be taken and spread onto a microscope slide. Viewed under transmitted visible or UV light at 200 to 400 times magnification, the slide shows the degree to which the polymer phase is incorporated. For example, a compatible system shows a virtually continuous single phase system with a very fine grain whereas an incompatible system shows two phases with a coarse grain. Photographs 5.8a and b show photomicrographs of compatible and incompatible systems.

5.6.3 SBS polymer content

A sample is dissolved in carbon disulphide and an infared spectrum run over the range 1200 to 625 cm^{-1}. Peak heights at 700 and 970 cm^{-1} are measured and, after calculation of extinction coefficients and comparison with spectra from standard solutions, the polymer content can be calculated. It should be noted that this method measures styrene content and so the user must know the styrene content of the polymer in order to calculate polymer content. Obviously the technique can be used to measure polymer contents with other styrene-containing polymers such as SIS (styrene-isoprene-styrene), SBR (styrene-butadiene rubber), etc. Figure 5.5 shows a spectrum of a bitumen/SBS mixture.

5.7 Other tests

5.7.1 Density (or relative density)

Density is the mass of a substance divided by its volume. Relative density is the ratio of the density of a substance at temperature 1 to the density of pure water at temperature 2. Usually both temperatures are 15°C but need not be so. Specific gravity is the ratio of the mass of a given volume of liquid to mass of an equal volume of pure water at the same temperature, usually 60°F. Density is not specified in BS 3690 but is specified in other standards which use bitumen, eg BS 4147. It is widely specified in other parts of the world although the reasons for this are not clear. It can be measured in several ways:-

Grade	Relative density @ 25°C/25°C
Penetration grades	
300 pen	1.010 -1.020
200 pen	1.015 -1.025
100 pen	1.020 -1.030
70 pen	1.020 -1.030
50 pen	1.025 -1.035
40 pen HD	1.025 -1.035
35 pen	1.025 -1.035
25 pen	1.030 -1.040
Oxidised grades	
75/30	1.015 -1.025
85/25	1.020 -1.030
85/40	1.010 -1.025
95/25	1.015 -1.030
105/35	1.000 -1.015
115/15	1.020 -1.035
Hard grades	
H80/90	1.045 -1.055
H100/120	1.055 -1.065
Cutback grades	
50 second	0.992 -1.002
100 scond	0.995 -1.005
200 scond	0.997 -1.007

Table 5.9 — Typical densities of some bitumens

5.7.1.1 Pyknometer method[37], IP190, ASTM D70

A small sample is weighed into a pyknometer and the pyknometer filled with water. The pyknometer is weighed at the required temperature, usually 15 or 25°C, and the density calculated. This is the most accurate method giving densities to four decimal places.

5.7.1.2 High temperature density

There are no published methods for determination of bitumen density at application temperatures. Hydrometers cannot be used because of the inaccuracies caused by bitumen on the stem and also because temperature corrections at such high temperatures are not valid. Density can be measured at high temperature using an electronic density meter. A calibrated cell is filled with sample and made to oscillate at high frequency. The damping in the cell is related to the bitumen density which is calculated and displayed.

Densities measured using this technique correlate well with values extrapolated from measurements made at ambient temperature. Table 5.9 shows typical relative densities for a range of bitumens.

5.7.1.3 British Standard BS 4147

BS 4147 describes a method for determination of density of bitumens used for protecting iron and steel. A brass mould is used to make a solid cube of bitumen with 18 mm sides. The bitumen is weighed in air and water at 25°C and the density calculated. The method is quick and simple but is only approximate and hence no repeatability limits are given.

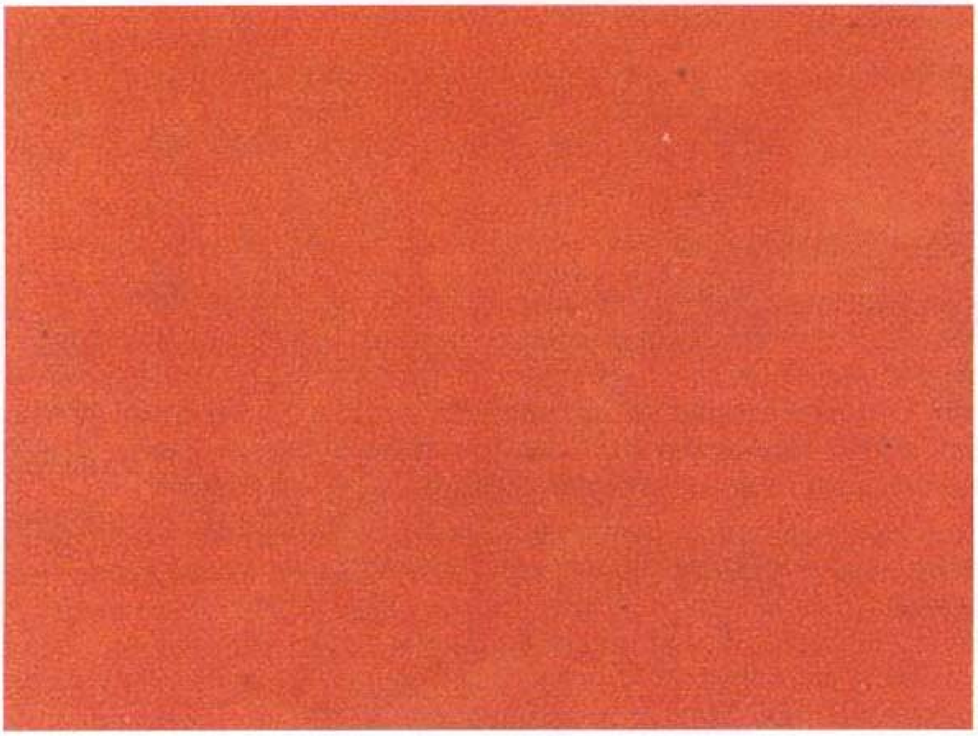
5.7.2 Durability of bitumen

Long-term studies have shown that if a bituminous surfacing is to achieve its design life it is important that the bitumen is not excessively hardened during storage, during the manufacturing process or in service. Bitumen, in common with many organic substances, is affected by the presence of oxygen, ultra-violet radiation and by changes in temperature. In bitumen these external influences cause it to harden, resulting in a decrease in penetration, an increase in softening point and an increase in penetration index (PI).

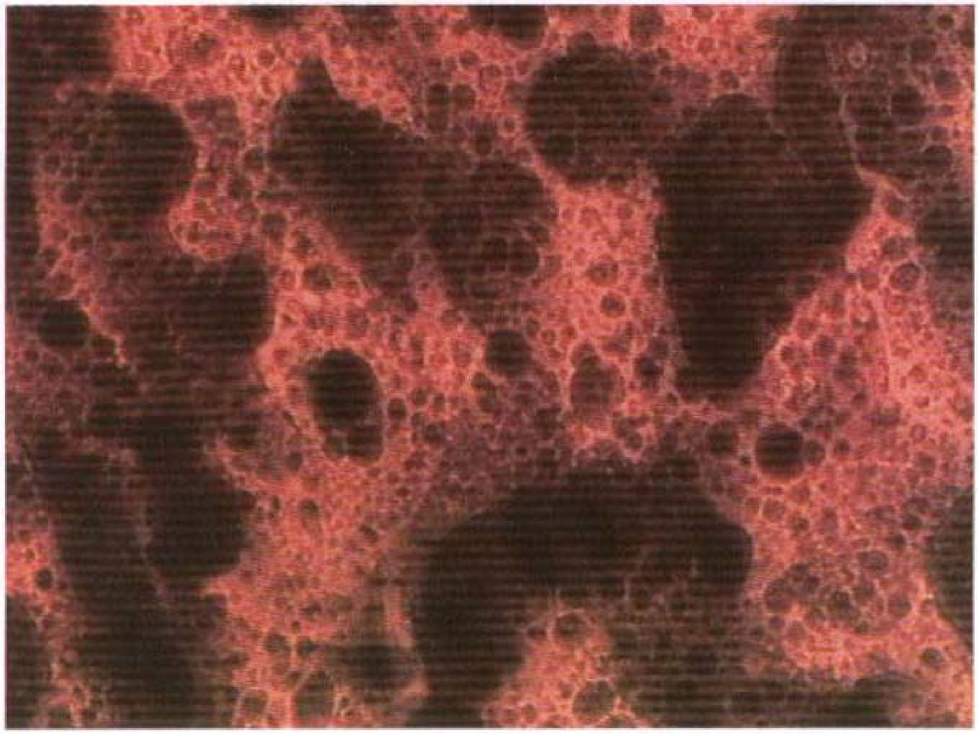
5.7.2.1 Bitumen hardening

The tendency for bitumen to harden under atmospheric influences has been known and studied for many years. Four principal mechanisms of bitumen hardening have been identified:

- oxidation;
- loss of volatiles;
- physical hardening;
- exudative hardening (loss of oils).



Photograph 5.8a — Compatible bitumen



Photograph 5.8b — Incompatible bitumen

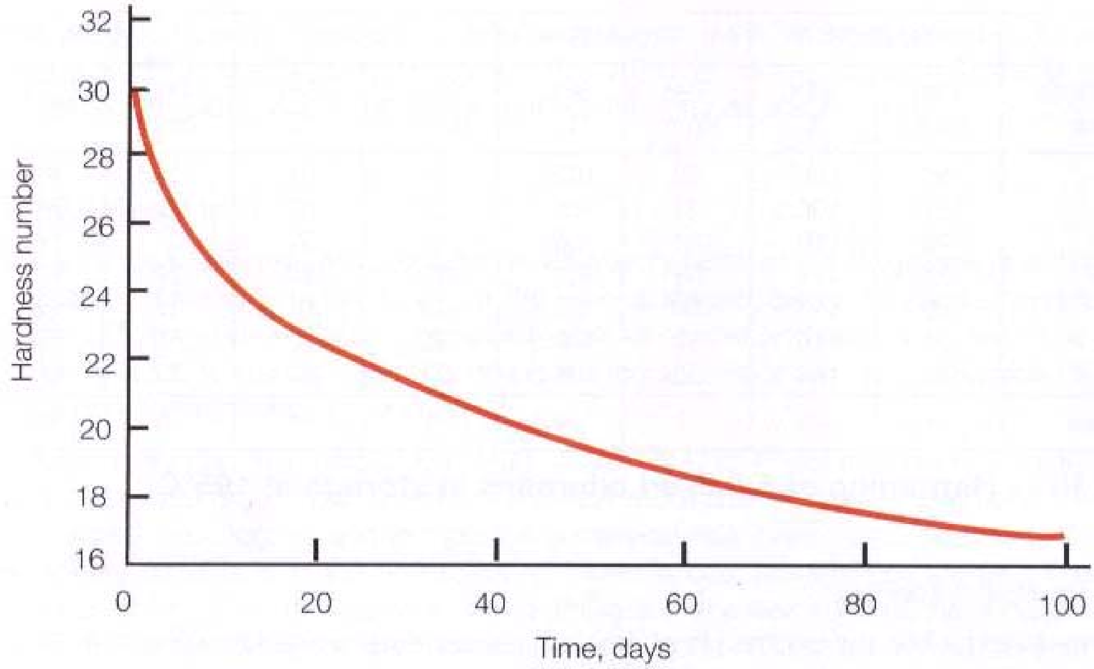


Figure 5.6 — Change in hardness number with time for roofing grade mastic asphalt

5.7.2.1.1 Oxidation

Like many organic substances, bitumen is slowly oxidised when in contact with atmospheric oxygen. The polar oxygen-containing groups formed tend to associate into micelles and thereby increase the viscosity of the bitumen. Polar hydroxyl, carbonyl and carboxylic groups are formed resulting in larger and more complex molecules which make the bitumen harder and less flexible. The degree of oxidation is highly dependent on the temperature, time and the thickness of the bitumen film. Oxidation rate approximately doubles for each 10°C increase in temperature above 100°C. Hardening due to oxidation has long been held to be the main cause of ageing to the extent that other factors have hardly been considered. However, it has been shown that although other factors are generally less important than oxidation they are certainly measurable.

5.7.2.1.2 Loss of volatiles

Evaporation of volatile components depends mainly upon temperature and the conditions of exposure. Penetration and oxidised grade bitumens are relatively involatile and therefore the amount of hardening resulting from loss of volatiles is usually fairly small. However, most oxidised bitumens are fairly hard and even small amounts of volatile loss may be sufficient to cause significant hardening.

	Mexphalte grade							
	R105/35		R105/35		R95/25		R85/25	
Storage time weeks	Pen dmm	SPt °C	Pen dmm	SPt °C	Pen dmm	SPt °C	Pen dmm	SPt °C
0	30	106	32	102	24	91	23	85
1	27	106.5	31	105	22	92	21	86
2	26	110	31	106	21	92	21	86
3	26	111	31	107	22	94	20	87
4	26	113.5	30	108.5	22	92	18	90
5	26	114	30	108.5	22	92	18	90
6	26	114	30	108.5	22	92	17	90
Change	-4	+8	-2	+6.5	-2	+1	-6	+5

Table 5.10 — Hardening of oxidised bitumens in storage at 195°C

5.7.2.1.3 Physical hardening

Physical hardening when the bitumen is at ambient temperature is well known(13, 38, 39, 40) and is usually attributed to reorientation of bitumen molecules and the slow crystallisation of waxes. Physical hardening is reversible in that upon reheating the original viscosity of the bitumen is obtained.

This phenomenon can be easily reproduced in the laboratory by measuring the penetration of a sample of bitumen (without reheating) over a period of time. As time progresses the penetration of the sample will fall.

In one study(41) of mastic asphalt it was shown that a 40 per cent reduction in hardness number occurred within the first year with a further 20 per cent in the next year (see figure 5.6).

5.7.2.1.4 Exudative hardening

Exudative hardening results from the movement of an oily component which can migrate from the bitumen into the substrate, eg stone, concrete, wood etc. It is a function of both the bitumen and the porosity of the substrate (sections 5.4.2 and 8.1.3.11.2).

5.7.2.2 Hardening of bitumen in bulk storage

When bitumen is stored in bulk at high temperature very little hardening occurs. This is because the surface of the bitumen exposed to the oxygen is very small in relation to the large volume. However, if the bitumen is being circulated and is falling from the pipe entry at the top of the tank to the surface of the bitumen, significant hardening may occur. This is because the surface area of the bitumen falling from the entry pipe will be relatively large, providing the opportunity for the oxygen to react with the bitumen (see chapter 3, section 3.2).

Although there is little published data on the extent of hardening during storage, experience of bitumen manufacturers shows it is small. However, it is realised that the extent of hardening is highly dependent on the storage tank geometry and storage conditions. Table 5.10 shows the effect of long term storage under ideal conditions in an oil refinery, ie large volume to surface ratio, static surface, submerged heater system, etc.

5.7.2.3 Ageing tests

There are two types of test used for bitumens; binder tests, which are carried out on a liquid sample and generally measure a combination of oxidation and volatile loss, and weatherometer tests, which are carried out on membranes and coatings.

5.7.2.3.1 Binder tests

It is clearly desirable that there should be laboratory tests which determine quantitatively the resistance of bitumens to hardening at the various stages during the production process. A number of tests already exist to measure the effect of heat and air on bitumen. The main aim of these tests is to identify bitumens which are too volatile or are too susceptible to oxidation to give good performance in service.

The loss on heating test(7) (BS 2000 : Part 45, ASTM D 6, IP 45) described in section 5.2.2 is a part of many bitumen specifications. This test is suitable for ranking bitumens according to their tendency to harden and indicates if a material has been contaminated with light oils. The ageing conditions in the test relate to those in bulk storage but are far removed from those during processing. The main disadvantages of the test are that the surface-to-volume ratio of the sample is too low and an oxidised skin tends to form quickly on the surface of the bitumen, which hampers further oxidation and evaporation.

The thin film oven test (TFOT) (ASTM D 1754) simulates practical conditions somewhat better. In this test the bitumen is stored at 163°C for five hours in a layer 3.2 mm thick. It is claimed that in this test the amount of hardening that takes place is about the same as that obtained in practice. However, in this test diffusion in the bitumen film is also limited and it is not possible to obtain homogeneous hardening or ageing, and therefore the test is far from ideal.

In 1963 the State of California Department of Public Works, Division of Highways, developed a test which simulates far better what happens to a bitumen during asphalt manufacture, the rolling thin-film oven test (RTFOT). In this test eight cylindrical glass containers containing 35g of bitumen are fixed in a vertically rotating shelf. During the test the bitumen flows continuously around the inner surface of each container in a relatively thin film with pre-heated air periodically blown into each glass jar. The test temperature is normally 163°C for a period of 75 minutes. The method ensures that all the bitumen is exposed to heat and air, and continuous movement ensures that no skin develops to protect the bitumen. A homogeneously aged material is obtained. Clearly the conditions in the test are not identical to those found in practice but experience has shown that the amount of hardening in the RTFOT correlates reasonably well with that observed in a conventional batch-type asphalt plant.

The RTFOT was accepted in 1970 by the American Society for Testing and Materials as method ASTM D 2872. Although there is much experience with this test for penetration grades, because of its widespread adoption by the road construction industry, there is little data for oxidised grades.

5.7.2.3.2 Weatherometer testing

Samples of bituminous membrane or plates coated with bituminous paint are hung in a climate-controlled cabinet. The environment within the cabinet can be controlled with respect to temperature, humidity, atmosphere, light including UV level and wavelength and water spray. A sequence of 'weathering' is programmed and the samples subjected to a preset number of cycles.

This is perhaps the closest to artificial weathering that can be achieved in the laboratory although the correlation with natural weathering is not known. A major drawback is the cost of such machines and the time taken to achieve a significant degree of 'weathering', typically many thousands of hours. Also, there is no inter-laboratory repeatability data and therefore comparison of results is difficult. Hence, use of weatherometers is not widespread.

5.7.2.3.3 Ageing index

Samples of binder are 'aged' in an 'oxidation' test and the ratio of measured property before and after ageing is termed the ageing index. The 'oxidation' test may be loss on heating(7) eg BS 3690 : Part 1, Rolling thin film oven test (RTFOT) or Thin film oven test (TFOT). The property of the binder is usually penetration, viscosity or, more rarely, softening point. Some national standards include ageing index for penetration grades primarily to control the amount of hardening during mixing at asphalt plants. This is not ageing in the true sense but is rather hardening through a combination of oxidation and volatile loss.

5.8 The Shell Bitumen Test Data Chart(42,43)

In the late 1960s, Heukelom developed a system to enable penetration, softening point Fraass breaking point and viscosity data to be described as a function of temperature on one chart as shown in figure 5.7. This is known as the bitumen test data chart (BTDC). The chart consists of one horizontal scale for the temperature and two vertical scales for the penetration and viscosity. The temperature scale is linear, the penetration scale is logarithmic and the viscosity scale has been devised so that penetration grade bitumens with 'normal' temperature susceptibility or penetration indices (PIs, see section 5.9) give straight-line relationships.

The BTDC shows how the viscosity of a bitumen depends on temperature, but it does not account for loading time. However, as the loading times for penetration, softening point and the Fraass breaking point tests are similar, these test data can be plotted with kinematic viscosity test data on the BTDC as shown in figure 5.8. As the test results on this chart form a straight-line relationship it is possible to predict the temperature/viscosity characteristics of a penetration grade bitumen, over a wide range of temperatures, from only two measurements, ie. a penetration and a softening point value.

The chart can also be used for comparing the temperature/viscosity characteristics of different types of bitumens. Three classes of bitumen can be distinguished using the BTDC:

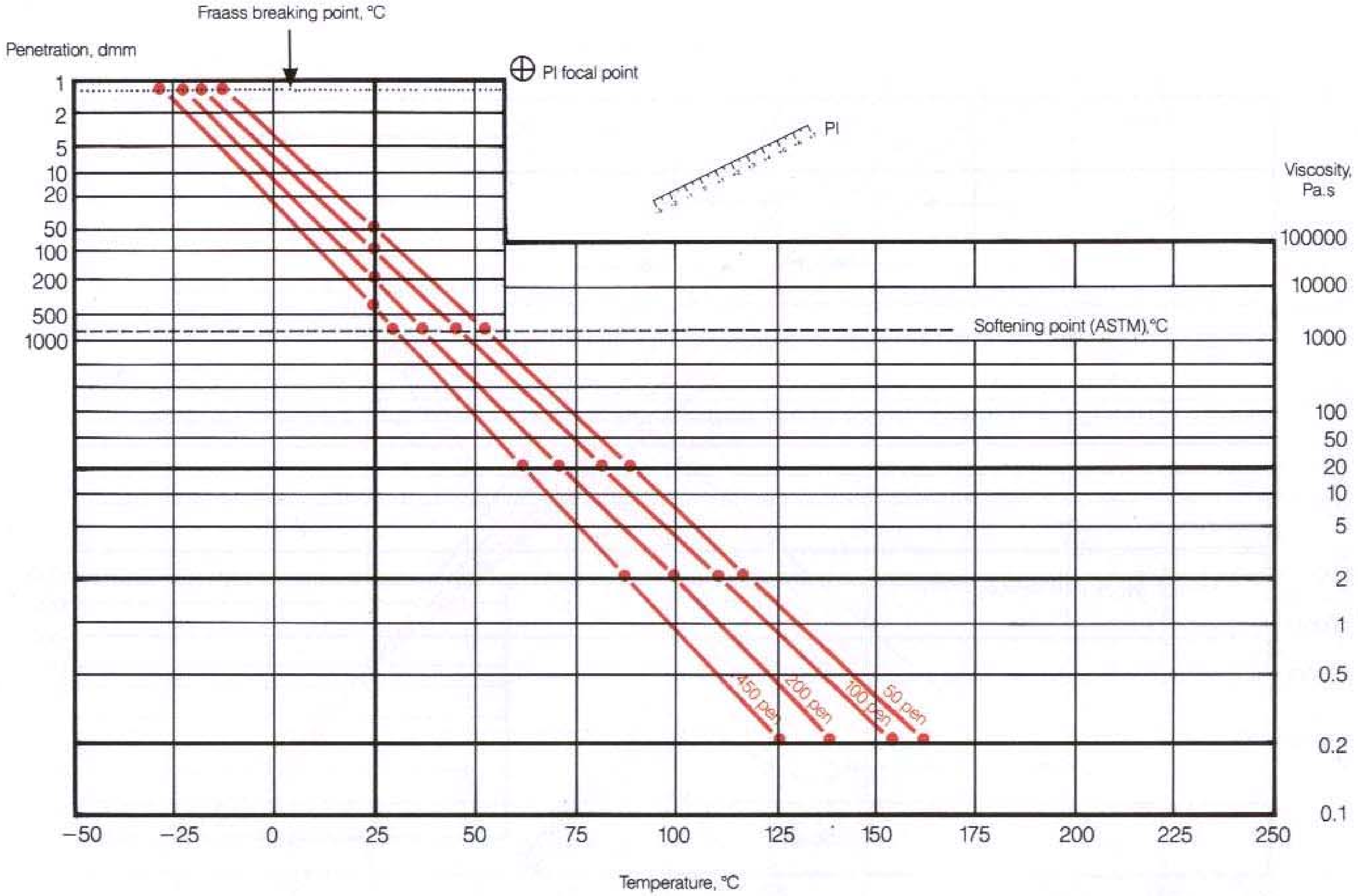


Figure 5.7 — A Bitumen Test Data Chart comparing penetration grade bitumens from one feedstock origin(43)

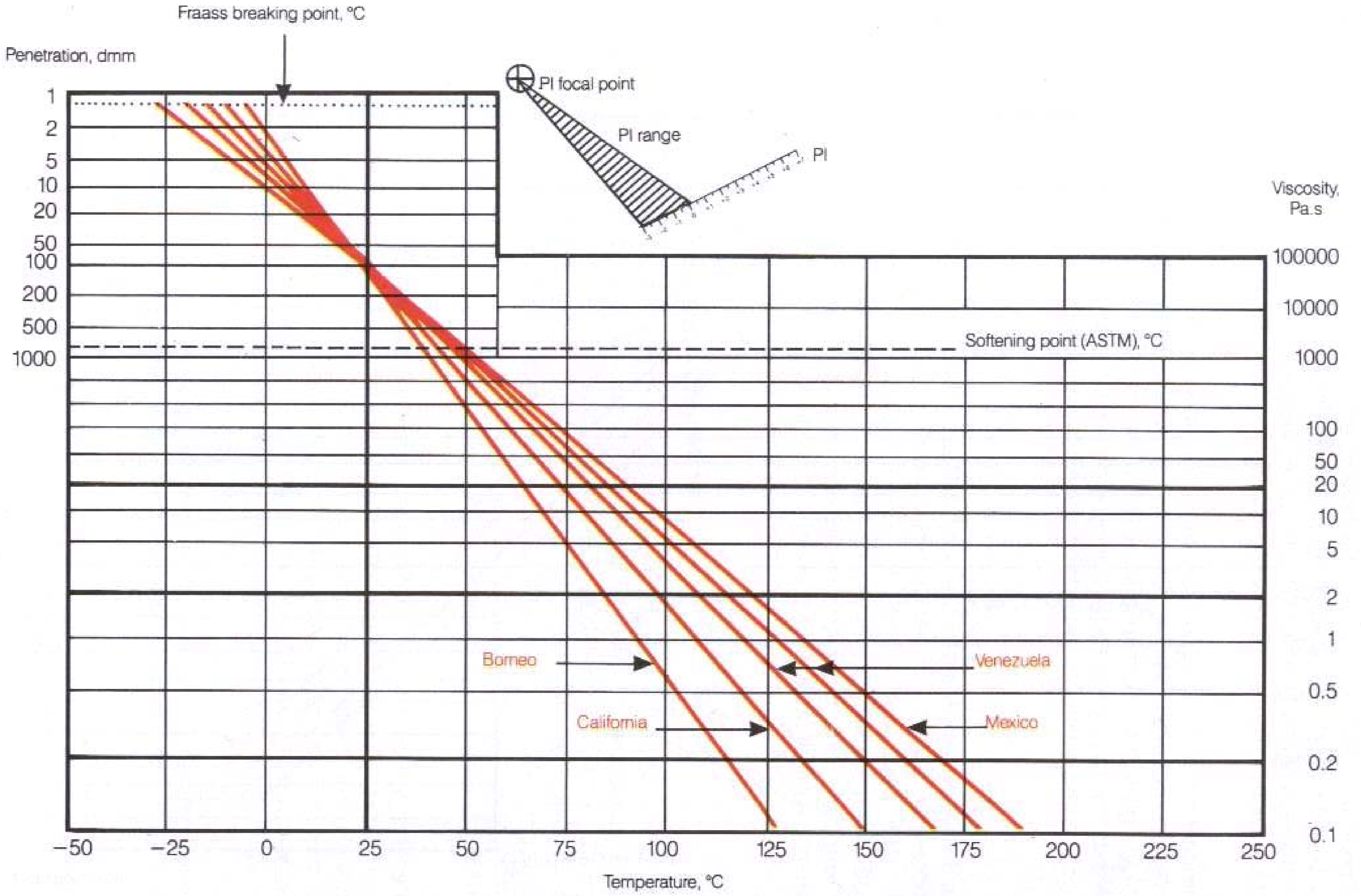


Figure 5.8 — A Bitumen Test Data Chart comparing several 100 pen bitumens manufactured from different feedstock types[44]

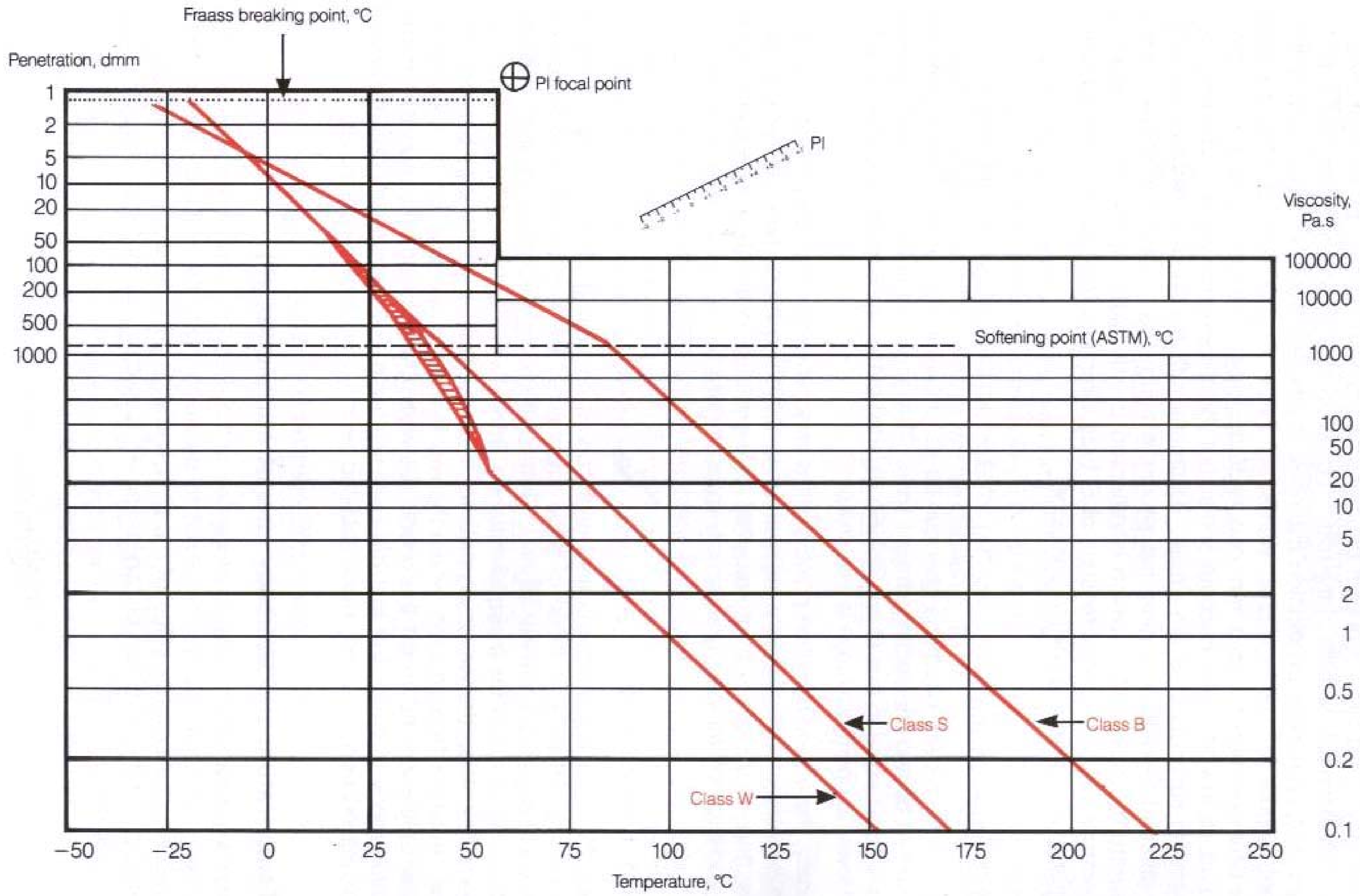


Figure 5.9 — Typical examples of Class S, B and W bitumens on the Bitumen Test Data Chart

5.8.1 S-type bitumens

The test data for a large group of bitumens can be represented by straight lines on the BTDC, within the repeatability of the test. This group, which has been designed S-type (S for straight line), comprises penetration bitumens of different feedstock origin with limited wax content. Figure 5.7 shows a chart with straight lines for a number of different penetration grade bitumens manufactured from one feedstock type. The lines move towards the left of the chart as the bitumens become softer, but their slopes are equal, indicating that their temperature susceptibilities are similar. Bitumens with the same penetration at 25°C, but from different feedstock origins, are shown in figure 5.8. The origin may influence the temperature susceptibility, which is reflected by the slope of the line. Therefore the temperature viscosity characteristics of S type bitumens may be determined from their penetration and softening point values alone.

5.8.2 B-type bitumens

B-type (B for blown) bitumens give curves as shown in figure 5.9. The curves can be represented by two intersecting straight lines. The slope of the line in the high temperature range is about equal to that of an unblown bitumen of the same feedstock origin, but the line in the lower temperature range is less steep.

Physically, there is no transition point, but it is very convenient that they are still straight lines in the penetration and viscosity regions; each of them can be characterised with two test values; thus, in all, four tests are required for a complete description; penetration, softening point and two high temperature viscosity measurements.

5.8.3 W-type bitumens

W-type (W for waxy) bitumens also give curves consisting of two straight lines which, however, are dissimilar to those of blown bitumens. The two branches of the curve give nearly equal slopes, but are not aligned. Figure 5.9 shows an example of an S type bitumen together with a curve for a similar bitumen with a wax content of 12 per cent. At low temperatures, when the wax is crystallised, there is hardly any difference between the two curves. At higher temperatures, where the wax is molten, the curve for the waxy bitumen is considerably lower down on the chart. Between the two straight branches there is a transition range in which the test data are scattered because the thermal history of the sample influences the viscosity result obtained over this range of temperatures.

5.9 Temperature susceptibility - penetration index (PI)

All bitumens display thermoplastic properties, ie they become softer when heated and harder on cooling. Several expressions exist to define the way the viscosity (or consistency) changes with temperature. One of the best known is that developed by Pfeiffer and Van Doormaal(14). If the logarithm of penetration, P, is plotted against temperature, T, a straight line is obtained such that:

$$\log P = AT + K$$

where A is the temperature susceptibility

K is a constant.

The value of A varies from about 0.015 to 0.06 showing that there may be a considerable difference in temperature susceptibility. Pfeiffer and Van Doormaal developed an expression for the temperature susceptibility which would assume a value of about zero for road bitumens. For this reason they defined penetration index (PI) as:

$$\frac{20 - PI}{10 + PI} = 50\,A$$

or

$$PI = \frac{20(1 - 25\,A)}{1+50A}$$

The value of PI ranges from about -3 for high temperature susceptibility bitumens to about +7 for highly blown, low temperature susceptible (high PI) bitumens. The PI is an unequivocal function of A and hence it may be used for the same purpose. The values of A and PI can be derived from penetration measurements at two temperatures, T_1 and T_2, using the equation:

$$A = \frac{\log \text{pen } T_1 - \log \text{pen } T_2}{T_1 - T_2}$$

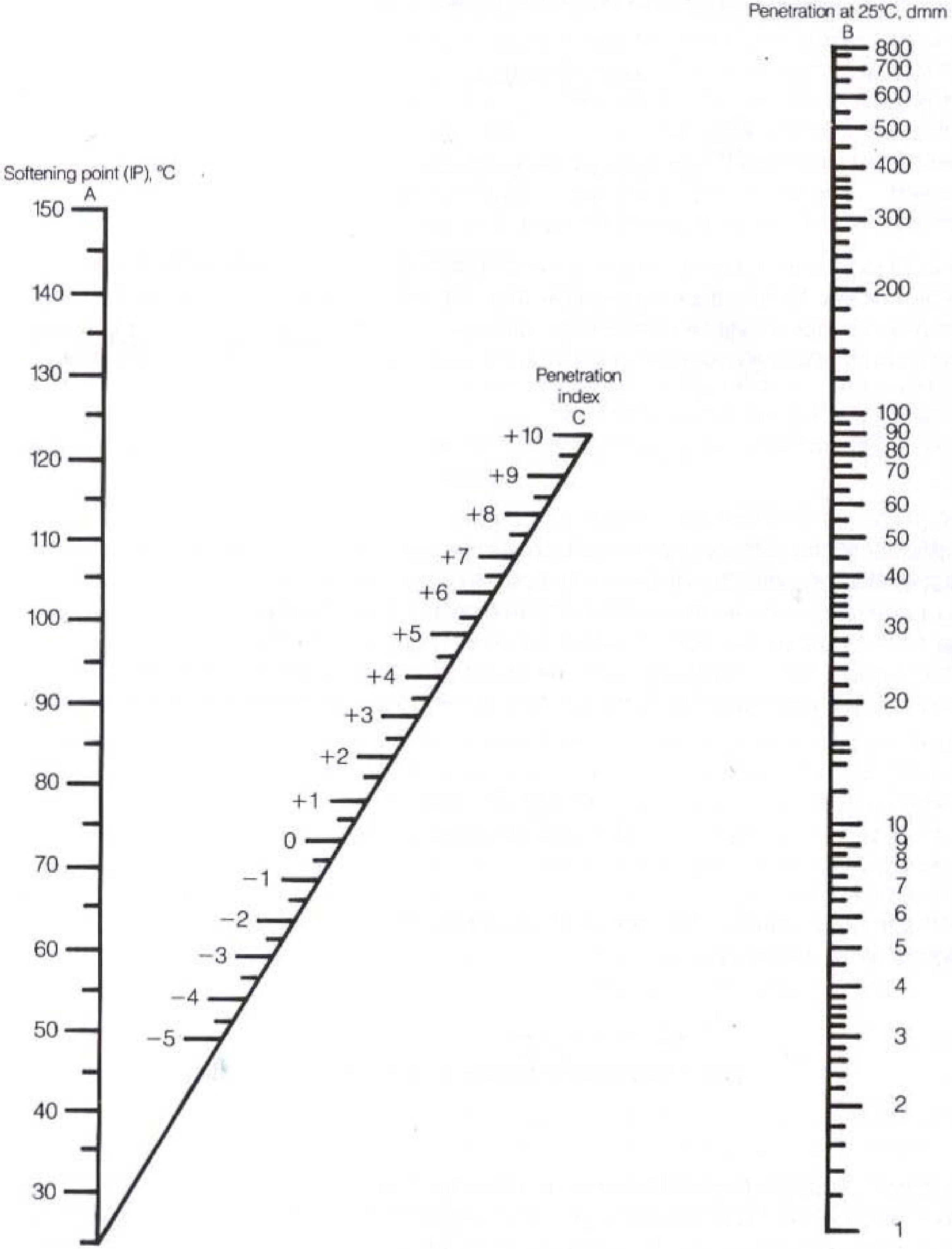
The consistency at the softening point can be expressed in terms of penetration, both by linear extrapolation of logarithm of pen vs temperature and by direct measurement with an extra long penetration needle at the ASTM softening point temperature. Pfeiffer and Van Doormaal found that at the ASTM softening point temperature most bitumens had a penetration of about 800. Replacing T_2 in the above equation by the ASTM softening point temperature and the penetration at T_2 by 800 they obtained the equation:

$$A = \frac{\log \text{pen } T_1 - \log 800}{T_1 - \text{ASTM softening point}}$$

Substituting this equation in the above PI equation and assuming a penetration test temperature of 25°C, we have:

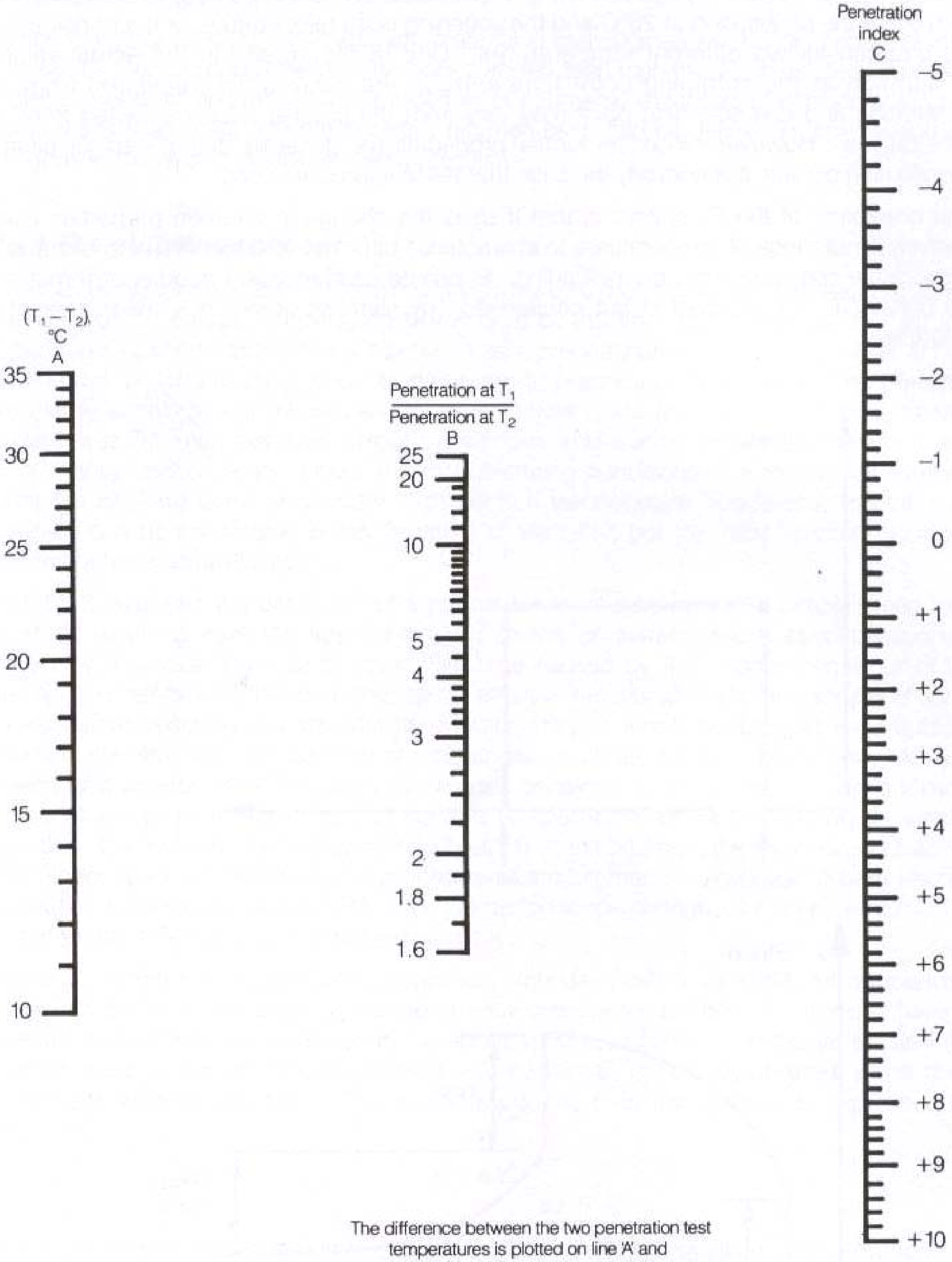
$$PI = \frac{1952 - 500 \log \text{pen} - 20 \text{ softening point}}{50 \log \text{pen} - \text{softening point} - 120}$$

The assumption of penetration of 800 dmm at the softening point temperature is not valid for all bitumens and hence many bitumens give PIs calculated from penetration and softening point values which are different to PIs calculated from two penetration measurements. Whilst it is advisable to calculate the temperature susceptibility using penetration at two temperatures, T_1 and T_2, it is usual practise to calculate PI from penetration and softening point values.



Draw a line between the softening point (line 'A') and penetration (line 'B') values. The intercept on line 'C' is the PI of the bitumen

Figure 5.10 — Nomograph for penetration index (softening point/penetration)



The difference between the two penetration test temperatures is plotted on line 'A' and the ratio of the two penetrations is plotted on line 'B'. A line is drawn through these two points and where it intercepts line 'C' is the PI of the bitumen.

Figure 5.11 — Nomograph for penetration index (pen/pen)

The nomographs shown in figures 5.10 and 5.11 enable the PI to be deduced approximately from either the penetration at 25°C and the softening point temperature, or the penetration of the bitumen at two different temperatures. Due to the spread in the actual value of penetration at the softening point temperature, the value of PI calculated from one penetration and one softening point may vary from the precise value calculated from two penetrations. However, since the former properties are generally determined for bitumen specification control, it is normally the case that these figures are used.

One drawback of the PI system is that it uses the change in bitumen properties over a relatively small range of temperatures to characterise bitumen. Extrapolations to extremes of temperature can sometimes be misleading. PI can be used to give a good approximation of the behaviour to be expected but confirmation by stiffness or viscosity measurements is desirable.

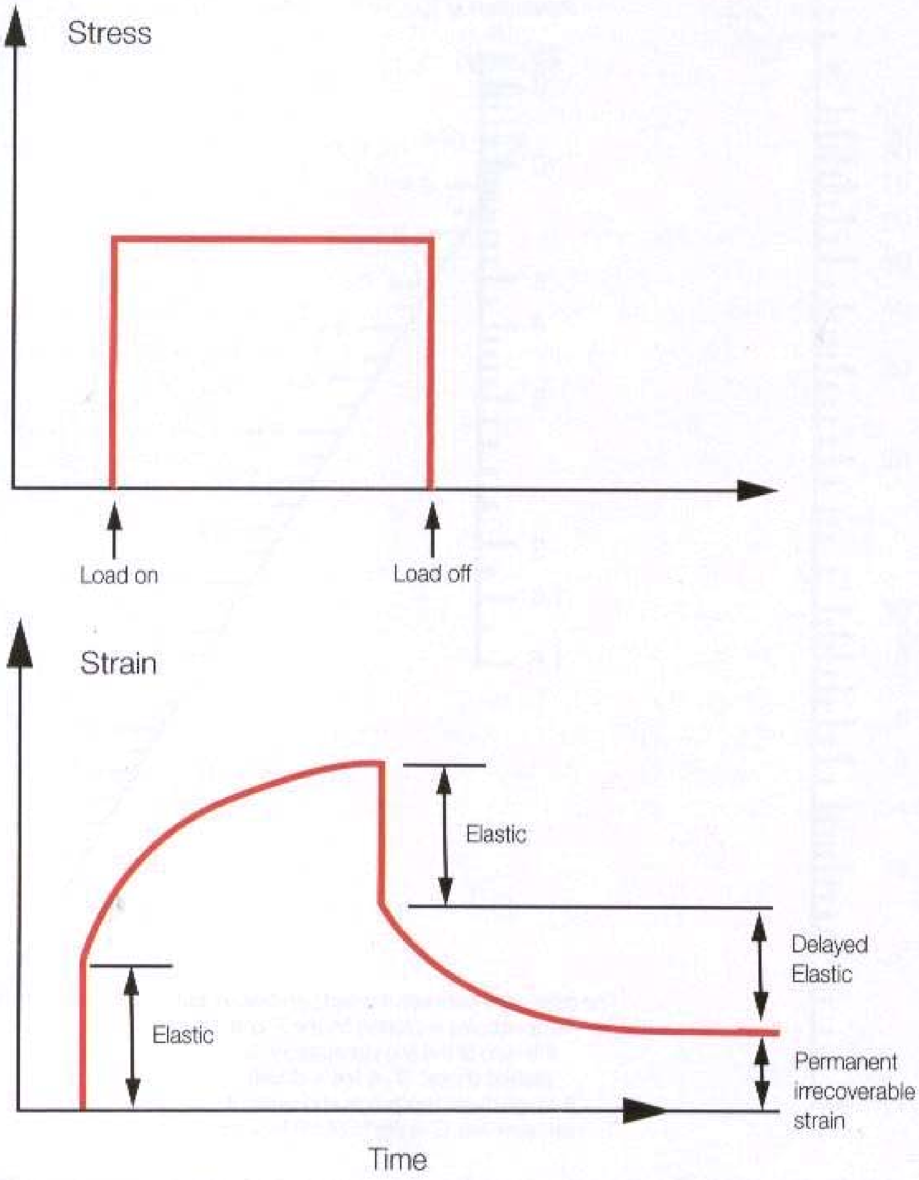


Figure 5.12 — Visco-elastic response of bitumen to a static load

5.10 Engineering properties of bitumen

Bitumen is widely used as a construction material in civil engineering, building and industrial fields, but its mechanical properties are more complex than materials such as steel or cement concrete. However, the mechanical properties of bitumens, which are of considerable value to both the civil engineer and the industrial bitumen user, can be defined in terms which are analogous to the elastic moduli of solid materials.

5.10.1 The stiffness concept

As well as being thermoplastic, bitumen is a visco-elastic material whose behaviour changes from viscous to elastic, depending upon time of loading and temperature. At low temperatures or short loading times it behaves as a predominantly elastic solid, whilst at high temperatures or long loading times its behaviour is predominantly viscous. The transition from mainly elastic to mainly viscous behaviour takes place gradually. At normal service temperatures bitumen behaves in both a viscous and elastic manner, although it is a predominantly viscous solid. Under the manufacturing conditions of a roofing felt line or a carpet tile backing plant and under high service temperature conditions, the bitumen properties can be considered purely in terms of viscosity, but for most service conditions bitumens behave visco-elastically.

Figure 5.12 illustrates the behaviour of a normal bitumen subjected to a simple creep test. The strain resulting from the applied loading shows an instantaneous elastic response, followed by a gradual increase of strain with time caused by the viscous behaviour of the material. On removal of the load, the elastic strain is recovered instantaneously and some delayed elastic recovery occurs with time. Ultimately, a small residual permanent strain remains in the bitumen. The addition of a plastomer, such as atactic polypropylene (APP) or ethylene vinyl acetate (EVA), modifies the viscous behaviour of the bitumen, making it more viscous or stiffer at the appropriate service temperature without changing its elastic properties. On addition of an elastomer such as TR to the bitumen, the visco-elastic balance of the binder changes, improving the properties of the bitumen in resistance to both viscous deformation and flexural fatigue. The principal performance changes are an improvement in cold temperature flexibility and increased viscosity.

In order to define the visco-elastic properties, Van der Poel(44), in 1954, introduced the concept of stiffness modulus as a fundamental parameter to describe the mechanical properties of bitumens, by analogy with the elastic modulus of solids. In this latter case, if a tensile stress, σ, is applied at loading time $t = 0$, a strain, E, is instantly attained, which does not increase with loading time. The elastic modulus, ε, of the material is expressed by Hooke's law:

$$E = \sigma / \varepsilon$$

In the case of visco-elastic materials such as bitumen, a tensile stress σ, applied at loading time $t = 0$, causes a strain ε_t, which increases, but not proportionately, with loading time. The stiffness modulus, S_t, at loading time t, is defined as the ratio between the applied stress and the resulting strain at loading time t:

$$S_t = \frac{\sigma}{\varepsilon_t}$$

It follows from this that the value of the stiffness modulus is dependent on the loading time which is due to the special nature of bitumen. Similarly the stiffness modulus will also depend on temperature, T; consequently it is necessary to state both temperature and time of loading of any stiffness measurement:

$$S_{t,T} = \frac{\sigma}{\varepsilon_{t,T}}$$

The effect of changes in temperature and loading time on the stiffness of three different bitumens is shown in figure 5.13a, 5.13b and 5.13c. Figure 5.13a shows a bitumen of low PI, -2.3. At very short loading times the stiffness modulus is virtually constant, asymptotic towards 2.5 to 3.0 x 10^9 Pa, and is, in this region, largely independent of temperature and loading time, ie S = E. The effect of PI is clearly illustrated by comparing figures 5.13a and 5.13b. The bitumen with the higher PI (+ 5) is considerably stiffer at higher temperatures and longer loading times, ie it is less temperature susceptible.

In order to appreciate fully the significance of the stiffness modulus and its measurement, it is necessary to consider the deformation under stress of simple solids and liquids. The deformation behaviour of visco-elastic materials can then be derived.

5.10.2 Determination of the stiffness modulus of bitumen

The methods to measure the stiffness modulus of bitumen are based on shear deformation, as shown in figure 5.14. The resistance to shear is expressed in terms of the shear modulus, G, which is defined as:

$$G = \frac{\tau}{\gamma} = \frac{\text{Shear stress}}{\text{Shear strain}}$$

The elastic modulus and shear modulus are related by the equation:

$$E = 2(1 + \mu)G$$

where μ = Poisson's ratio.

The value of μ depends on the compressibility of the material and may be assumed to be 0.5 for almost incompressible pure bitumens, while values of <0.5 have to be considered for asphalt mixes. Thus we have:

$$E \approx 3G$$

Shear stress can be determined statically in a creep test or dynamically by application of a sinusoidal load. In a creep test, the shear stress is applied from the starting time of the test. The deformation at loading times from about 1 second to 10^5 seconds or longer can be

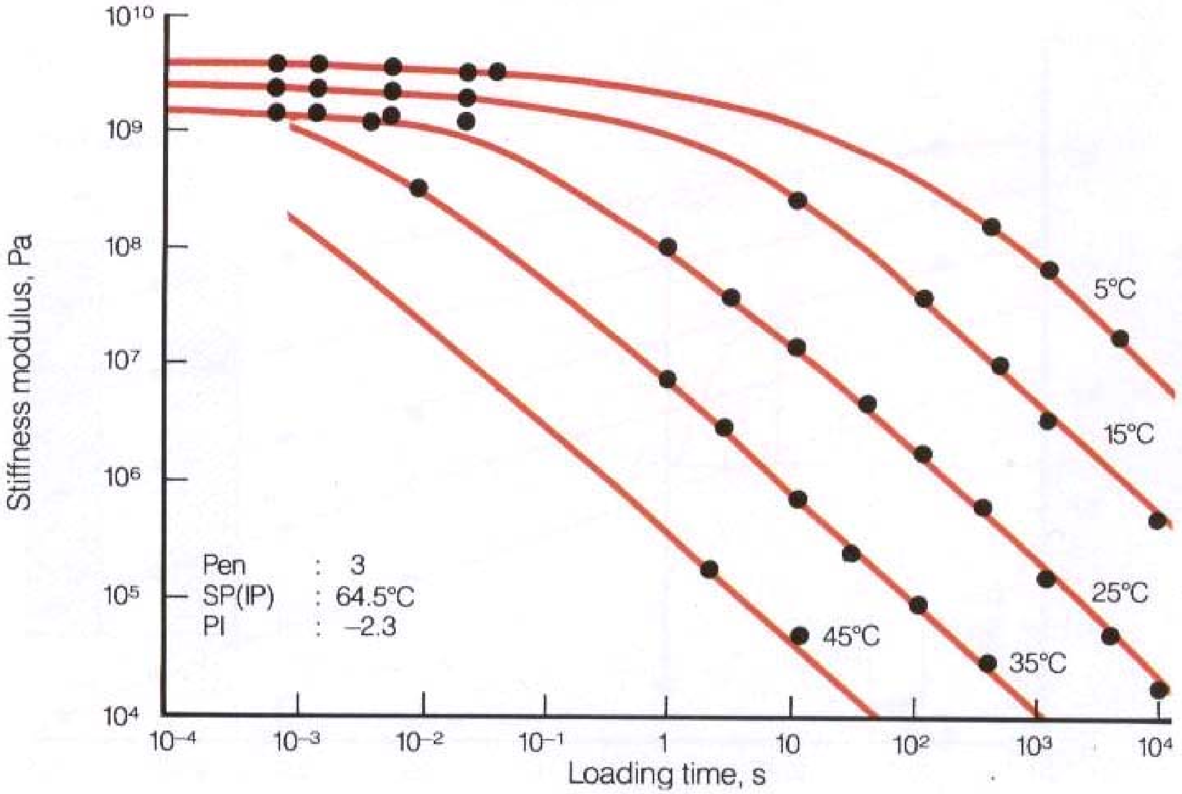


Figure 5.13a — The effect of temperature and loading time on the stiffness of a low PI bitumen

measured. In dynamic tests, the shear stress is usually applied as a sinusoidally varying stress of constant amplitude and fixed frequency. The deformation of the material under test also varies sinusoidally, with the same frequency as the applied stress. This is illustrated in figure 5.15.

The shear modulus, G_f, at frequency, f, is given by the ratio of the amplitudes of shear stress, γ, and shear strain, τ, according to:

$$G_f = \left(\frac{\tau}{\gamma}\right)_f$$

It follows that the stiffness modulus under dynamic conditions is:

$$S_f = 3G_f$$

Figure 5.15 shows the phase difference, φ, between shear stress and shear strain. This phase lag is a measure of the degree of elasticity of the bitumen under the test conditions. A purely elastic material would not show any phase difference between the stress and strain, whereas in the case of a purely viscous material there would be a phase lag of 90° or one-quarter cycle. With a visco-elastic material such as bitumen, the phase lag between stress and shear is between 0° and 90°, depending on the type and grade of bitumen, temperature and frequency. Small phase angles are found at low temperature and high frequency, and vice-versa, indicating that under these conditions the bitumen approximates respectively to elastic and viscous behaviour.

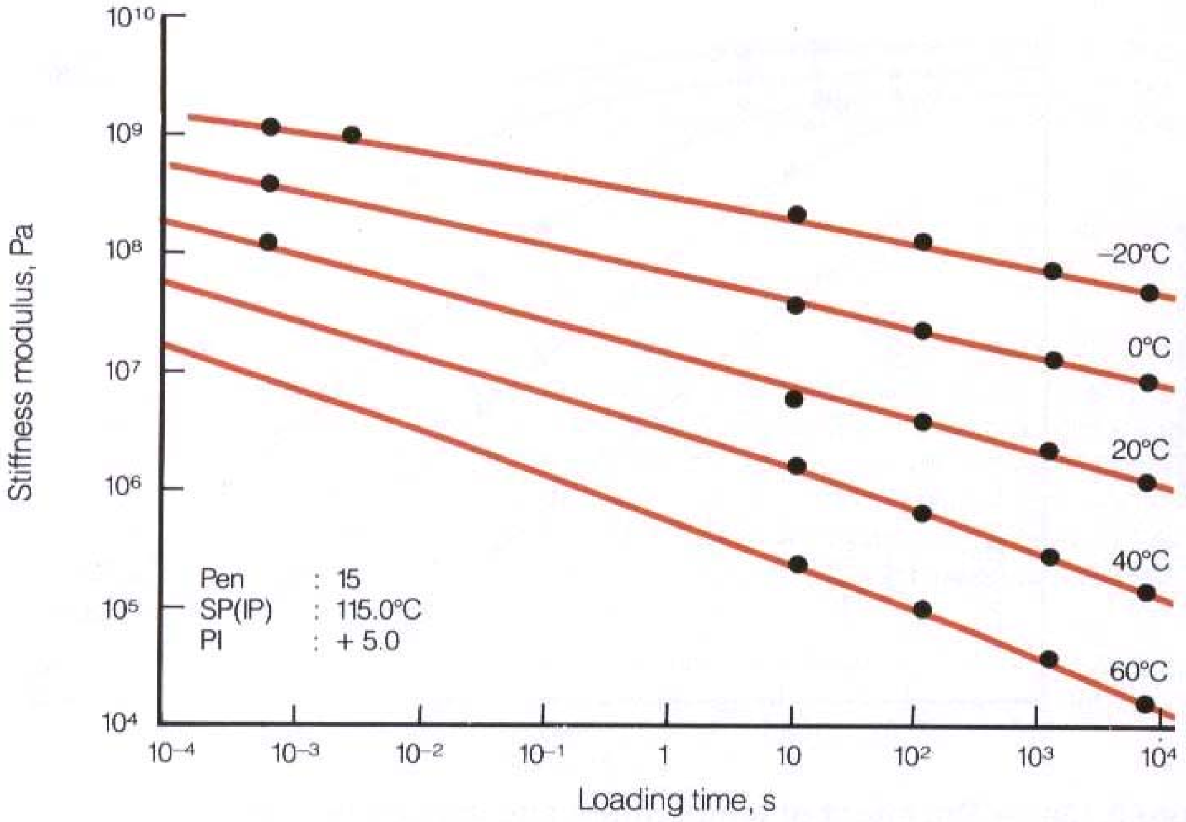


Figure 5.13b — The effect of temperature and loading time on the stiffness of a high PI (115/15) bitumen

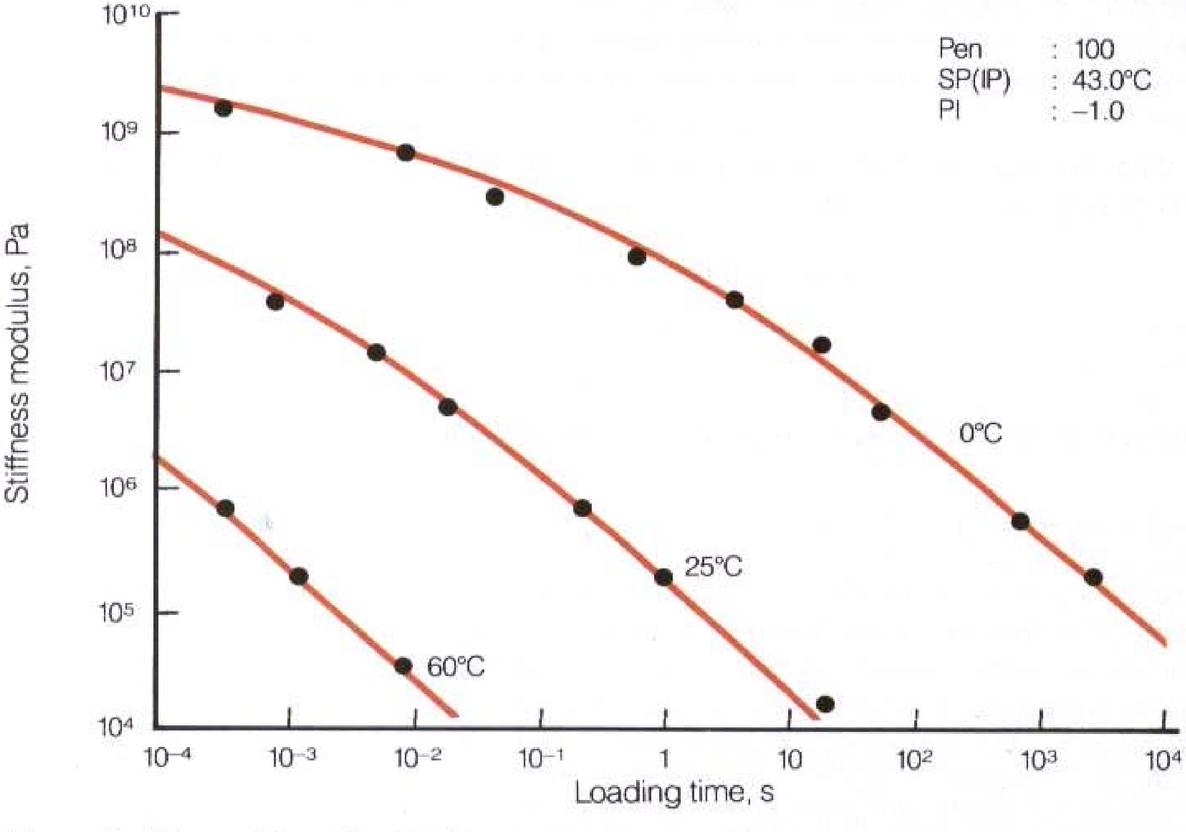


Figure 5.13c — The effect of temperature and loading time on the stiffness of 100 pen bitumen

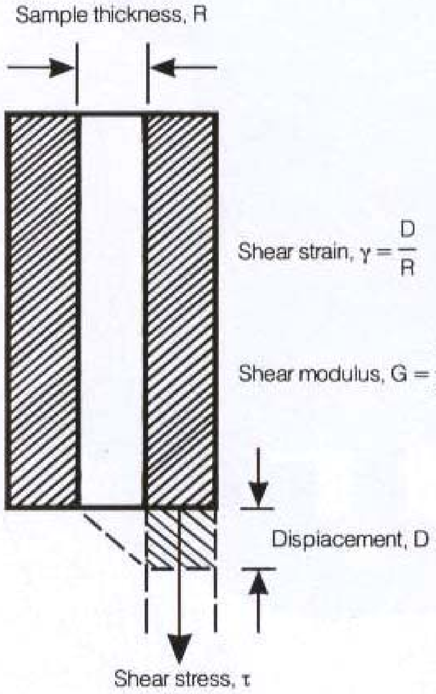


Figure 5.14 — A creep test in shear

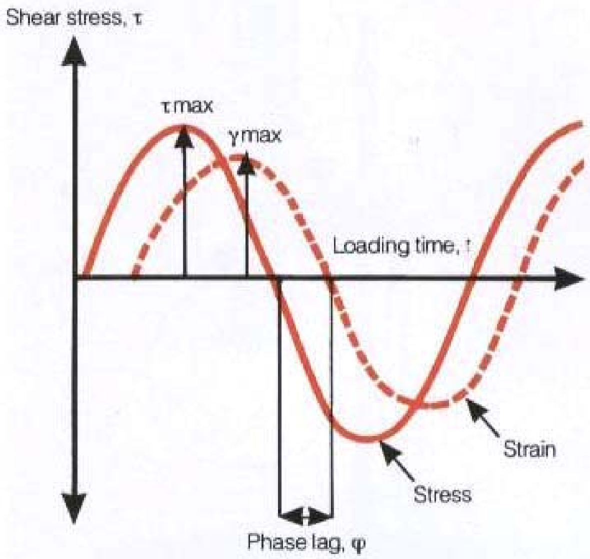


Figure 5.15 — A dynamic test in shear

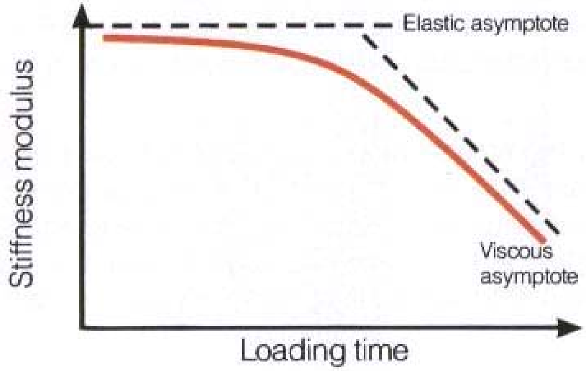


Figure 5.16 — Stiffness modulus as a function of loading time or frequency

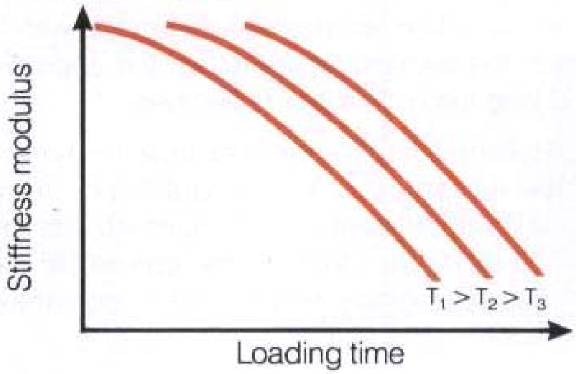
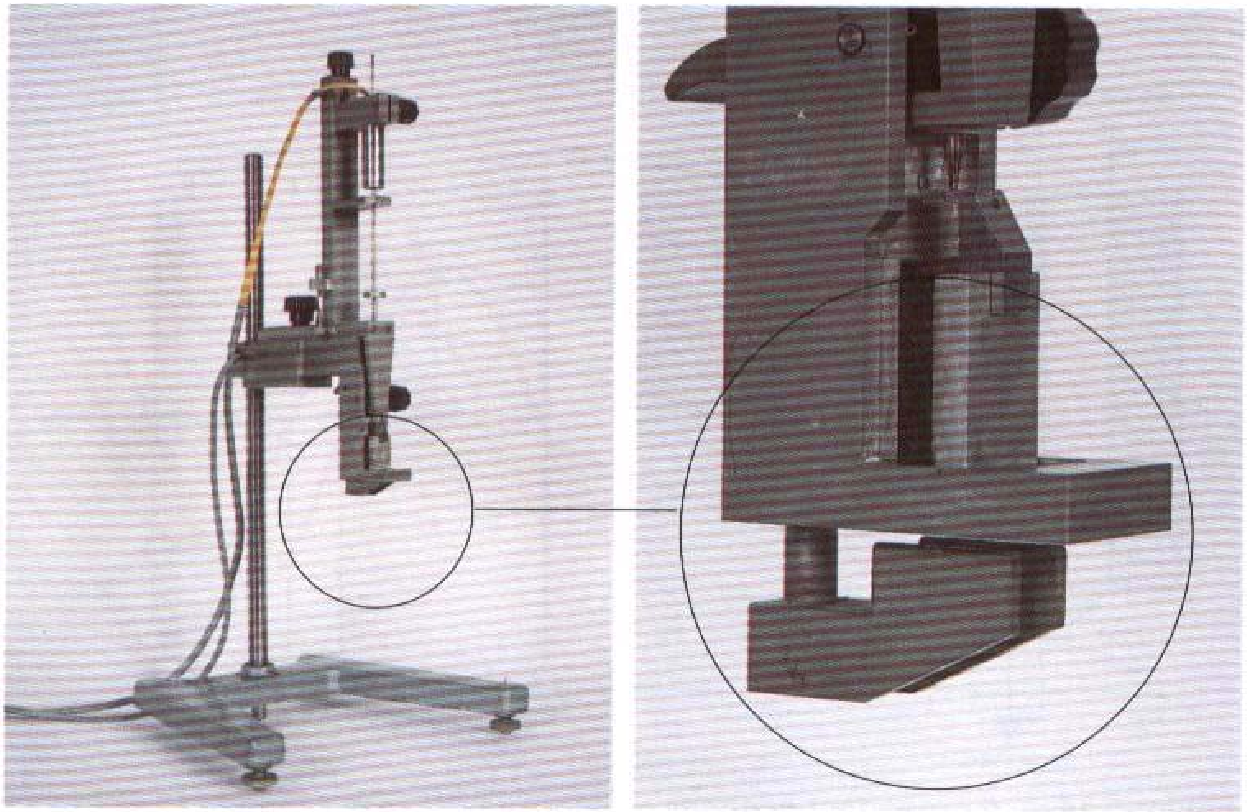


Figure 5.17 — Stiffness modulus as a function of loading time at different temperatures



Photograph 5.9 — The sliding plate rheometer

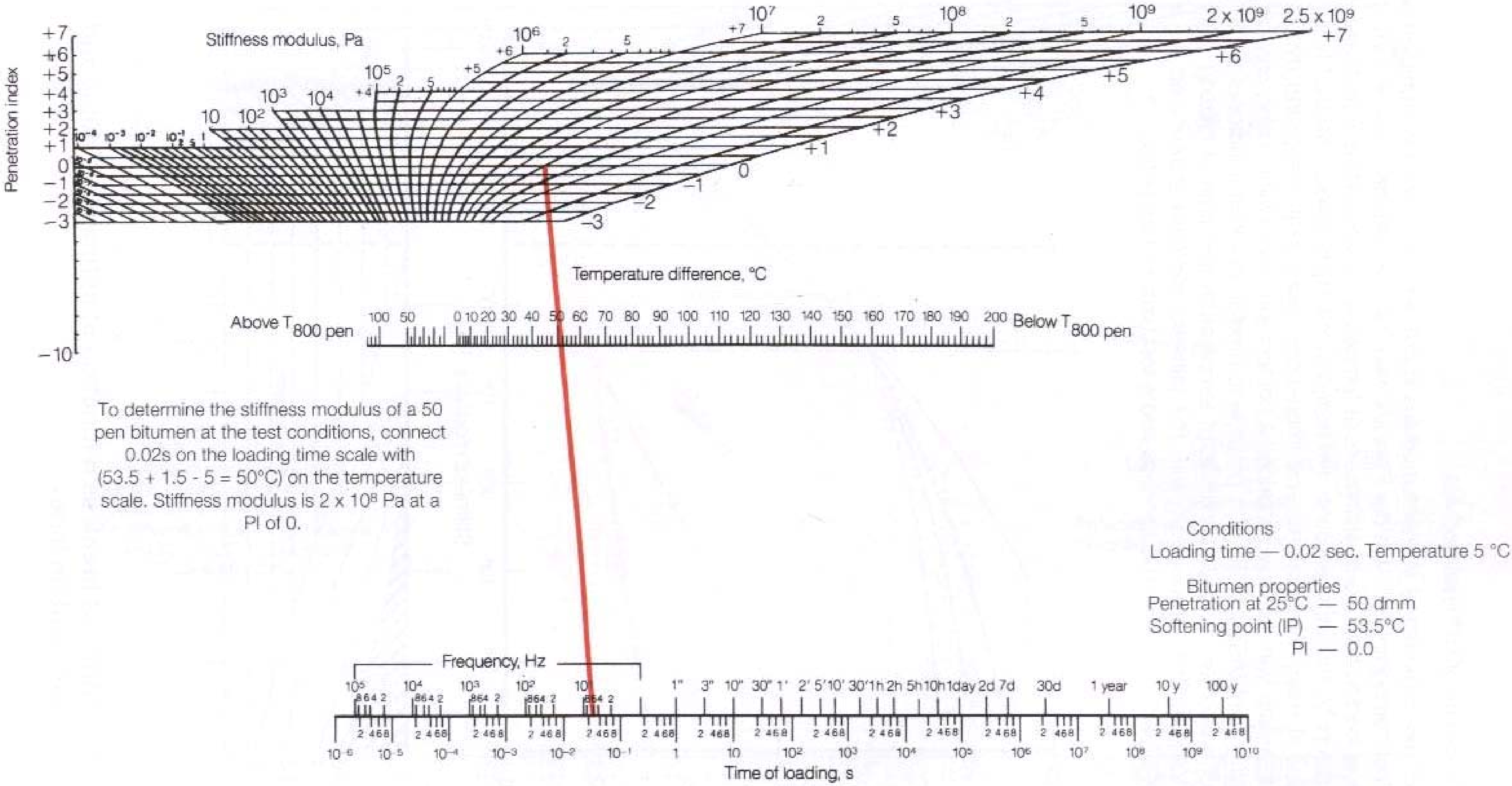
vice-versa, indicating that under these conditions the bitumen approximates respectively to elastic and viscous behaviour.

By combining creep tests with dynamic tests, a considerable range of stiffness moduli and loading times can be covered. The stiffness modulus as a function of loading time is, therefore, often represented in a graph with logarithmic scales as illustrated in figure 5.16, in which the asymptotes represent the approximation of elastic and viscous response at short and long loading times, respectively.

Measurements of the stiffness as a function of loading time at various temperatures result in a graph as represented in figure 5.17. It appears that the stiffness/loading time curves obtained at different temperatures on one grade of bitumen all have the same shape and if shifted along the loading time axis would coincide. In this case the bitumen is said to be 'thermorheologically simple'. Most penetration and oxidised grade bitumens belong to this category.

5.10.2.1 Measurement of stiffness modulus

The majority of instruments used to measure stiffness modulus are sophisticated and therefore expensive to purchase. However, in the late sixties the bitumen department of the Shell Laboratory Amsterdam developed the sliding plate rheometer(22), which combines simplicity and reliability. This test is similar to the sliding plate viscometer but uses thicker specimens between the plates. This instrument locks one plate in position and applies a load to the other plate (see photograph 5.9). The displacement (D) of this plate is recorded;



To determine the stiffness modulus of a 50 pen bitumen at the test conditions, connect 0.02s on the loading time scale with (53.5 + 1.5 - 5 = 50°C) on the temperature scale. Stiffness modulus is 2 x 10^8 Pa at a PI of 0.

Conditions
Loading time — 0.02 sec. Temperature 5 °C

Bitumen properties
Penetration at 25°C — 50 dmm
Softening point (IP) — 53.5°C
PI — 0.0

Figure 5.18 — Nomograph to determine the stiffness modulus of bitumen

5.10.2.2 Prediction of stiffness modulus

If the direct measurement of stiffness modulus is not feasible, it can be predicted using the Van der Poel nomograph(44). Van der Poel showed that two bitumens of the same PI at the same time of loading have equal stiffnesses at temperatures which differ from their respective softening points by the same amount. He tested over forty bitumens, whose PIs varied from +6.3 to -2.3 at many temperatures and frequencies, using both creep and dynamic tests. From the test data Van der Poel produced a nomograph, from which, using only penetration and softening point (ASTM D 36), it is possible to predict, to within a factor of 2, the stiffness modulus of a bitumen for any conditions of temperature and time of loading. Figure 5.18 shows a Van der Poel nomograph with the stiffness modulus determined for a 50 pen bitumen at a loading time of 0.02 seconds and a test temperature of 5°C.

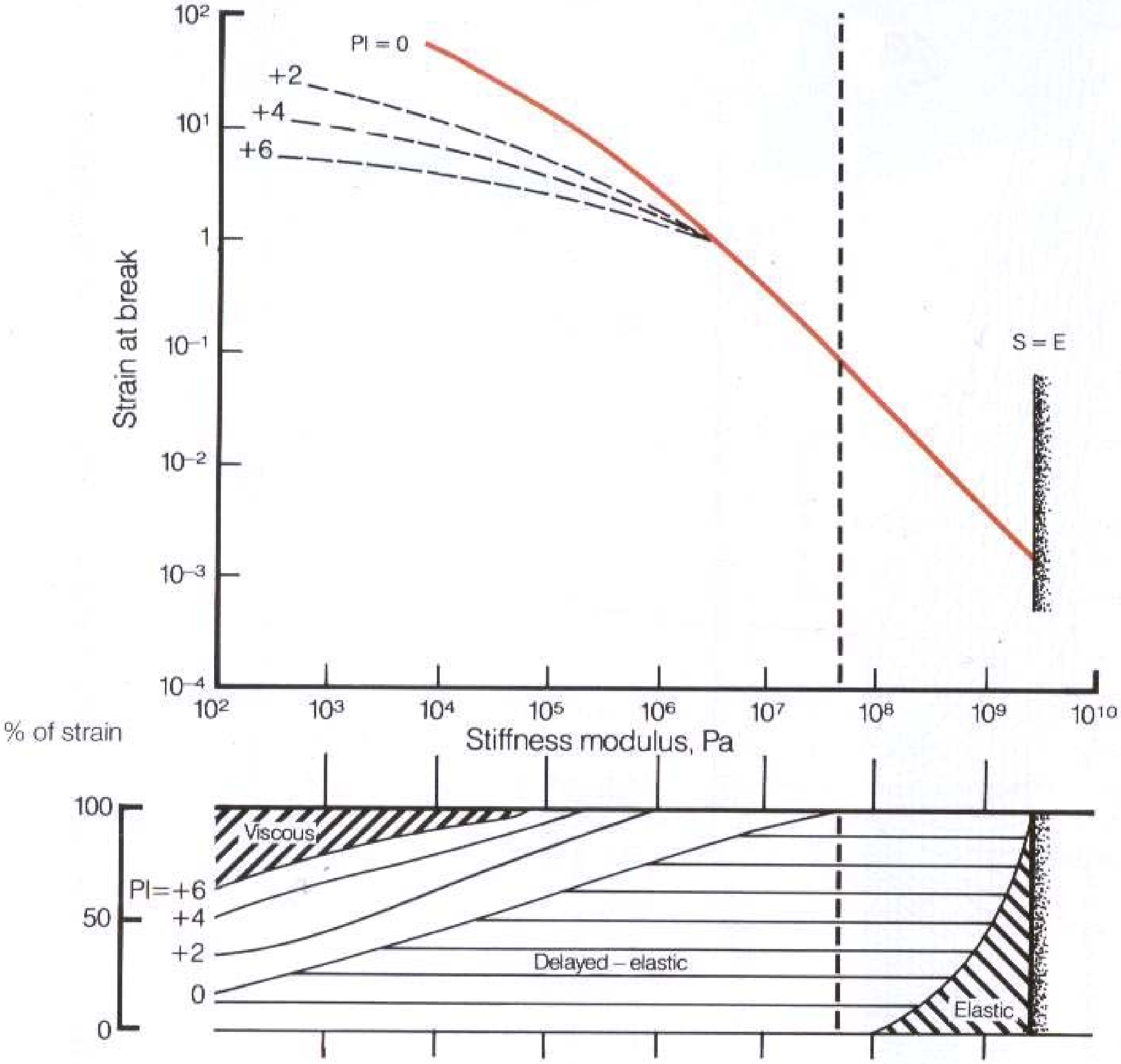
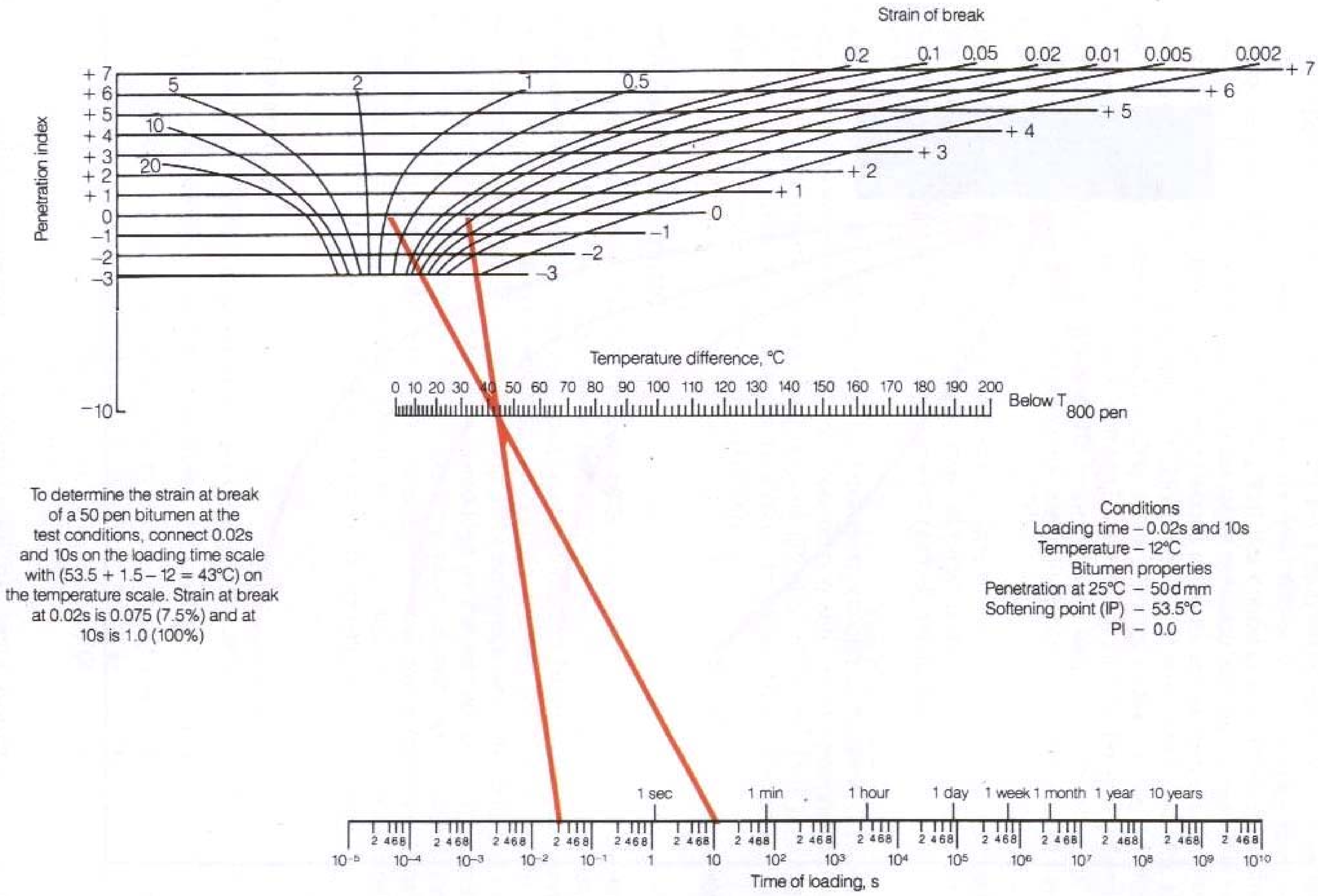


Figure 5.19 — Strain at break as a function of stiffness modulus and penetration index



To determine the strain at break
of a 50 pen bitumen at the
test conditions, connect 0.02s
and 10s on the loading time scale
with (53.5 + 1.5 – 12 = 43°C) on
the temperature scale. Strain at break
at 0.02s is 0.075 (7.5%) and at
10s is 1.0 (100%)

Conditions
Loading time – 0.02s and 10s
Temperature – 12°C
Bitumen properties
Penetration at 25°C – 50 d mm
Softening point (IP) – 53.5°C
PI – 0.0

Figure 5.20 — Nomograph to estimate the strain at break of bitumen

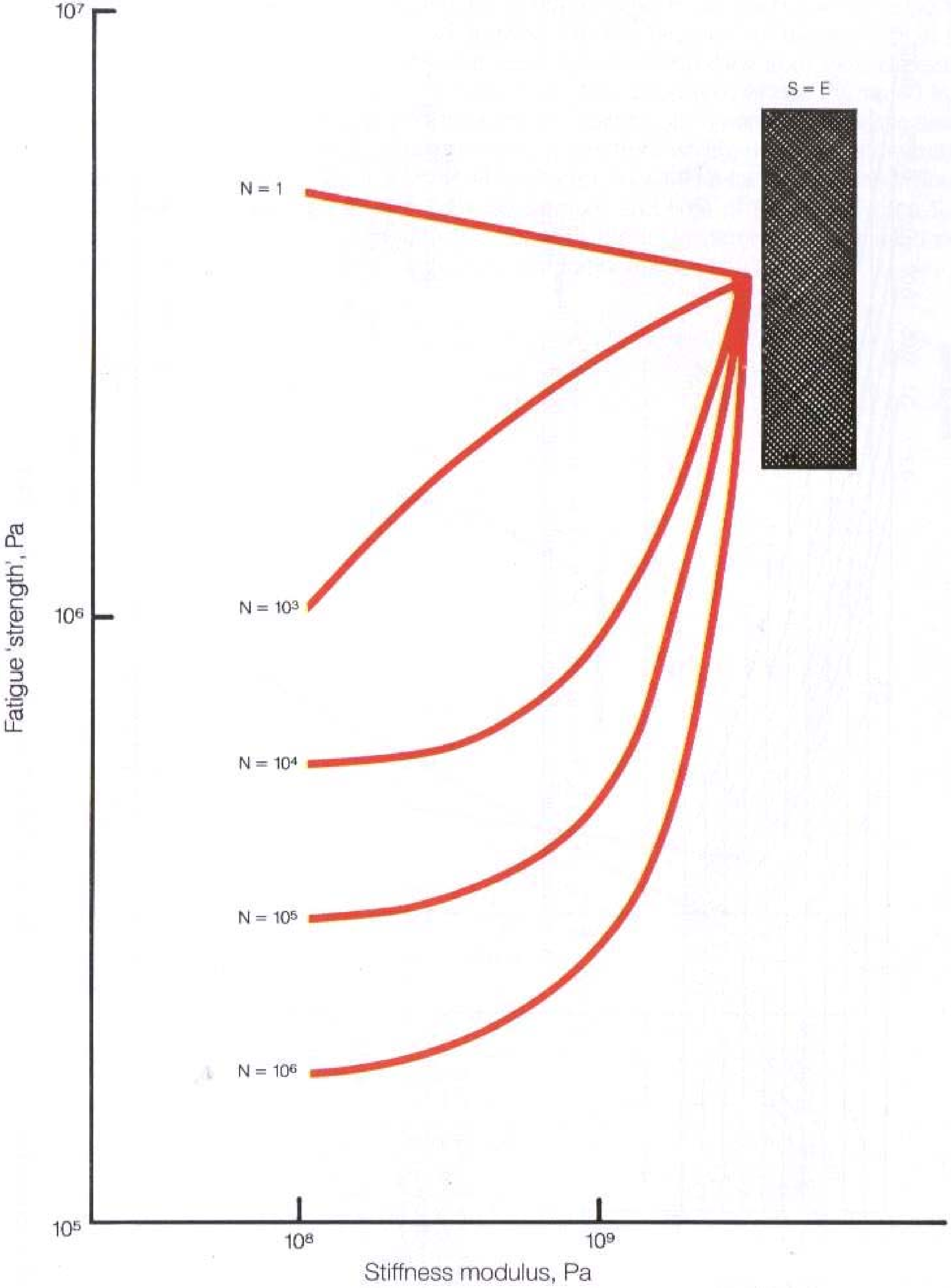


Figure 5.21 — Fatigue 'strength' as a function of stiffness modulus

5.10.3 Tensile strength

Another important engineering property of bitumen is its breaking stress and/or tensile strain at break. The tensile properties of bitumen are, like stiffness modulus, dependent on both temperature and loading time. Assuming that the breaking properties of bitumen are dependent on its rheology at the instant of failure, its behaviour can be expressed in terms of the amounts of elastic, delayed elastic and viscous strain as shown in figure 5.19(45). This shows, accepting the above assumption, that for a stiffness greater than 5 x 10^6 Pa, strain at break is a function of stiffness modulus. Only at low stiffness, where viscous deformation is large, is PI a significant factor. At high stiffness S = E. As the strain at break is defined as the ratio between change in length and the instantaneous length, it will be equal to the elongation, ie increase in length divided by the initial length, as long as the increase in length remains low.

In practice break takes place under conditions of large stress. Large stresses normally occur at low temperatures, ie at high stiffness; strain at break is then at its minimum. At higher temperatures, ie at low stiffness moduli, there will normally be no break at the same load but there will be deformation.

Strain at break can be predicted using the Heukelom nomograph(46), shown in figure 5.20, which has been derived from the Van der Poel nomograph. In the example (figure 5.20) strain at break of a bitumen with a softening point (IP) of 53.5°C and a PI of zero is given at 12°C. At a loading time of 0.02 seconds the strain at break is 0.075 (7.5%) and at a loading time of 10 seconds the strain at break is 1.00 (100%).

5.10.4 Fatigue 'strength'

The strength of bitumen, like that of many other materials, can be reduced by repeated loading, ie it fatigues. This is illustrated in figure 5.21 where the curves for fatigue 'strength' and breaking strength are shown as a function of stiffness modulus. All the tests have been carried out by bending at constant stress amplitude. The fatigue 'strength' is the stress which causes failure after 10^3, 10^4, 10^5, and 10^6 load cycles while the breaking strength corresponds to one cycle. The strength is reduced as the number of loadings increases. Figure 5.21 shows that at high stiffness moduli the effect of load repetitions is significantly reduced and at the maximum stiffness modulus (S = E = 2.7 x 10^9 Pa) fatigue 'strength' is independent of the number of load repetitions. For a single bend the fatigue strength is virtually constant, at about 4 x 10^6 Pa for stiffness moduli greater than 5 x 10^7 Pa.

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Chapter 6 - Emulsions and cutback bitumens

6.1 Introduction

Bitumen is the oldest known thermoplastic material in use today. Its usefulness and appeal derive from its simple thermoplastic property of being a thin liquid at high temperature and a virtual solid at ambient temperature. For the vast majority of applications bitumen is used in the temperature range 140 to 230°C at a viscosity of around 200 cSt (20 Pa.s). For many applications these conditions are both essential and desirable allowing rapid throughput from hot bulk bitumen delivery through to final use without any reheating. There are limitations to the coating film thickness that can be achieved using hot-applied techniques and for some applications it is necessary to apply at a lower temperature and/or viscosity. The reasons may be a combination of the process requirements, the application techniques, safety and environmental requirements or final product properties. The two methods used mostly to modify bitumen properties are emulsification with water and dilution with hydrocarbon solvent enabling the bitumen to be applied cold, up to about 80°C for emulsions or up to about 150°C for cutbacks, depending on the dilution and solvent used.

6.2 Emulsions

Bitumen emulsions are heterogeneous, two-phase systems consisting of two immiscible liquids, bitumen and water, stabilised by a third component, the emulsifier. The bitumen is dispersed throughout the continuous aqueous phase in the form of discrete droplets, typically 0.5 to 5 microns in diameter, which are held in suspension by electro-static charges.

Bitumen emulsions can be divided into three classes of which the first two, in volume terms, are by far the most important:

- cationic emulsions;
- anionic emulsions;
- nonionic emulsions.

The terms cationic, anionic and nonionic refer to the overall particle charge on the bitumen droplet imparted by the emulsifier. If an electric charge is passed through an emulsion containing negatively charged particles of bitumen, the droplets will migrate to the anode, hence the emulsion is termed anionic. Conversely, positively charged particles will migrate to the cathode and these emulsions are known as cationic emulsions. Bitumen droplets in nonionic emulsions are neutral and consequently will not migrate to either pole. Such nonionic emulsions include clay emulsions.

In 1906 Schade van Westrum(1) took out a patent covering the application of bituminous dispersions in water for road building. Initially efforts were made to form emulsions by purely mechanical means, but it soon became apparent that whilst a dispersion could be formed by mechanical shear, the dispersion was not stable unless a third component, the emulsifier, was present. Initially naturally occurring organic acids in naphthenic bitumens were utilised. The addition of sodium or potassium hydroxide to the aqueous phase saponified (turned into soap) the acids and stabilised the dispersion(2).

Since the pioneering days of bitumen emulsions a great variety of materials have been used as stabilisers. These include such obscure items as ox blood and casein through to more efficient surfactants such as fatty acid distillation residues, rosin acids and lignin sulphonates. Since the early 1950s cationic surfactants have become increasingly important as emulsifiers due to their ability to be adsorbed onto a variety of solid surfaces. This affinity for solid surfaces has led to their almost total dominance of the road construction market because good adhesion of the bitumen to different types of mineral aggregate is essential. However, cationic emulsions are seldom used for industrial purposes because their affinity for natural surfaces tends to make them break too quickly for most applications. Cationic emulsifiers most widely used are long chain fatty amine derivatives such as mono- and diamines, amido amines and imidazolines(3).

6.2.1 Emulsifiers

The properties of an emulsion depend greatly on the material used as the emulsifier. The emulsifier coats the surface of the dispersed phase and consequently inhibits coagulation of the droplets. It is this surface activity which determines whether or not the emulsion will be stable when subjected to either mechanical action or chemical activity.

Chemical emulsifers, those used to produce anionic and cationic emulsions, consist of a long hydrocarbon chain terminated with a polar functional group. The hydrocarbon chain is lipophilic (oil loving) and consequently has an affinity for the bitumen, whereas the polar group is hydrophilic (water loving) and consequently has an affinity for water. The emulsifier molecule orientates itself so that the hydrocarbon chain is firmly bound in the bitumen with the polar functional group located at the interface between the bitumen and water. As the functional group is electrically charged the surface of the bitumen droplet behaves as though it is charged and consequently, if the emulsion is brought into contact with a material of the opposite charge, the droplet will be attracted to it. Conversely, if the bitumen droplet and the substrate to which it is applied bear the same overall charge, there will be no attraction. Electrostatic attraction can be exploited to cure or break the emulsion, particularly in the case of those emulsions used for road surface dressing where cationic emulsions are typically used. Aggregate surfaces generally have a weak negative charge, the emulsion droplets are attracted to this and adhere to the aggregate, thereby breaking the emulsion.

Cationic emulsifiers are typically mono- di- or polyamine derivatives of fatty acids and may be functionalised by ethoxylation. The emulsifier solution is prepared by the reaction of the emulsifier with dilute hydrochloric or acetic acid, the pH of the solution being carefully controlled so as to produce the amine salt as follows:

$$R - NH_2 + HCl \longrightarrow R - NH_3^+ + Cl^-$$

Fatty amine + hydrochloric acid ——> Amine hydrochloride

Anionic emulsifiers are generally fatty acids which are saponified using a strong alkali, eg sodium or potassium hydroxide. Excess alkali can also saponify the natural acids found in the bitumen which can also act as emulsifiers. The typical reaction is as follows:-

$$R - COOH + NaOH \longrightarrow R - COO^- + Na^+ + H_2O$$

Fatty acid + sodium hydroxide ——> Fatty acid soap + water

Nonionic emulsifiers may be chemical surfactants or natural materials such as inorganic clays. Emulsions stabilised by the use of clay are most widely used for roofing. Clays are made up of flat, plate-like particles that associate at the surface of the bitumen droplets forming a physical barrier to coalescence. The aqueous phase of a clay emulsion is prepared as an aqueous dispersion of clay known as a 'slip'. Clays are sometimes used in conjunction with anionic emulsifiers to make soap/clay emulsions.

6.2.2 Manufacture

6.2.2.1 Soap emulsions

Emulsifier solutions for manufacture of bitumen emulsions are often referred to as 'soap" because anionic emulsions using saponified fatty acids were the first to be widely used. At the present time soap emulsions are almost always manufactured on some form of colloid mill. Such mills consist of a rotor, which may be grooved or smooth and revolves at between 1,000 and 6,000 rpm within a stator, which may also be grooved or smooth. The clearance between the rotor and stator is typically between 0.25 and 0.50 mm (0.01 and 0.02 inches) and may be adjustable. The hot bitumen and aqueous phases are fed separately, but simultaneously into the mill and are subjected to intense shear forces between the rotor and stator. The temperatures of the bitumen and aqueous phase vary, depending on the grade and percentage of bitumen in the emulsion. However, the viscosity of the bitumen entering the mill should not exceed 0.2 Pa.s (2 Poise); to achieve this viscosity, bitumen temperatures in the range 100 to 140°C are used. The temperature of the aqueous phase is adjusted so that the temperature of the emulsion is at or around 90°C, although temperatures above 100°C can be tolerated if the system can be pressurised. As the bitumen and aqueous phase are subjected to shear in the mill, the bitumen breaks up into tiny droplets which are intimately mixed with the emulsifier solution. The coated droplets are kept from coalescing by the emulsifier coating.

Schematic diagrams of continuous and batch emulsion manufacturing plants are shown in figures 6.1 and 6.2 respectively. The bitumen and aqueous phases are metered into the colloid mill separately by proportional metering pumps or under manual control in conjunction with flow meters.

The method of adding the emulsifier to the water varies; some emulsifiers such as amines, must be mixed and reacted with acid to attain water solubility; whereas others such as fatty acids must be saponified by heating with alkali before addition to water. Nonionic systems, such as clays, require the preparation of a dispersion before manufacture.

6.2.2.2 Clay emulsions

Bitumen emulsions containing clay as the only emulsifier can not be made easily on a colloid mill; clay is an excellent stabiliser but a poor emulsifier. Clay emulsions are made in a slow-moving powerful mixer because of their consistency. Batch mixing times are long, increasing disproportionally as the batch size is increased because of the problem of removing heat (introduced with the bitumen) from the mass. Continuous production of clay emulsions is possible on specially-designed equipment.

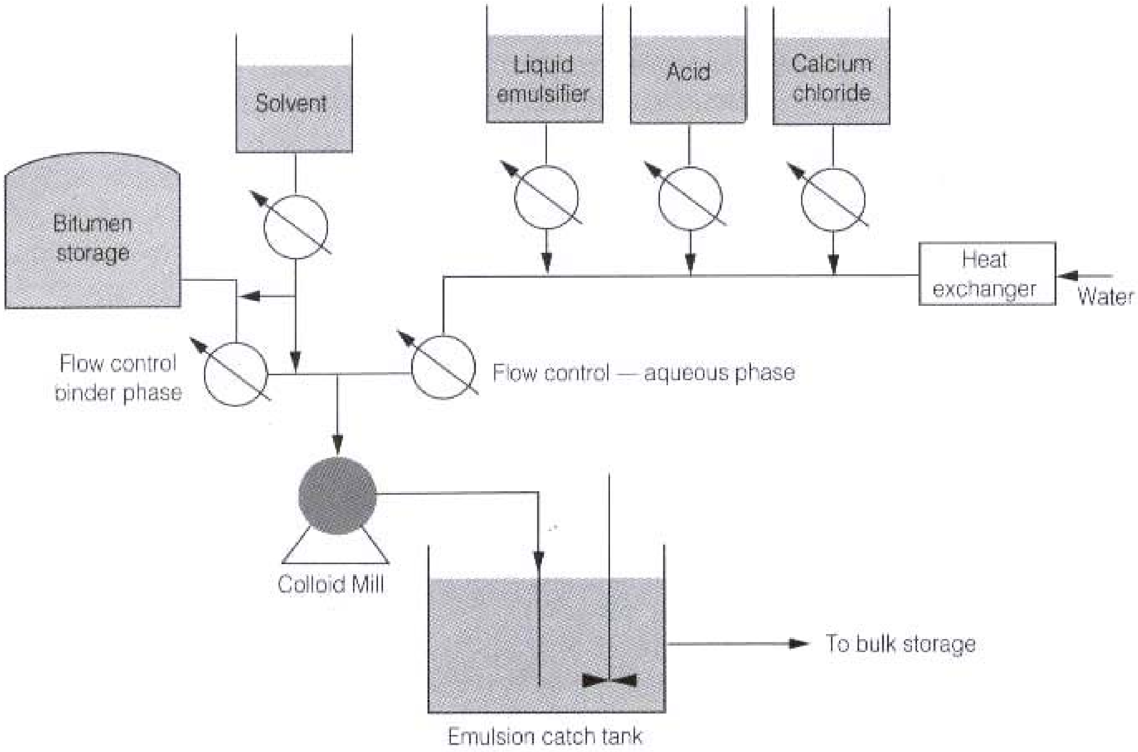

Figure 6.1 — Schematic diagram of a continuous emulsion plant

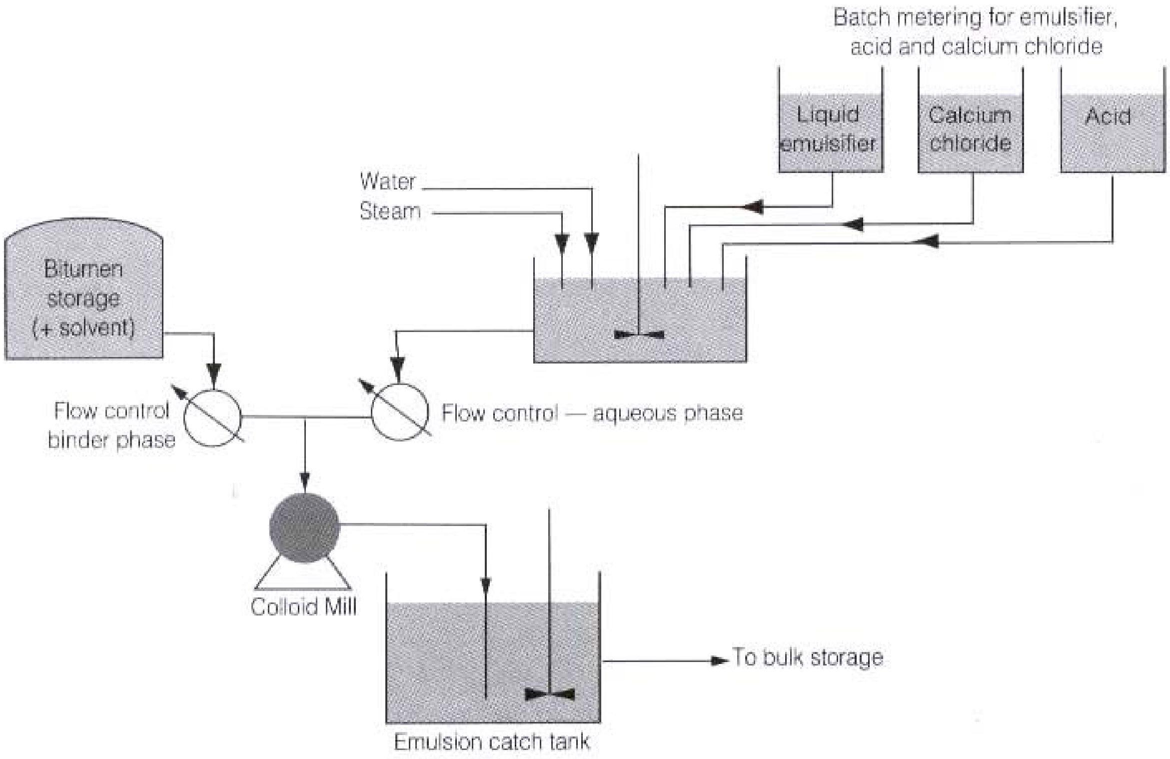

Figure 6.2 — Schematic diagram of a batch emulsion plant

6.2.2.3 Soap/clay emulsions

Soap/clay emulsions merit inclusion as, although they represent only a small percentage of the world bitumen market, they are widely used in applications where composite films incorporating fillers and having very high resistance to flow at high temperatures are needed. Soap/clay emulsions were developed as a means of producing clay emulsions at a high rate of throughput on a colloid mill instead of the slow batch process. Their formulation is complex although no special manufacturing equipment is needed. The aqueous phase consists of a clay 'slip' to which an anionic emulsifier is added. A base emulsion is manufactured on a colloid mill and cooled. The base emulsion, a relatively low viscosity liquid, is then mixed with a 'conversion agent' which disables the anionic emulsifier. When the reaction process is complete, the emulsion has changed from a thin soap-stabilised emulsion to a thixotropic clay-stabilised emulsion.

6.2.3 Formulation

The properties required of a bitumen emulsion are highly dependent upon the end use to which it is to be put. However, the emulsion should generally be mechanically stable to facilitate storage, handling and transport without significant deterioration in dispersion quality. The chemical stability of the emulsion will vary depending upon whether the emulsion is required to undergo mixing with aggregate or filler, or break quickly after application. Emulsion viscosity is also critical to the performance of most emulsions as it determines the method and thickness of application to the desired substrate. From a technological viewpoint the most important properties can be summarised as follows

- the stability of the emulsion;
- the adhesivity of the emulsion;
- the viscosity of the emulsion.

6.2.3.1 Emulsion stability

6.2.3.1.1 Storage stability

Inadequate storage stability of an emulsion manifests itself initially by settlement of the bitumen, generally resulting in a bitumen-rich lower layer and a bitumen-lean upper layer, although in unusual circumstances the opposite can occur. Settlement of an emulsion is the result of gravity acting upon the denser dispersed bitumen droplets. The velocity of the downward movement of these particles can be estimated using Stokes' Law(4), which expresses the velocity as follows:

$$v = \frac{2}{9} \frac{gr^2 (d_1 - d_2)}{\eta}$$

where g = force due to gravity

r = particle radius

d_1 = specific gravity of the bitumen

d_2 = specific gravity of the aqueous phase

η = viscosity of the aqueous phase

In practice Stokes' Law tends to overestimate the rate of settlement due to the fact that in a bitumen emulsion the droplets are so tightly packed that they are not entirely free to move.

In addition to gravity there are other forces acting on the droplets, repulsive forces originating from the electrostatic double layers created by the ionised emulsifier (see figure 6.3) and attractive forces associated with the mass of the droplets. The rate of settlement is also affected by the rheology (flow characteristics) of the continuous phase and by the particle size of the emulsion which controls the amount of Brownian motion occuring.

Breakdown of an emulsion follows settlement in two stages. Firstly bitumen droplets agglomerate into clumps. This phenomenon is known as flocculation and can be reversed by stirring or agitation of the emulsion. The second stage, which is irreversible, is termed coalescence in which the flocculated particles fuse together to form larger globules. This process may be spontaneous or induced by mechanical action.

6.2.3.1.2 The breaking process

6.2.3.1.2.1 Anionic/cationic emulsions

The mechanism by which emulsion coalescence occurs is dependent upon the type of emulsion and the substrate to which it is applied. An emulsion contains emulsifier molecules in both the aqueous phase and on the surface of the bitumen droplets. Some of the free emulsifier ions form micelles, or, in the case of clay emulsions, the clay particles agglomerate. In a stable emulsion an equilibrium exists between the free and bound emulsifier; if some of the free emulsifier ions are removed from the aqueous phase, the balance is restored by ions from the micelles and the surface of the droplets. This phenomenon is exploited in some systems in order to break the emulsion. Mineral aggregates tend to have negatively charged surfaces, which, when brought into contact with cationic emulsion, rapidly absorb emulsifier ions from the aqueous phase, weakening the charge on the surface of the bitumen droplet

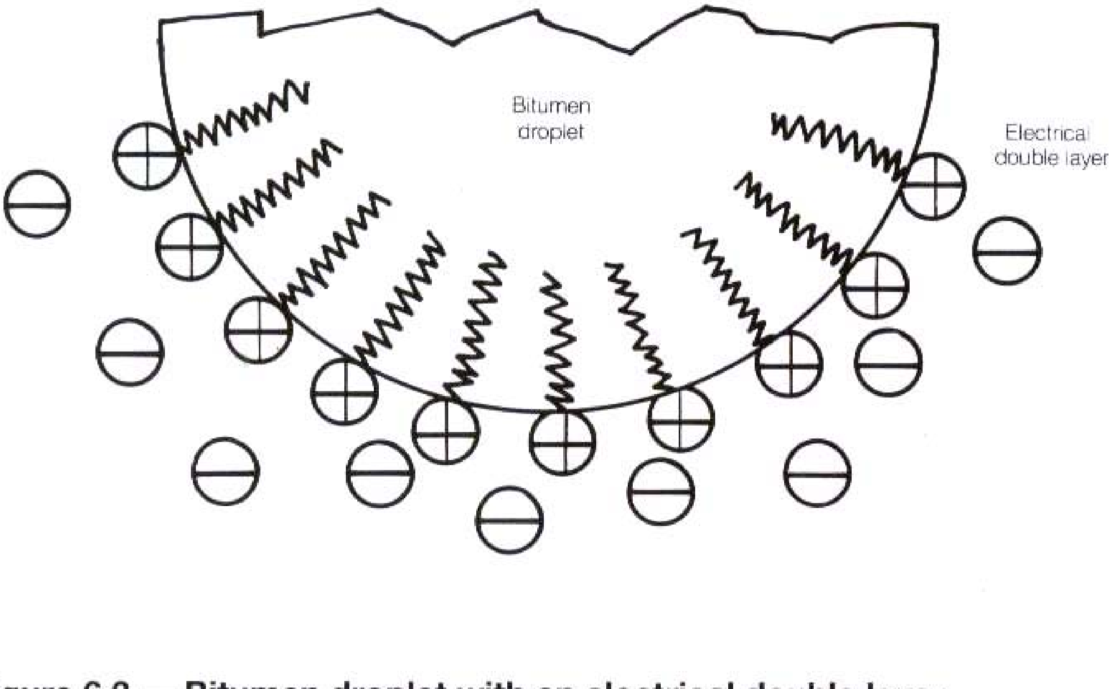

Figure 6.3 — Bitumen droplet with an electrical double layer

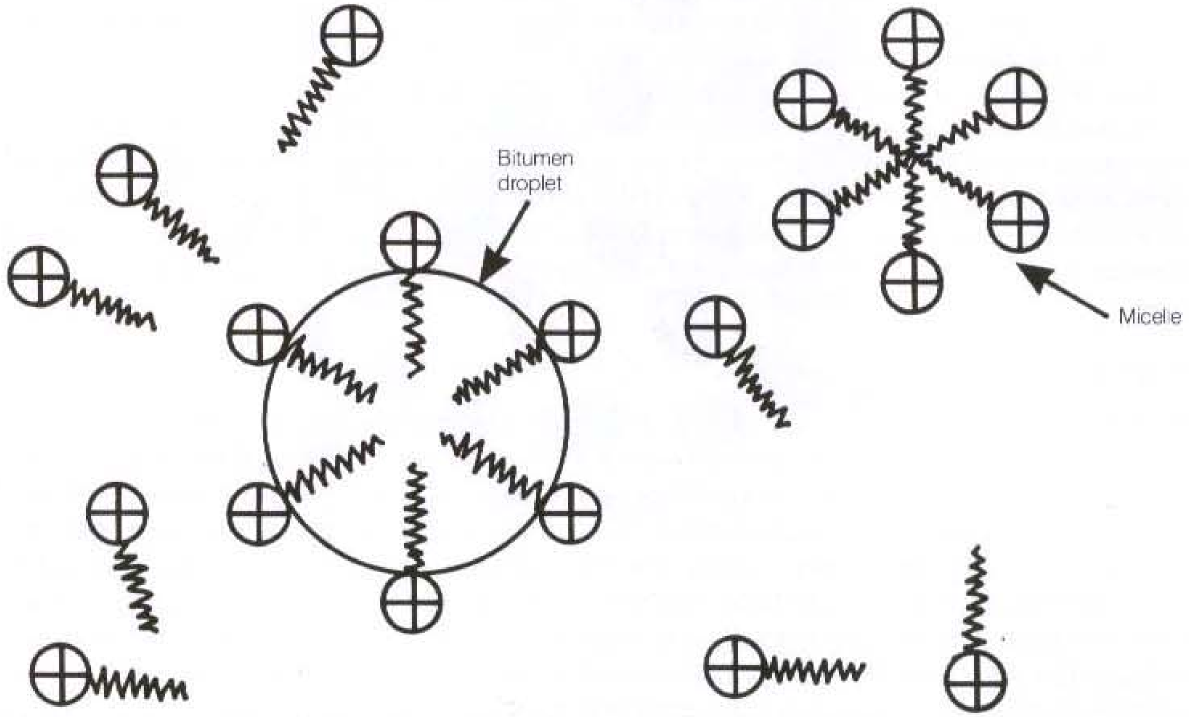

Figure 6.4a — Emulsifier ions forming micelles in a stable solution

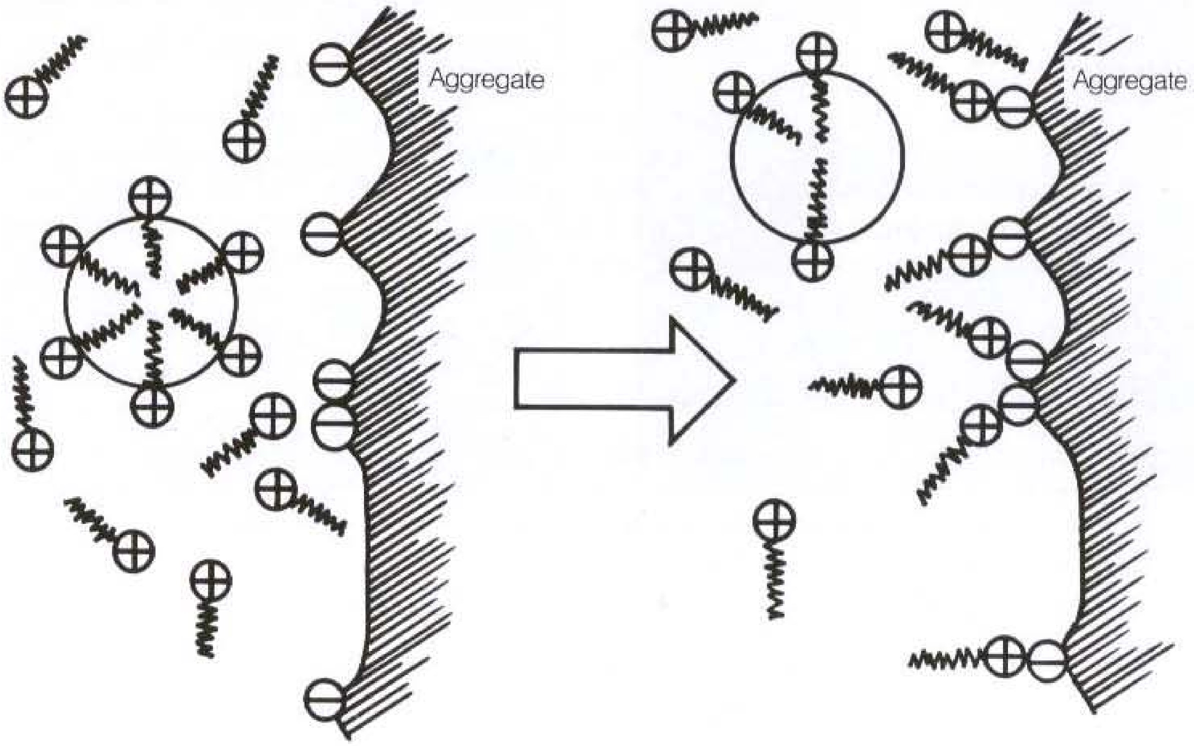

Figure 6.4b — Schematic diagram of the breaking process

and initiating the breaking process. This is shown schematically in figures 6.4a and 6.4b. A point is reached where the charge on the surface of the droplets is so depleted that rapid coalescence takes place. The aggregate, now covered in hydrocarbon chains, has a high affinity for bitumen and strong adhesion of the bitumen to the stone results. Industrial bitumen emulsions are generally required to be stable to mixing with filler or fibres and the above mechanism may not be desirable. In these cases anionic or nonionic emulsions are used where there is little or no affinity for the substrate and consequently the emulsion is still stable after mixing. In these emulsions breaking occurs predominantly by evaporation of water until the particles first flocculate and subsequently coalesce. With these emulsions full adhesion to the substrate is only obtained after complete evaporation of the water.

6.2.3.1.2.2 Soap/clay emulsions

The inclusion of clay in a soap/clay emulsion fulfils two functions. Firstly, during manufacture the clay acts as a stabiliser to prevent contact coalescence of the bitumen droplets, and secondly, in the dried film, the clay particles form a skeleton which gives the binder addtional strength and reduced hot flow properties. Emulsions containing clay are highly stable and consequently break very slowly. Unless the bitumen droplets are in some way charged to make them attracted to the substrate onto which they are applied, then the breaking process of the emulsion will be predominantly by evaporation. As the water evaporates from the emulsion the clay skeleton forms as illustrated in figures 6.5a, 6.5b and 6.5c. For most applications of soap/clay emulsions the breaking mechanism is by evaporation.

Whilst the emulsion is in its stable form, depending upon its viscosity, it can be poured, brushed, trowelled or sprayed.

6.2.3.2 Viscosity

The viscosity of the emulsion is of prime importance because it ultimately determines mode of application of the emulsion. The relationship between shear applied and viscosity, ie the rheology of the emulsion, also plays a large part in the suitability of an emulsion for a particular purpose(5). A consequence of this is that when stating the viscosity of an emulsion it is essential to state the conditions under which that viscosity was determined. For details of viscosity tests see chapter five.

6.2.4 Modification of emulsion properties

There are a number of measures an emulsion manufacturer can take to modify the basic properties of a bitumen emulsion, ie viscosity, storage stability, breaking rate and particle size distribution. Contrary to popular belief, the bitumen is not the sole controlling agent, although its influence is, of course, very important.

There are three basic ways in which changes to emulsion properties can be induced:

by changing the grade, concentration or (sometimes) origin of the bitumen;

by changing the emulsion formulation; eg pH, inclusion of additives such as calcium chloride;

by changing the type of emulsifier and/or its concentration.

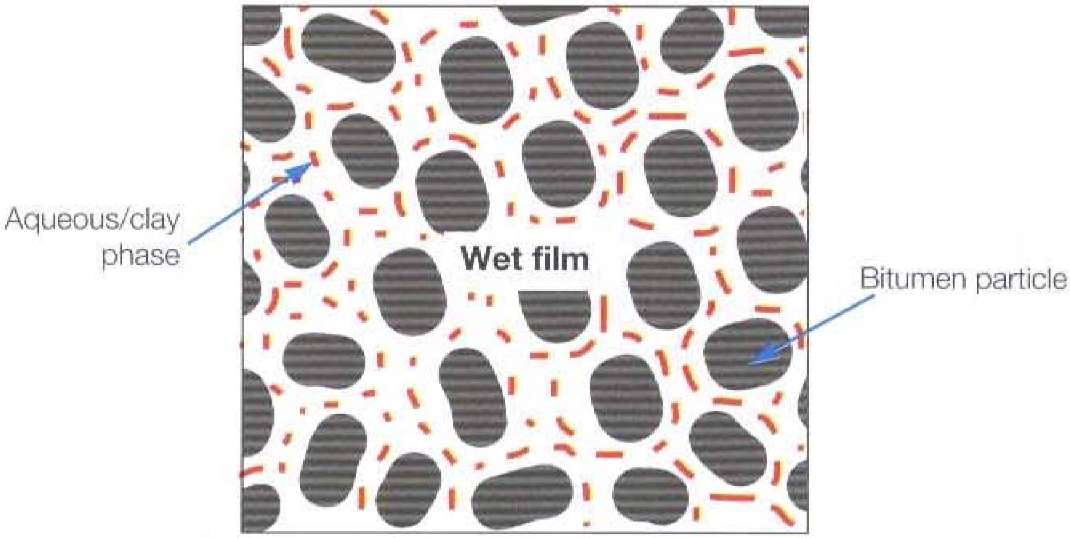

Figure 6.5a

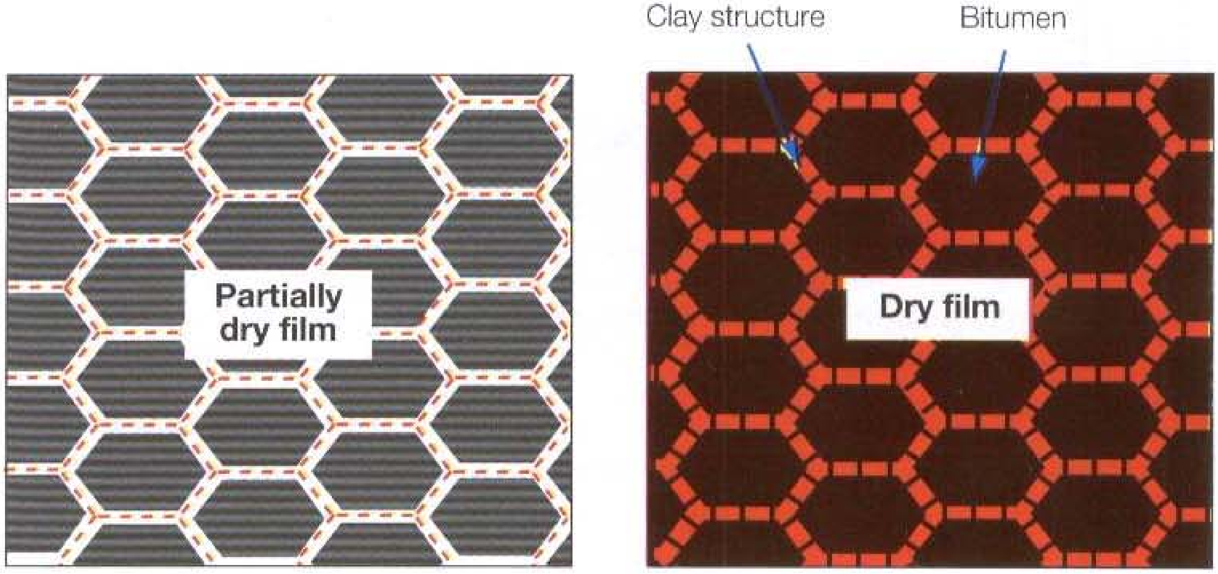

Figure 6.5b **Figure 6.5c**

Figure 6.5 — Breaking of a soap/clay emulsion

6.2.4.1 Viscosity

6.2.4.1.1 Bitumen content

This is subject to some limitations; firstly increasing the bitumen content could be considered too expensive and, secondly, if the content is already high, a small increase in concentration can induce a dramatic viscosity increase, see figure 6.6. Below 60 per cent by mass of bitumen the effect is small and the degree of latitude is restricted by the bitumen content in the specification. The data shown in figure 6.6 is specific to aparticular formulation but the effect is general.

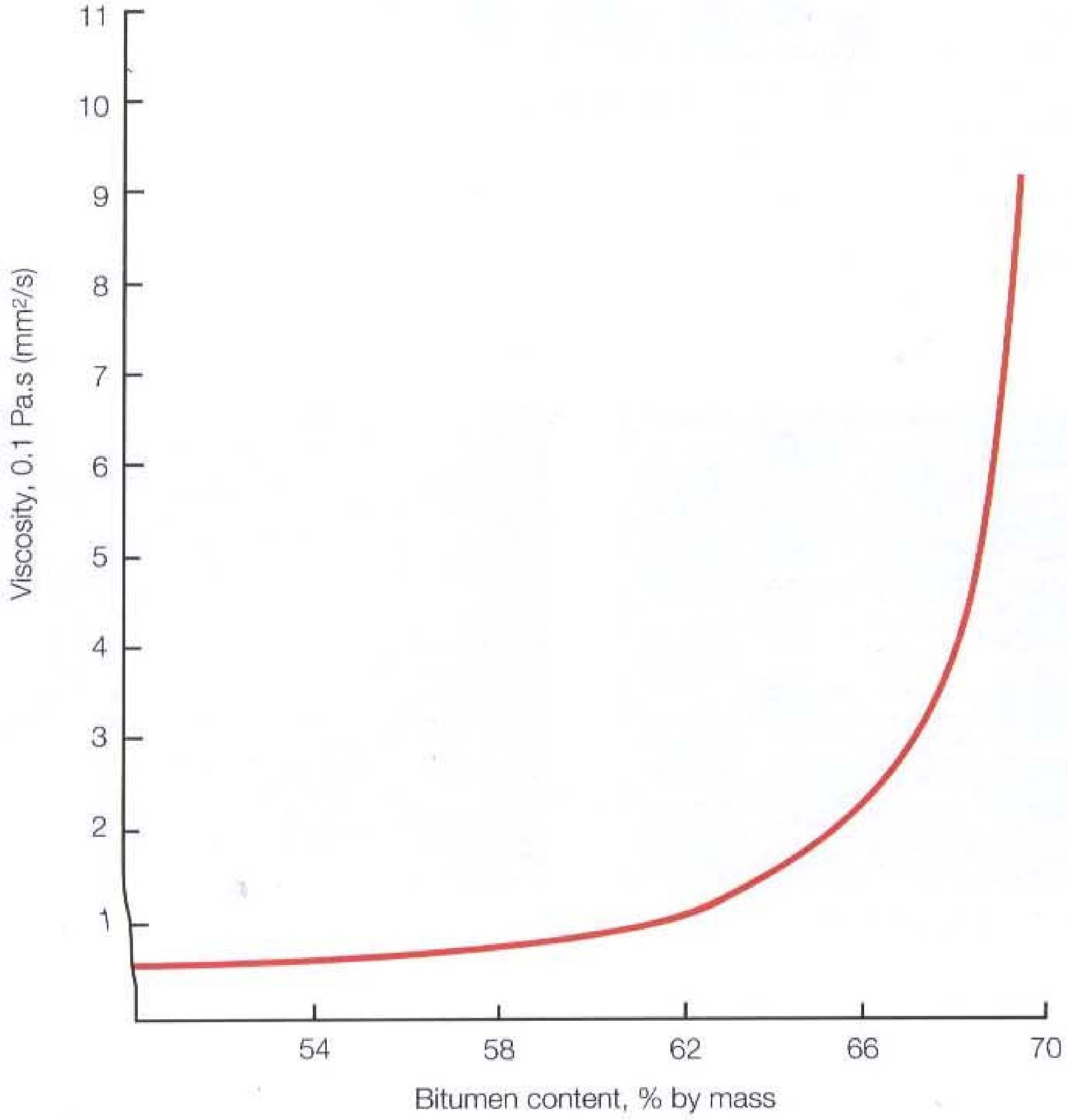

Figure 6.6 — Emulsion viscosity as a function of bitumen content

6.2.4.1.2 Aqueous phase

The viscosity of a bitumen emulsion is highly dependent on the aqueous phase composition. It has been shown that viscosity can be increased by altering the pH, increasing the emulsifier content or by increasing the neutralisation ratio between the acid and amine contents in a cationic emulsion. Apart from increasing or decreasing the viscosity of an emulsion, such changes can also affect the rheology, or flow characteristics, to introduce non-Newtonian behaviour. However, it should be borne in mind that other properties are strongly dependent on aqueous phase composition, such as breaking time and storage stability.

6.2.4.1.3 Manufacturing conditions

By increasing the flow rate through the mill, the particle size distribution of the emulsion will be changed. At bitumen contents less than 65 per cent by mass the viscosity of the emulsion is virtually independent of flow rate. However, at bitumen contents greater than 65 per cent by mass where the globules of bitumen are packed relatively close together, inducing a change in the particle size distribution by changing the flow rate has a marked effect on viscosity, as shown in figure 6.7.

6.2.4.1.4 Bitumen viscosity

If the viscosity of the bitumen entering the colloid mill is lowered, the particle size of the emulsion will be reduced which will tend to increase the viscosity of the emulsion. This can be achieved by adding a small quantity, say two to four per cent by mass, of a hydrocarbon solvent to the bitumen.

6.2.4.1.5 Particle size distribution

Particle size distribution has a large effect on viscosity. A theoretical emulsion having single-sized spherical particles would have infinite viscosity at about 70 per cent bitumen content (assuming non-deformable bitumen) but practical surface dressing emulsions of 80 per cent bitumen content are possible if a rubber polymer is incorporated in the bitumen. This is because the polymer gives a wide particle size distribution. The effect can be demonstrated by adding 60 per cent latex to 60 per cent bitumen emulsion. The resulting mixture has lower viscosity than either component.

6.2.4.2 Breaking rate

The breaking rate of an emulsion can be modified by changes to certain key parameters.

6.2.4.2.1 Aqueous phase composition

The breaking rate of a bitumen emulsion has been shown to be increased by reducing the acid content, increasing the emulsifier content or by altering the neutralisation ratio of the emulsifier.

6.2.4.2.2 Bitumen content

Increasing the bitumen content of an emulsion induces an increase in its breaking rate, the size of the effect depending on the aqueous phase composition.

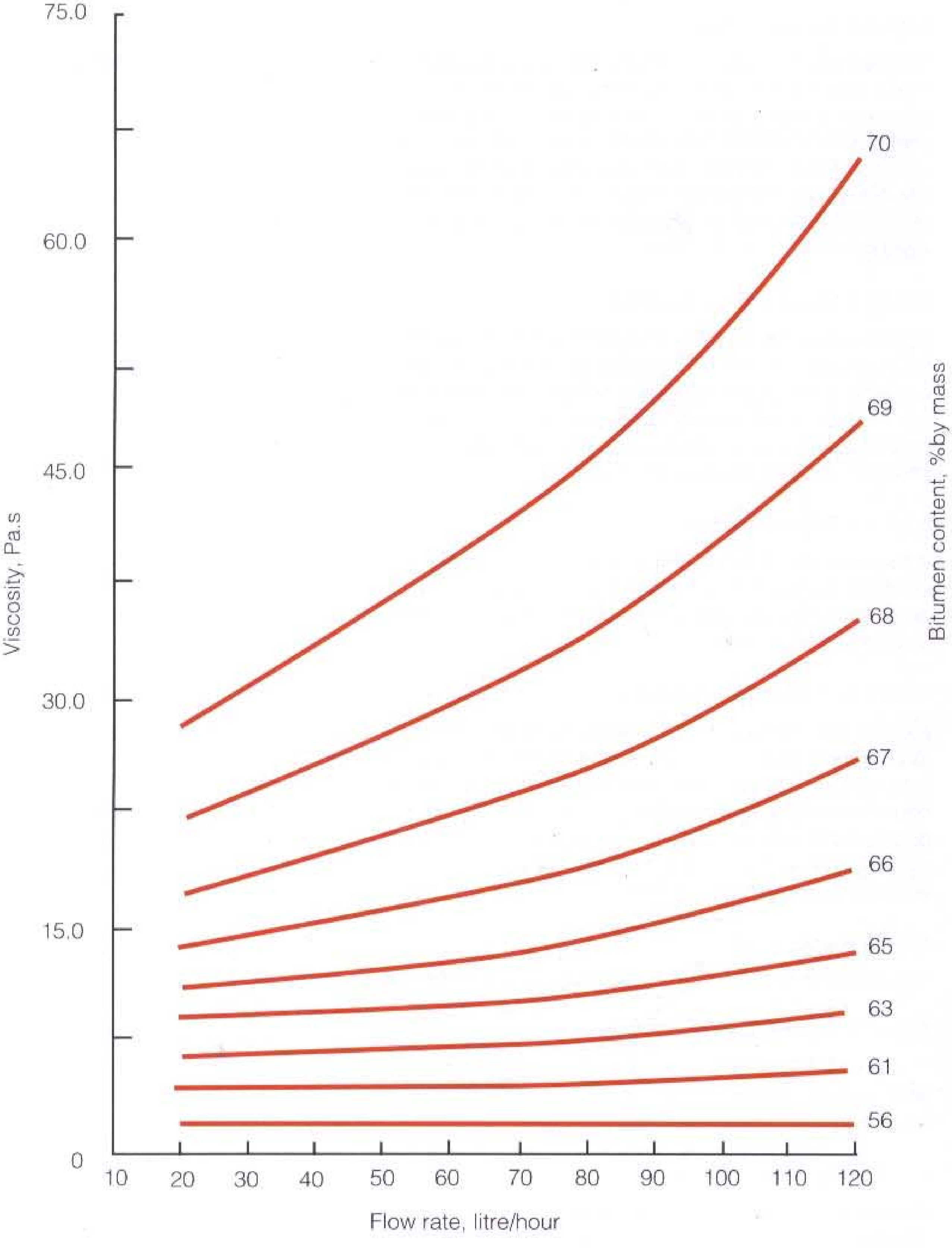

Figure 6.7 — Emulsion viscosity as a function of flow-rate

6.2.4.2.3 Breaking agents

The use of breaking agents can accelerate the breaking of an emulsion. For some emulsions it is possible to include a chemical breaking agent just after application of the emulsion. Breaking agents generally have a double role as they may also improve adhesion between the bitumen and substrate.

6.2.4.2.4 Other parameters

Several other parameters may influence the breaking rate of an emulsion and can be summarised as follows:

- the type of emulsifier;
- the bitumen particle size and distribution; the finer the particle size and smaller the dispersion the slower the breaking rate;
- temperature; the higher the ambient temperature the faster the breaking rate of the emulsion.

6.2.4.3 Storage stability

It is usual for any deficiency in the storage stability of an emulsion to show itself in the form of settlement for which there are several causes:

6.2.4.3.1 Bitumen specific gravity

Bitumen with a high specific gravity will tend to settle when emulsified. The problem can be reduced by:

- decreasing the specific gravity of the bitumen by the addition of kerosene before emulsification; however, this will result in an increased emulsion viscosity and a reduced viscosity of the binder on the substrate.
- by increasing the specific gravity of the aqueous phase by the addition of a salt such as calcium chloride.

6.2.4.3.2 Emulsion viscosity

Low viscosity emulsions are more prone to settlement than high viscosity emulsions because the particles have more freedom to move. The storage stability can be improved by increasing the viscosity as discussed above. Increasing the emulsifier content will also decrease the settlement rate.

6.2.4.3.3 Electrolyte content

The presence of electrolytes in the bitumen can reduce the storage stability of the emulsion. In cationic emulsions a high sodium concentration in the bitumen may induce breaking during storage. This can be counteracted by the addition of a salt to the aqueous phase.

6.2.4.4 Particle size distribution

The size distribution of the emulsion droplet is dependent on the interfacial tension between the bitumen and the aqueous phase (the lower the interfacial tension, the more easily the bitumen disperses) and on the energy used in dispersing the bitumen. For a given mechanical energy input, harder bitumens will produce coarser emulsions and high penetration or cutback bitumens will produce finer emulsions. It is possible to influence the particle size and distribution to achieve a finely divided emulsion with a narrow spread of particle sizes.

Bitumen emulsions with a broad spectrum of particle sizes are more prone to settlement than those with a relatively narrow size distribution. This is because large particles settle more rapidly due to the repulsion forces between the particles. Therefore emulsions with a relatively narrow particle size distribution are more storage stable.

6.2.4.4.1 Bitumen additives

6.2.4.4.1.1 Acids

Naphthenic acids can be added to paraffinic bitumens for the production of anionic emulsions. The acids react with the alkaline aqueous phase to form soaps which are surface active and which stabilise the dispersion.

The addition of naphthenic acids causes a decrease in the mean particle size of the emulsion without changing its relative size distribution. The specific surface area of the bitumen emulsion is increased, and the amount of emulsifier absorbed at the bitumen surface is increased. This results in a reduction in the emulsifier concentration in the aqueous phase and consequently the breaking rate is increased.

6.2.4.4.1.2 Electrolyte concentration

The presence of electrolytes such as sodium chloride in bitumen can have a profound effect on the emulsion viscosity. Finely divided bitumen can act as a semi-permeable membrane and if a bitumen droplet in an emulsion contains a higher electrolyte concentration than that of the aqueous phase, then transfer of water from the aqueous phase to the bitumen droplet will occur. This increases the volume occupied by the droplet thereby increasing the viscosity of the emulsion. However, if the electrolyte concentration of the bitumen phase is too high, then excessive absorption of water will occur and ultimately the particle will 'burst', releasing the electrolyte into the aqueous phase. This phenomenon manifests itself as a sudden drop in viscosity of the emulsion, together with a corresponding increase in the sieve residue. Water absorption by the bitumen will not occur if the electrolyte concentration of the aqueous phase exceeds that of the bitumen droplet and this can be controlled by the addition of electrolytes to the aqueous phase either before or after manufacture. Water absorption of the bitumen can be increased by adding electrolytes to the bitumen before manufacture in the form of an emulsion of brine in heavy fuel oil. However, considerable expertise is required in the use of such additives to avoid uncontrollable viscosity fluctuation during storage and subsequent use.

6.2.4.4.2 Manufacturing conditions

The manufacturing conditions substantially influence the particle size distribution of the emulsion, viz:

6.2.4.4.2.1 Temperature

Increasing the temperature of either the aqueous phase or the bitumen, thus reducing its viscosity, normally increases the mean particle size of the emulsion.

6.2.4.4.2.2 Bitumen content

Increasing the bitumen content increases the mean particle size and tends to reduce the size distribution.

6.2.4.4.2.3 Aqueous phase composition

For cationic emulsions manufactured with hydrochloric acid and an amine emulsifier the particle size can be decreased by increasing either the acid or emulsifier content; if the ratio of acid to amine is kept constant, the particle size can also be reduced by increasing the amine/acid content; the size distribution does not appear to be related to the concentration of these two components.

6.2.4.4.2.4 Colloid mill

The gap and rotational speed of the colloid mill strongly influence the particle size and distribution of the emulsion; a small gap will result in a small particle size with a relatively narrow range of sizes; high rotational speed will produce a small particle size.

The foregoing is an overview of the factors which influence the properties of emulsions and a number of alternative approaches are available to the emulsion manufacturer to adjust emulsion properties. However, it is clear that it is difficult to adjust one property of the emulsion without influencing others. This interdependence is shown in figure 6.8.

6.2.5 Uses of bitumen emulsions

In volume terms the vast majority of bitumen emulsions are used in surface dressing applications for roads, but their versatility makes them suitable for a wide variety of applications from road mixes to binding peat flower pots. The uses in industry are so diverse that a complete list is not possible; however, the following are some uses of industrial emulsions:

6.2.5.1 Concrete curing membranes

Within a short period of time, generally within one hour of placing, a thin layer of emulsion is applied to the surface of the concrete. The emulsion seals the surface and thus prevents desiccation of the surface. Typical emulsions used would be BS434(6) class K1-40 or A1-40. Emulsions are also used to protect concrete structures buried underground against sulphate attack and corrosion. These are often modified with natural rubber latex to enhance the impermeability.

6.2.5.2 Sand stabilisation(7)(8)

Bitumen emulsions can be used to stabilise sand and soil until plant life can take over. A light application of emulsion to give 25 to 50 mm depth of lightly stabilised surface on dunes and other areas where blowing sand or soil creates an environmental nuisance. This treatment can also be carried out in conjunction with the establishment of grass, trees or other vegetation(9) and has also been used in agricultural applications(10). The bitumen provides the

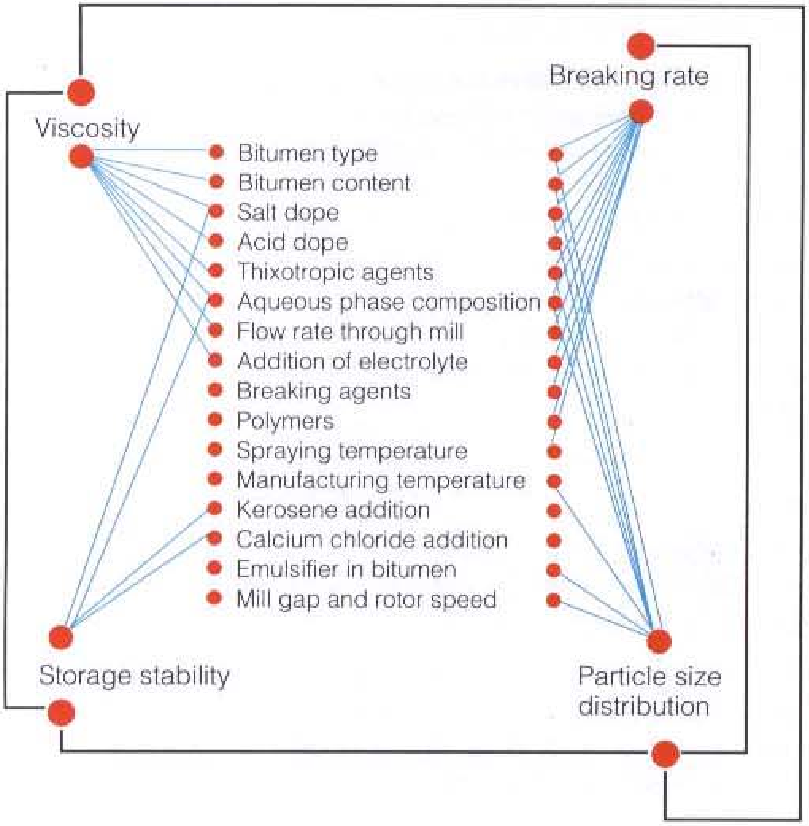

Figure 6.8 — Inter-relationships between manufacturing variables and properties for bitumen emulsions

surface with a coating which binds the soil/sand so that neither water nor wind can affect the vegetation. Other important effects which make the system productive are that evaporation of water is reduced and due to its dark colour the surface is warmed, increasing the rate of germination.

6.2.5.3 Soil injection

Specialised emulsions have been used for rendering porous soil impermeable(10). Such emulsions find uses where barrages or dikes are leaking. Bitumen emulsions can be injected under pressure with breaking agents and seal the structure, preventing further leakage. The ability to break the emulsion close to the injection point makes it possible to control seepage through structures and has advantages over other methods, such as cement grouts, in that these tend to be carried long distances by the seepage water before setting.

6.2.5.4 Clay and soap/clay emulsions

Bitumen emulsions are used in various ways to waterproof structures. These include spray applied systems which may include fibres, eg the Monoform(11) system, and soap/clay emulsions(12) which include both brushing and trowelling grades. These emulsions must exhibit flow resistant behaviour both on application and if subjected to prolonged heating, but the cured membrane must remain flexible during service to accommodate thermal expansion/contraction of the roof or structure in service.

Soap/clay stabilised emulsions, such as the Flintkote, Shellkote and Weatherkote systems, are used for a wide range of applications including industrial and domestic roofing, industrial flooring, damp-proofing, tennis court surfaces and coating timber ends in the lumber industry.

Clay and soap/clay emulsions normally dry purely by evaporation. However, in mastic flooring and some other applications thick films (up to 20 mm) will cure in hours because cement is mixed with the emulsion. The emulsion is sufficiently stable to withstand mixing with cement but the cement reacts with the water and thus breaks the emulsion.

6.2.5.4.1 Properties of Flintkote coatings

Flintkote/Shellkote systems are easy to maintain, self healing, oil resistant and mechanically strong. Typical data for mastic flooring Shellkote/Flintkote Type 3 a compound is given below.

Indentation resistance, measured by the State Testing Laboratory in Zurich, Switzerland, varies typically between:

> 0.17 mm at 20°C under a pressure of 2.5 N/mm^2 (2.5 M Pa), sustained for several hours, and
>
> 0.79 mm at 50°C under a pressure of 6.5 N/mm^2 (6.5 M Pa), sustained for seven days.

Abrasion resistance, as measured by a skidding steel trolley wheel at an angle of 30 degrees under a load of 4.5 kg at 20°C:

> dry conditions: 10,000 wheel passes, maximum 0.4 mm wear.

Thermal conductivity, as measured by the modified form of standard hot plate thermal conductivity apparatus described in American Federal Specification LLL-F-321A.

> K factor 0.8 cal/m^2/h/°C. 0.93 Wm/m^2°C. 6.42 Btu in/ft^2/hr/°F

Dielectric strength at 60 cycles per second is approximately 1260 volts per mm at 12 mm thickness. (32 volts per 0.001 inches at 0.5 inches thickness).

Volume resistivity is approximately 1.3 x 10^{11} ohm-cm at 12 mm thickness (5.0 x 10^4 megohm-inches at 0.5 inches thickness).

Loading capacity. The dead weight loading of Flintkote/Shellkote mastic of 12 mm thickness is approximately 24.5 kg/m^2 (240 Pa).

The material can be subjected to wheeled traffic to a maximum loading of 2.1 MN/mm^2.

6.2.5.5 Miscellaneous uses

Other uses of emulsions include binding of peat flower pots(13), fibreboard manufacture for waterproofing, thermal and soundproofing applications(14), industrial chimney linings and recovery of industrial fines(15).

6.3 Cutback bitumens

6.3.1 General

The term cutback refers to the practice of adding a low viscosity liquid to a high viscosity liquid in order to cut the viscosity back to the desired level. This is routinely done in the refining industry where the low viscosity component is referred to as 'cutter' or 'cut'.

Bitumen may be mixed with a wide variety of petroleum fractions for different applications. Volatile light fractions (white spirit, naphtha) are used for cutbacks and paints where rapid drying is required. Medium fractions (kerosene, gas oil) are used where a longer drying period is permissible. Heavier cuts (such as oils) are used where permanent softening is required, producing materials which are equivalent to a softer grade of bitumen. Two general rules apply to solvents for bitumen:

- the heavier the solvent fraction the better the solvent;
- the more aromatic the fraction the better the solvent.

6.3.2 Blending

Because of the flammability and/or toxicity of many hydrocarbon solvents great care is needed in the preparation of bitumen solutions. Where the ratio of the solvent to bitumen is high (ie greater than, say, 2:3) then hot bitumen can be added to cold solvent. It is recommended that the mixing vessel is stirred to minimise local boiling of the solvent and solidification of the bitumen. Where the ratio is lower than, say, 2:3, then cold solvent should be added to the bitumen in such a way that it enters the mixing vessel below the surface of the bitumen. Here again stirring is necessary during mixing to ensure efficient dispersion. In all cases the mixing vessel should be fitted with a condenser to trap any escaping solvent vapour. The condensed solvent should be returned to the solution below the level of the solution surface.

These precautions are a minimum requirement only and do not take into account other requirements such as spark/flame proofing of electric motors. In all cases it is necessary to liaise with the relevant authority to ensure that all statutory health and safety requirements are met.

Special precautions are not usually needed when blending oils, as the flash points of most oils are in the same range as that of bitumen. Oil is added hot or cold and simply stirred for a few minutes.

Figures 6.9, 6.10, 6.11 and 6.12 show blending curves for bitumen with kerosene, gas oil and an extract oil. All curves should be regarded as approximate only. This is particularly the case where waxy oils are used as the wax content has a strong effect on viscosity. There are no predictive relationships allowing the final properties to be calculated and it is necessary to make trial blends in the laboratory for each new batch of components.

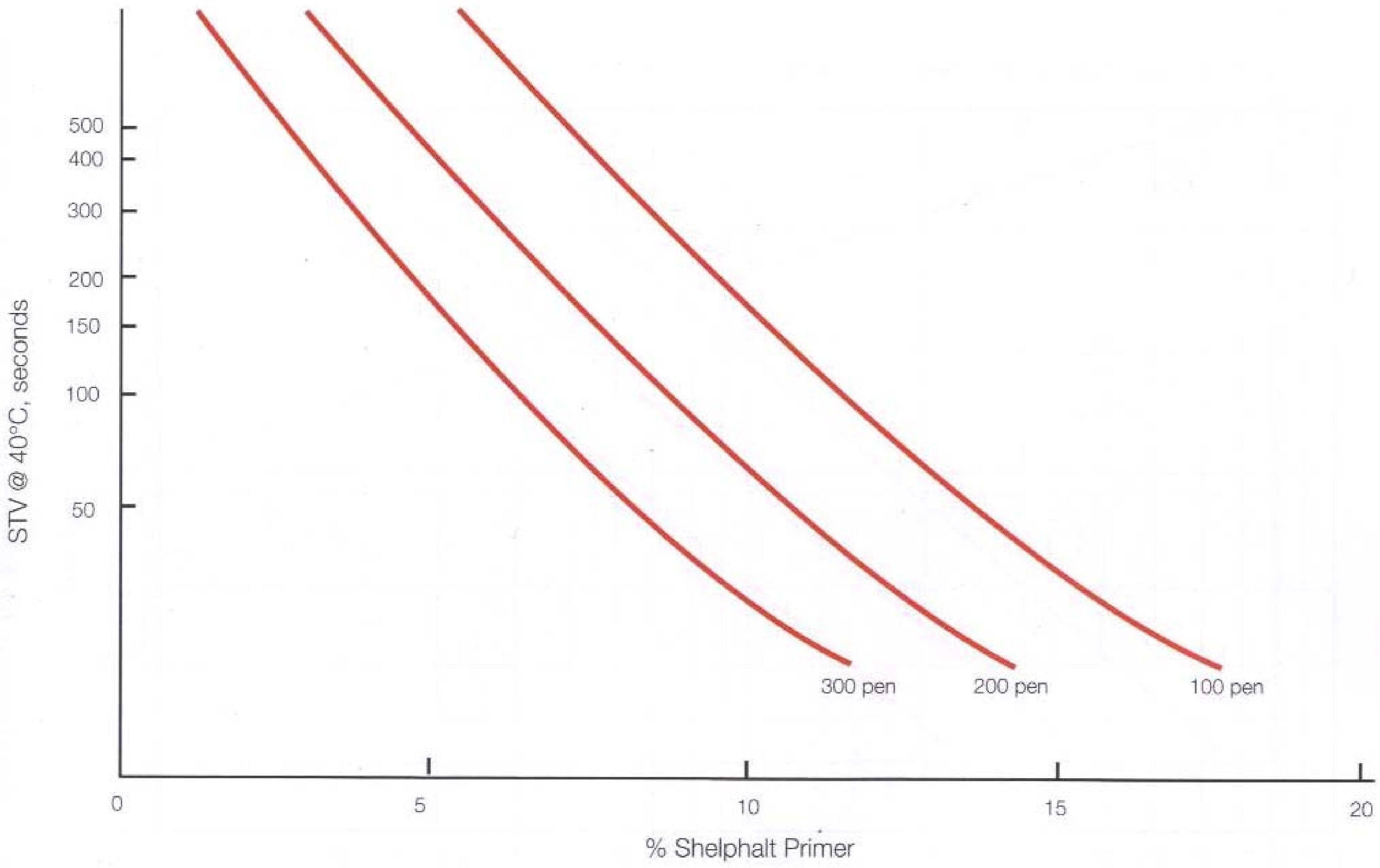

Figure 6.9 — Bitumen/Shelphalt Primer blending chart

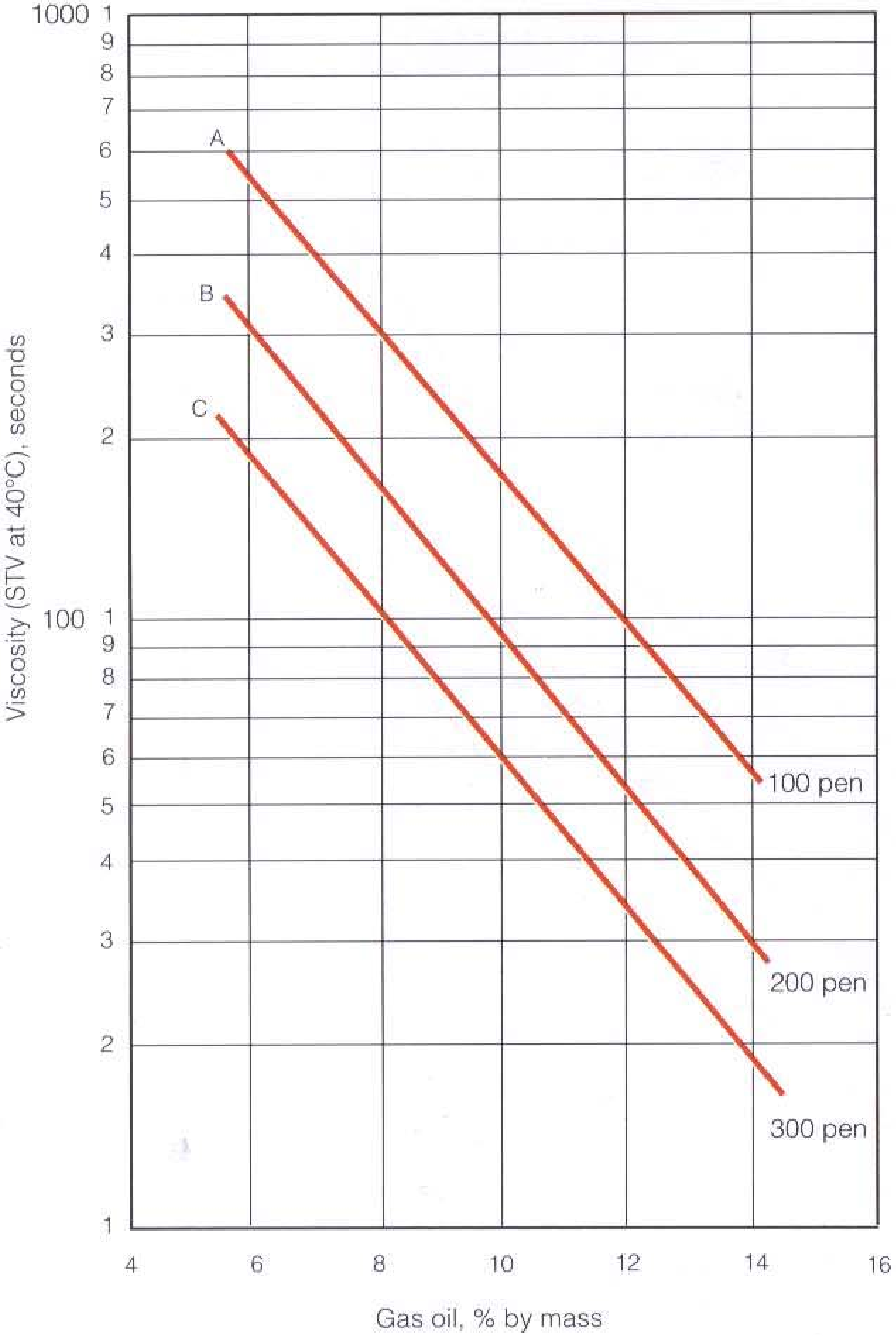

Figure 6.10 — Blend curves for Mexphalte 300, 200 and 100 penetration bitumen

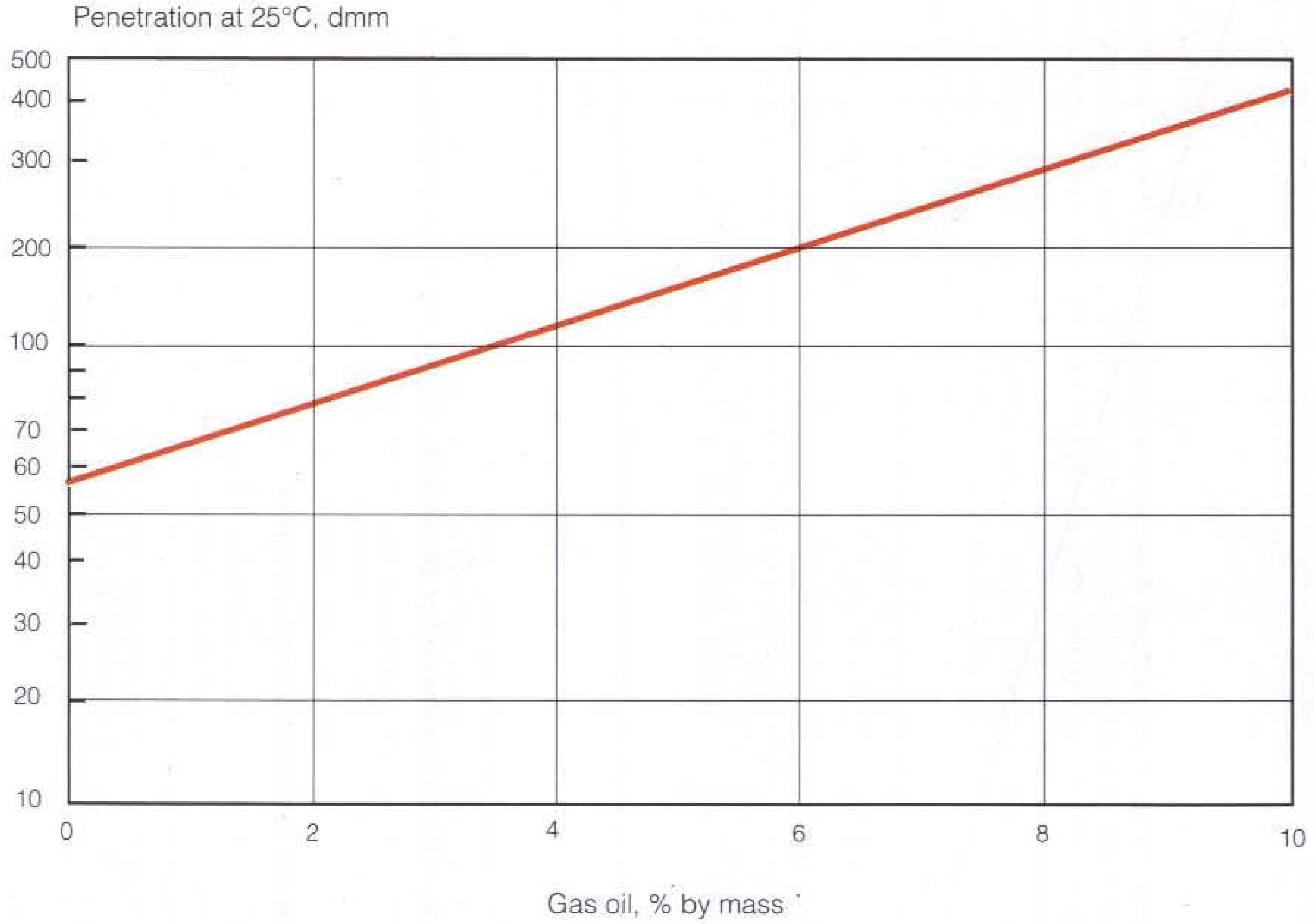

Figure 6.11 — Blend curve for Mexphalte 50 pen with gas oil

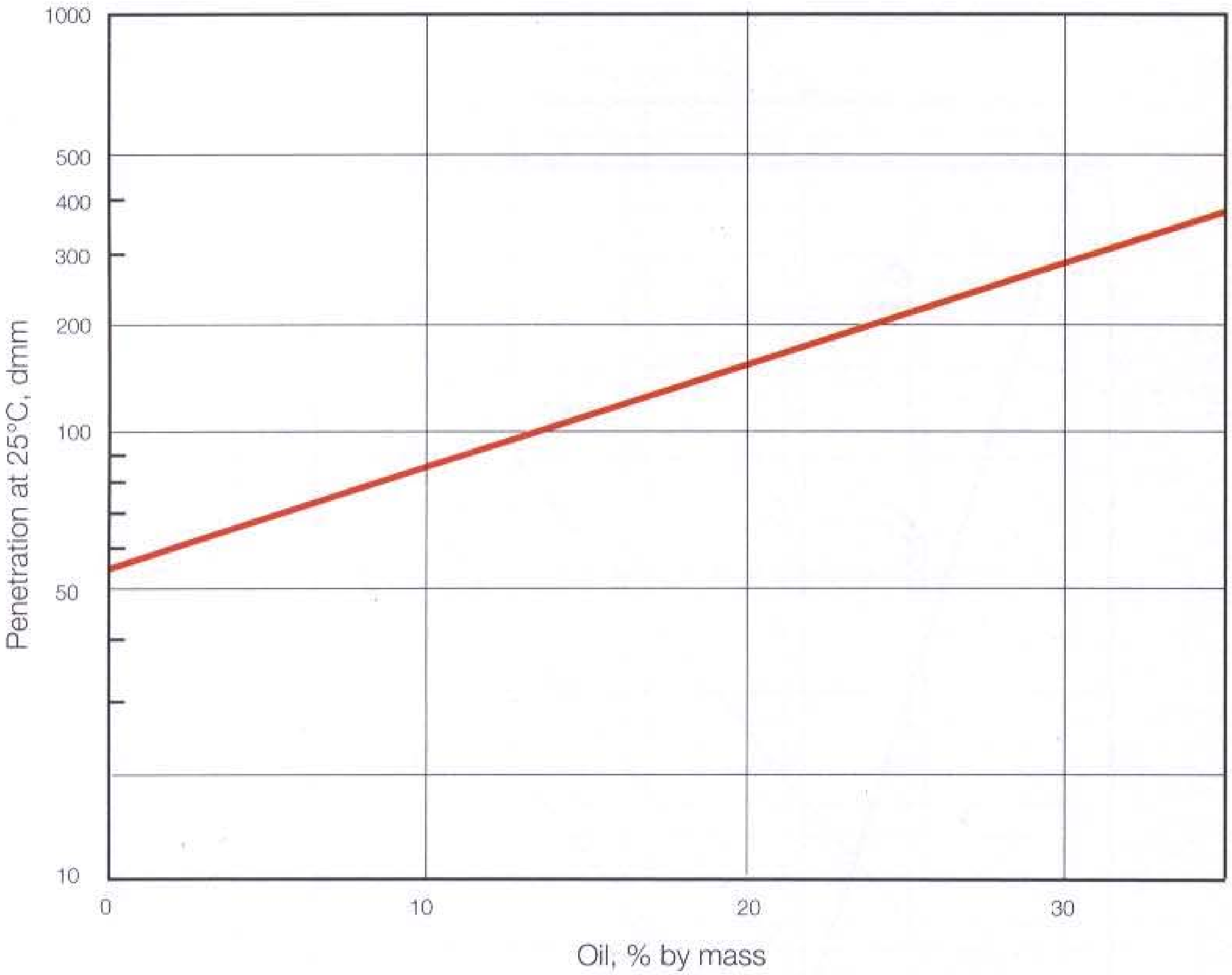

Figure 6.12 — Blending curve for Mexphalte 50 pen with an aromatic oil

6.3.3 Problems associated with cutback

In general, no problems will be experienced with any of the usual solvents for penetration grade bitumens. For blown grades, however, problems can occur. With highly dilute solutions precipitate or gel formation is sometimes observed. These problems are caused by insufficient solvation of the asphaltenes which either precipitate or reform their structure. Both problems can be overcome by the use of a more aromatic solvent, eg white spirit with a minimum 45 per cent aromatics, or white spirit with ten per cent toluene added.

6.3.4 Uses

The major use for cutback bitumen is in the road maintenance industry where it is used as an adhesive to stick chippings to the road surface. Other uses include:

6.3.4.1 Roofing

Cutback is used both as a waterproofing membrane (see chapter eight) and as an adhesive to stick chippings onto a flat, horizontal roof to minimise the effects of weathering from the sun on the felt. Typically 100 pen bitumen would be used, mixed with approximately 25 per cent kerosene, to produce a cutback which could be trowelled or brush applied.

6.3.4.2 Priming

Cutbacks are used to prime both concrete and steel structures subsequent to coating with either hot bitumen enamel or a bituminous membrane. The cutback serves to provide good adhesion by cleaning away any dust and grease and 'wetting' the pores of the surface to be coated. A primer would normally consist of a solution of the bitumen used in the final coating cut back to give a viscosity suitable for spray or brush application, approximately 30 to 60 per cent solvent depending on both the bitumen and solvent. Wetting agents are sometimes added to improve adhesion.

6.3.4.3 Damp-proof courses

Bitumen cutbacks are used as damp-proof membranes in concrete floors particularly for small repairs or where extensions are keyed-in to existing structures. A hard penetration grade such as 70 pen is mixed with kerosene to give a consistency suitable for trowelling or stiff brush application. The solvent should be sufficiently volatile to afford curing within about 24 hours.

6.3.4.4 Paints

6.3.4.4.1 Corrosion protection

H80/90 is used to give a virtually non-sticky coating to metal surfaces. Mixed with kerosene at 50 per cent by mass or sometimes higher, it is brushed, sprayed or dip-coated onto water pipes, cisterns and tanks. Solutions containing only 30 to 40 per cent by mass of bitumen are used to dip-coat spades, wheelbarrows and suchlike for the building industry. The requirement is mainly for corrosion resistance while the goods are stored in a warehouse or shop as once out on site they face severe conditions and are regarded as consumable. It is important to note that bitumen is not impermeable to water and will not protect ironware from rusting indefinitely. It does however have a very low moisture permeability (see section 12.7).

6.3.4.4.2 Anti-vandal paint

Used to coat, eg vertical drainpipes, anti-vandal paint is intended to deter thieves and vandals from climbing pipes and walls. The paint is designed to make the surfaces both sticky and slippery. A penetration grade such as 70 pen is used with kerosene to give a thick brushing consistency. Several applications are required to build up a good thick coat. Thickeners or fibres can also be incorporated to aid this. Because of the effects of weathering and dust in the atmosphere, the coating needs to be renewed periodically to retain its effectiveness.

6.3.4.5 Wire-rope maintenance

Wire ropes are washed with a cutback solution both to clean off dust and dirt and to provide a corrosion resistant film. The bitumen also acts as a lubricant on the rope. A hard penetration grade such as 35 or 50 pen or even a soft oxidised grade such as R75/30 is used with 40 to 50 per cent of a medium curing solvent (kerosene) or solvent mixture.

6.3.4.6 Adhesives

Bitumen adhesives are used in thousands of different applications. Bitumen is usually the principal adhesive agent, often in conjunction with wetting agents, polymers and aromatic oils to increase tack. Solvents may be used to modify initial viscosity and to control the 'cure' rate.

6.4 References

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Chapter 7 - Modified bitumens

7.1 General

There are many occasions when a bitumen user may wish to modify the properties of his bitumen in some way. There may be requirements for changes to:

- a basic bitumen property;
- method of application;
- an end-product property;
- cost of the system.

For the modifier to be effective and for its use to be both practicable and economic, it must:

- be readily available;
- resist degradation at process and application temperatures;
- blend with bitumen;
- improve resistance to flow at high service temperatures without making the bitumen too viscous at application temperatures or too stiff or brittle at low temperatures in service;
- be cost effective.

The modifier, when blended with bitumen, should have the following characteristics:

- maintain its premium properties during storage, application and in service;
- be capable of being processed by conventional equipment;
- be physically and chemically stable during storage, application and in service;
- achieve a coating viscosity at normal application temperatures.

Apart from emulsification (see chapter 6), which is perhaps the most radical modification of bitumen, all other modifications entail the addition of either a liquid or solid to the bitumen. The 'additives' can be loosely classified into five groups, eg:

- inert fillers;
- mouldable fillers;
- chemical agents, wetting/adhesion agents;
- solvents (including hydrocarbon extracts);
- polymers.

Table 7.1 shows the relationship between some commonly used modifiers and the properties affected.

Modifier	Property affected
Oil	Constitution of bitumen Tackiness Viscosity Penetration value Softening point
Filler Powders	Softening point Viscosity Stiffness Density Cost Mechanical Strength
Fibres	Thixotropy Crack resistance Viscosity
Wax	Viscosity (hot) Stiffness (cold) Tackiness Adhesion
APP (Atactic polypropylene) EVA (Ethylene vinyl acetate)	Stiffness Penetration value Fraass breaking point Softening point
SBS (Styrene-butadiene-styrene)	Penetration value Softening point Elastic recovery Brittleness at low temp
Solvent	Viscosity
Emulsification	Viscosity Wetting ability Application temperature
Wetting agents	Wetting ability Adhesion

Table 7.1 — The relationship between final property modified and some commonly used modifiers

7.2 Classes of modifier

7.2.1 Bitumens

Bitumens are routinely blended for a variety of reasons. For example, storage tanks may be available for only two grades and it may be more convenient to blend a third grade. Alternatively, a non-standard grade may be required for use in a product. Bitumens are miscible with each other in all proportions and the penetration and softening point of a blend of two bitumens can be calculated.

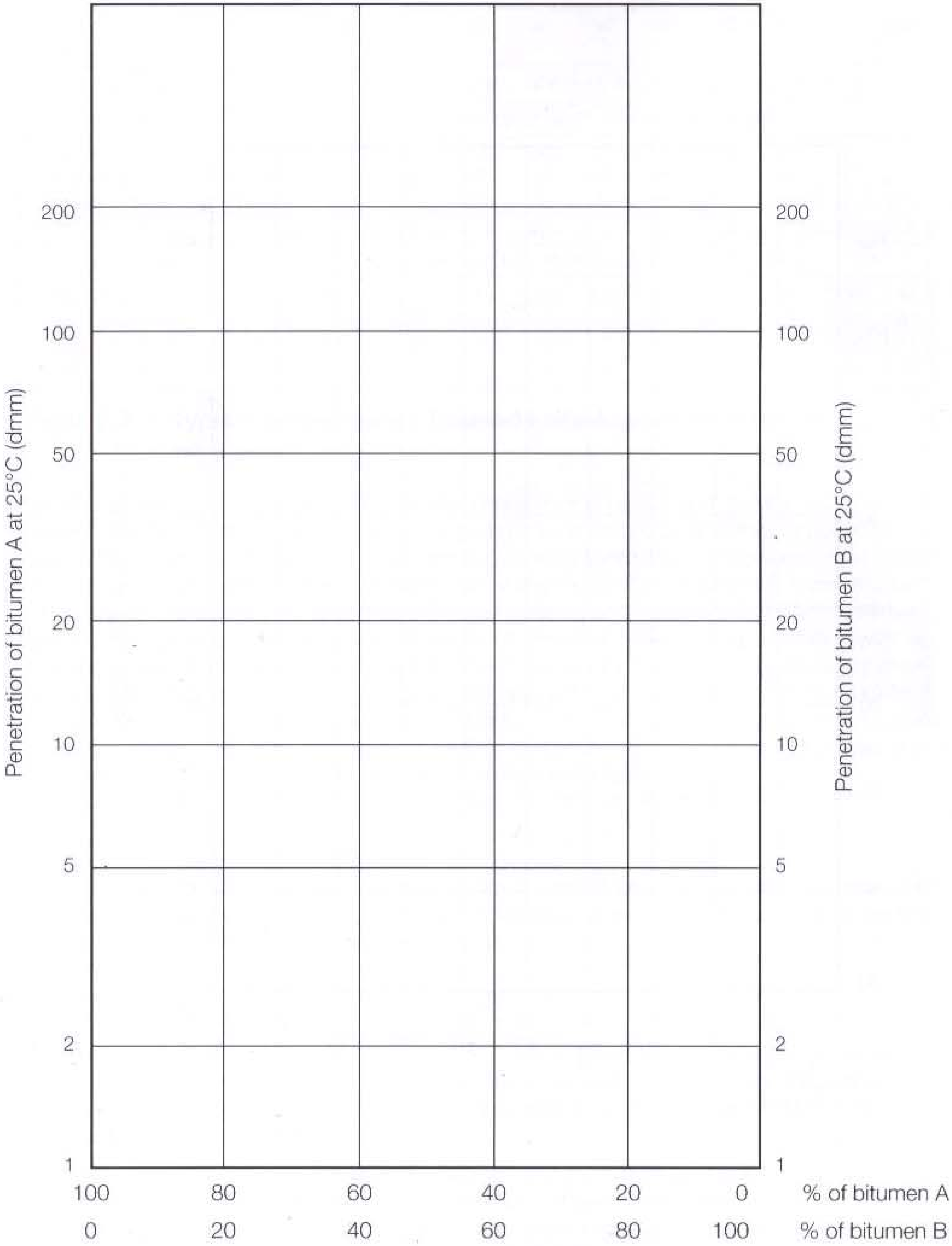


Figure 7.1 — Estimation of the penetration value of bitumen blends

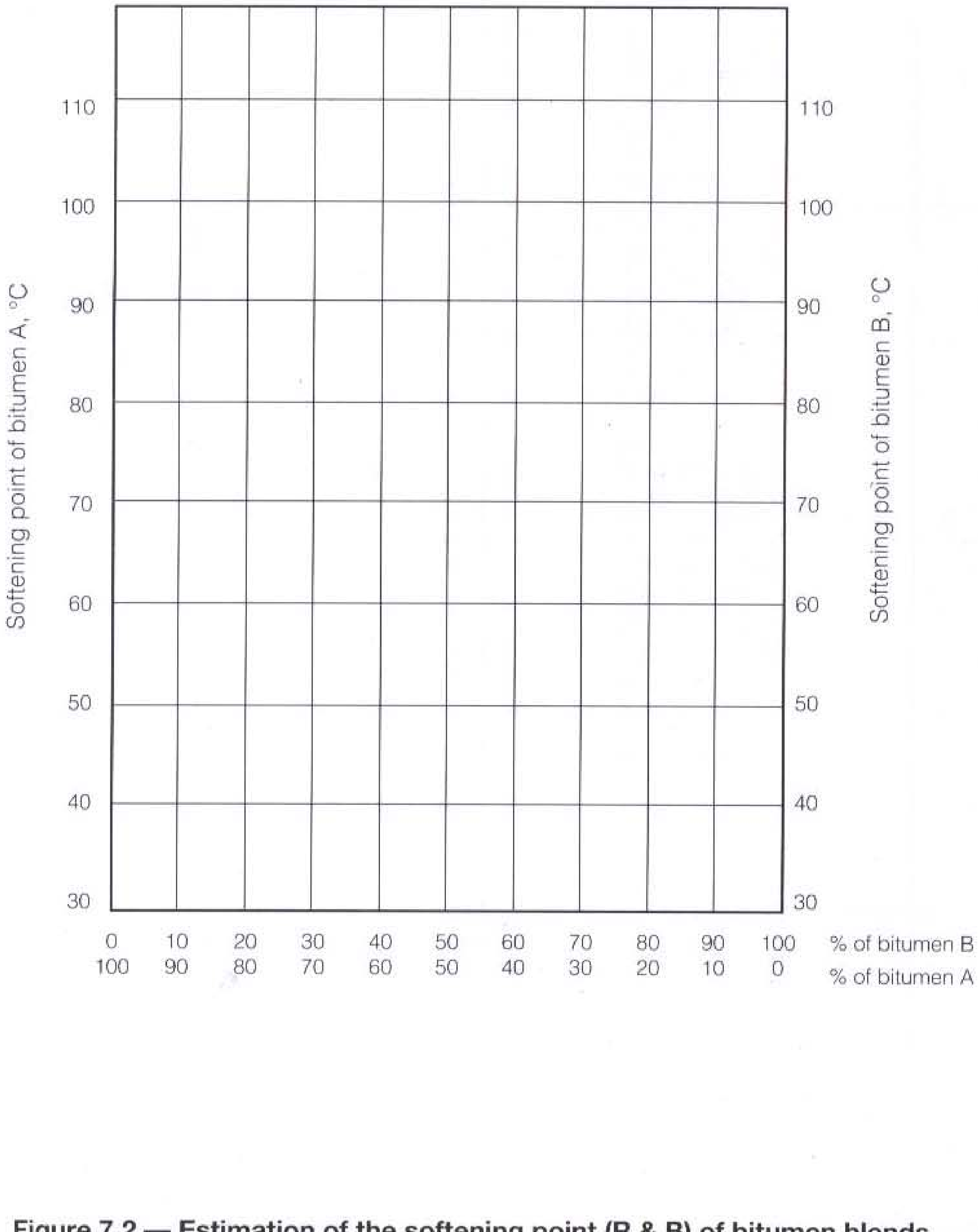


Figure 7.2 — Estimation of the softening point (R & B) of bitumen blends

TLA content % by mass	0	10	20	30	40	50	60	70	80	90	100
Ash % by mass	Trace	3.6	7.3	10.9	14.6	18.2	21.9	25.5	29.2	32.8	36.5
Bitumen grade	Penetration at 25 °C of resultant blend										
60/70 pen	70	57	48	40	30	23	17	12	6	4	2-3
90/110 pen	100	78	62	44	36	31	25	12	7	4	2-3
190/210 pen	197	132	97	78	50	38	32	17	10	4	2-3
280/320 pen	320	218	181	113	75	53	33	20	11	4	2-3
Bitumen grade	Specific gravity at 25°C/25°C of resultant blend										
60/70 pen	1.03	1.07	1.10	1.14	1.18	1.22	1.25	1.29	1.33	1.36	1.41
90/110 pen	1.02	1.05	1.07	1.11	1.14	1.17	1.22	1.26	1.31	1.34	1.41
190/210 pen	1.01	1.03	1.06	1.08	1.12	1.17	1.22	1.26	1.31	1.34	1.41
280/320 pen	1.01	1.03	1.06	1.08	1.12	1.17	1.22	1.26	1.31	1.34	1.41

Table 7.2 — Typical properties of Trinidad Lake Asphalt blends with bitumens

Blend properties can be estimated from the charts in figures 7.1 and 7.2 by joining with a straight line the points on the vertical scales giving the penetrations or softening points of the grades to be blended and then using the horizontal scale to read the proportions of the blend of the required properties. The relationship on which the charts are based is quite accurate for blends of the same bitumen type, ie two penetration or two oxidised grades. However, care should be taken when blending bitumens of dissimilar types, eg a penetration with an oxidised grade, as the chart predicts results which are usually too hard. The actual blend will usually have a higher penetration and lower softening point than predicted and the properties of such blends must be determined experimentally. This phenomenon is believed to be due to the reassociation of asphaltenes in the mixture, see section 4.1.1. Similar effects may also be observed with bitumens produced from dissimilar crude types.

7.2.1.1 Naturally occurring bitumens

Of all the naturally occurring bitumens throughout the world, only two are used to any extent, namely Trinidad Lake Asphalt and Gilsonite. Their main use is in mastic asphalt where the main effect is to harden the normal bitumen grade.

7.2.1.1.1 Trinidad Lake Asphalt

Also known as TLA, Lake Asphalt and Epuré, it has a penetration of about 2 dmm with a softening point of 95°C and is too hard to be used on its own. It is supplied cold, containing approximately 30-40 per cent of fine filler and is added to a mastic mixer in block form. It is not preblended with bitumen.

TLA behaves as though it is a penetration bitumen and the blending charts in figures 7.1 and 7.2 can be used. However, the actual penetrations observed are slightly softer than those predicted from the charts. This is almost certainly a consequence of the filler interfering with the penetration needle, thereby giving an apparently harder value than would be the case if TLA contained no mineral matter. If the penetration of TLA is taken as 7 dmm, then the charts are quite accurate for blends of up to about 85 per cent bitumen. Table 7.2 shows the properties of some bitumen/TLA blends.

7.2.1.1.2 Gilsonite (North American Asphaltum)

Gilsonite is a naturally occurring bitumen which was discovered by Sam Gilson in 1885 in the Uintah valley of eastern Utah. Although widely known as Gilsonite for a century, the ASTM name for the mineral group is North American Asphaltum and the name for this specific deposit is Uintaite.

Gilsonite is a pure hydrocarbon containing little or no mineral matter. It has a black, glossy appearance but is easily crumbled and milled into a free-flowing powder. It occurs in a series of parallel vertical seams ranging in width from 5 cm to 10 metres and to a depth of approximately 450 metres. The seams each have slightly different properties and hence Gilsonite is available in a range of softening points around 150-200°C.

Gilsonite is a petroleum-based solid and is therefore readily compatible with refined bitumens. It is, however, significantly different from bitumen in its composition, see table 7.3.

Its high nitrogen content results in good adhesion properties and its overall high molecular weight gives resistance to oxidation. Its uses include:

- paints (including varnish and japans);
- wire insulation;
- roofing;
- mastics;
- paving;
- clay pigeons.

It is commonly used in printing ink for newspapers and in mastic asphalt production as a blending component with a penetration bitumen (usually 50 pen).

	Gilsonite % by mass	Bitumen % by mass
Nitrogen	3.3	1.0
Sulphur	3.0	3.0
Asphaltenes	50-70	15
Maltenes	30-50	85
Saturates	2	10

Table 7.3 — Comparison of Gilsonite and bitumen

7.2.2 Inert fillers

Materials in this category include inorganic powders such as limestone filler, slate dust (slate flour), hydrated lime, cement, silica and gypsum as well as fibres such as asbestos and cellulose. Fillers usually have a particle size below 75 micron (µm).

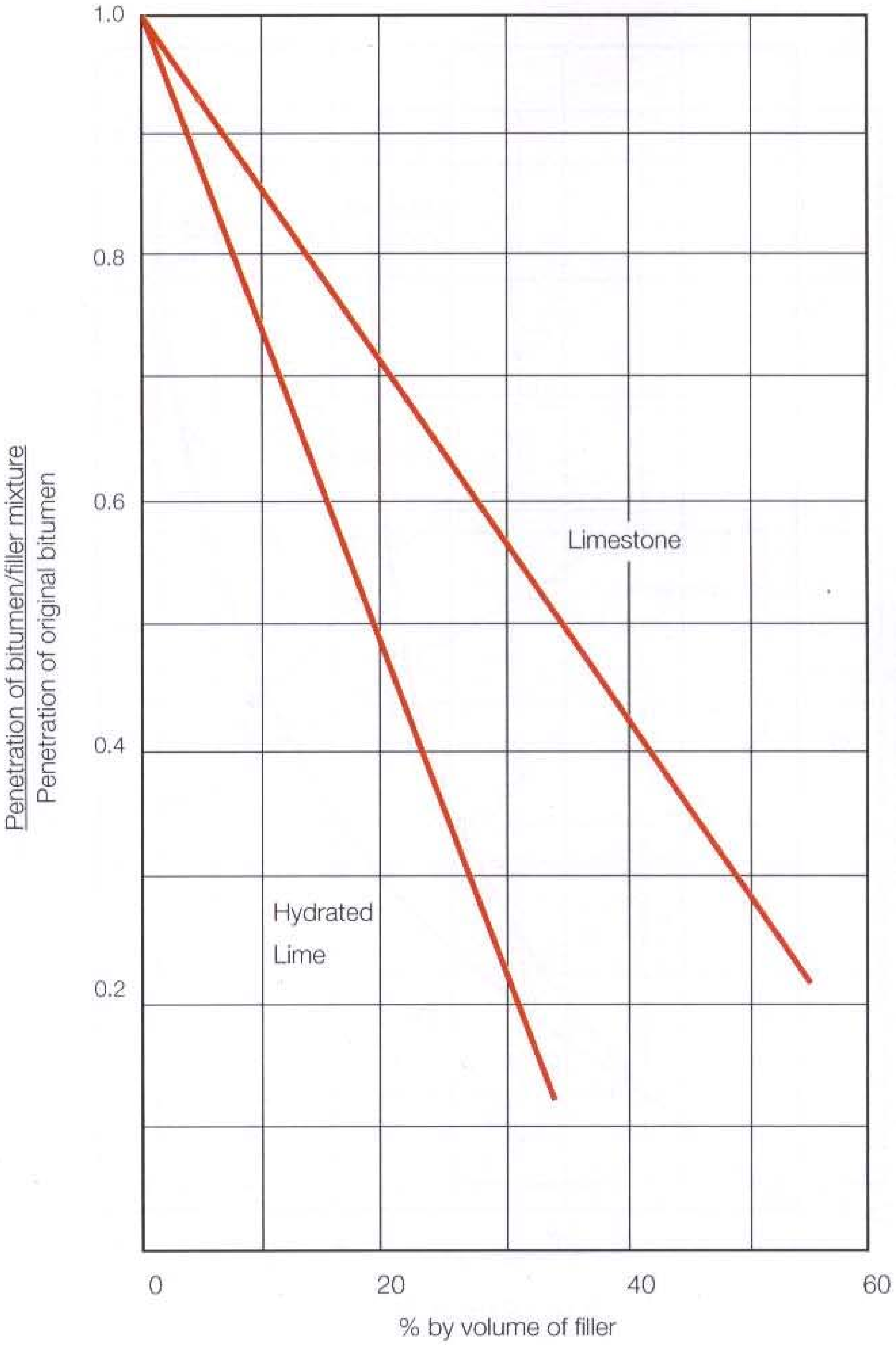


Figure 7.3 — Effect of filler on the penetration value of bitumen/filler mixtures

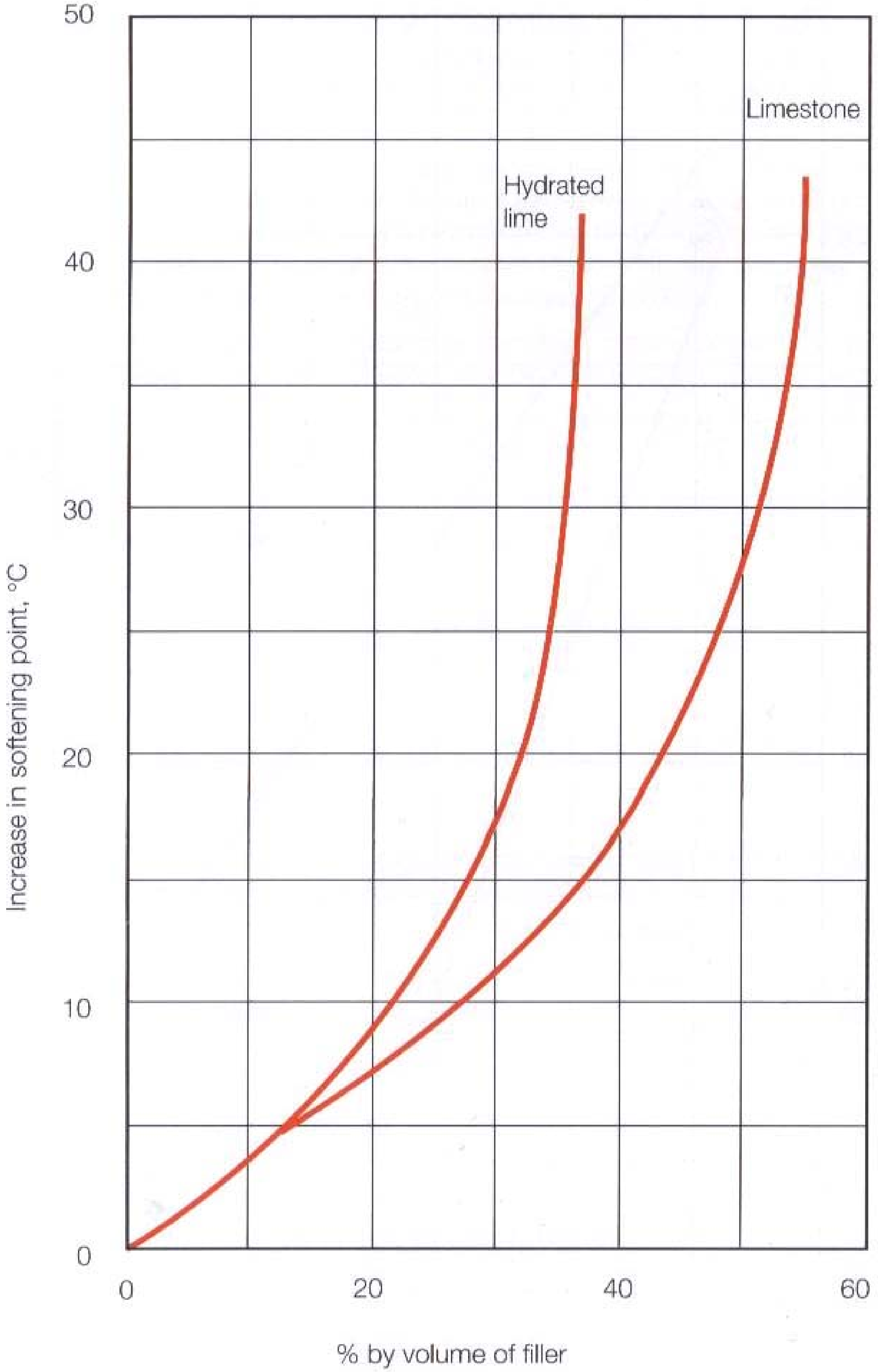


Figure 7.4 — Effect of filler on softening point (R & B) of bitumen/filler mixtures

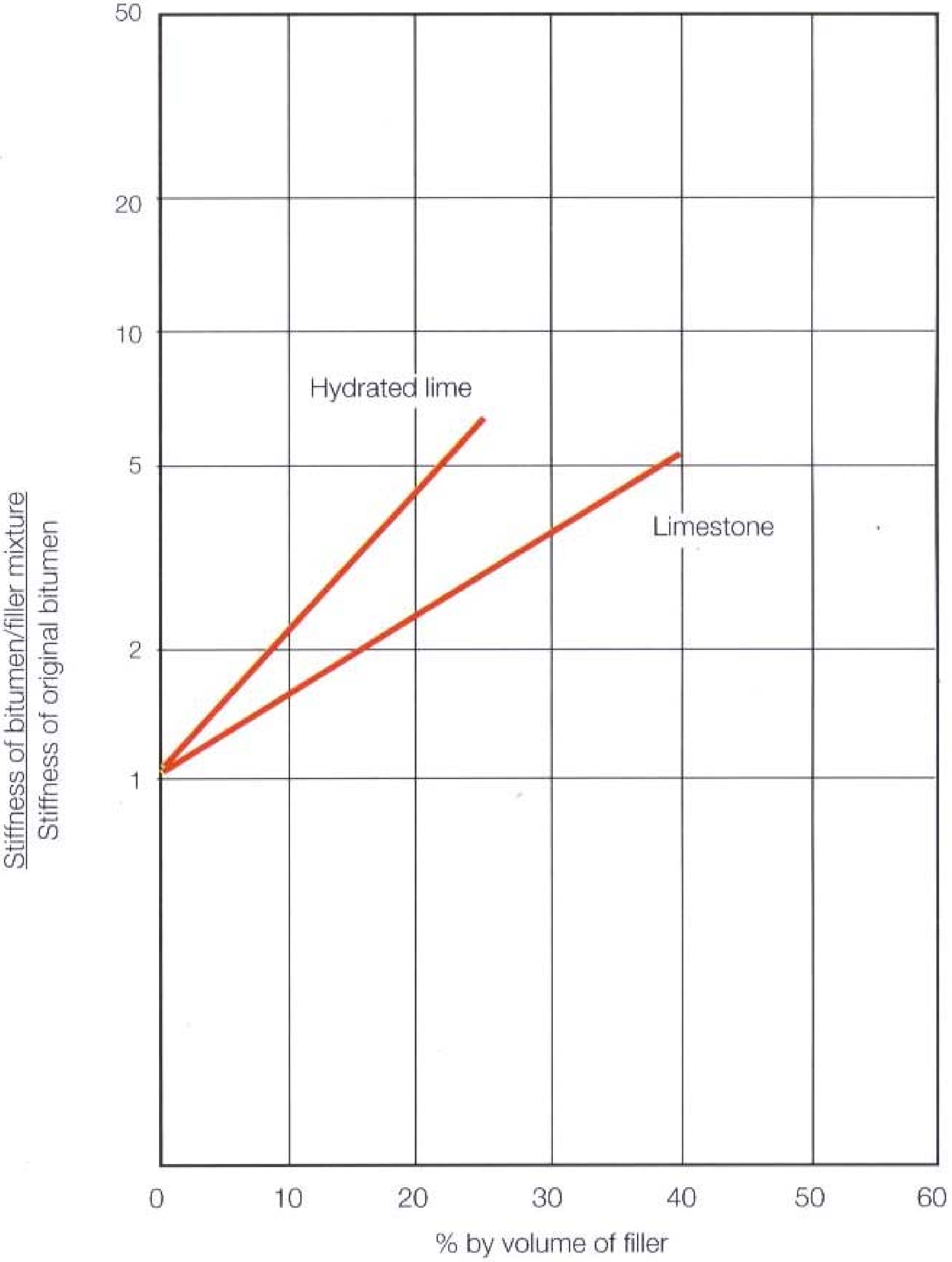


Figure 7.5 — Effect of filler on stiffness of bitumen/filler mixtures

Mass %	Volume %
10	4
20	8.5
30	14
40	20
50	27
60	36
70	46

Table 7.4 — Comparison of mass and volume percent for limestone filler

The general effect of adding filler to bitumen is to make it harder and stiffer. This in practical terms results in a reduction in the deformation or flow produced by a given load and is shown by an increase in softening point, a reduction in penetration and an increase in stiffness. The extent of this hardening or stiffening effect depends on the amount of filler added and its particle size, shape and grading. Rigden(1) showed that for non-fibrous fillers the effect of filler addition to bitumen is a function of the volume fraction of filler added, ie if the volume percent of filler added is constant, the change in stiffness is the same for a variety of fillers. The effects are not the same for all fillers, however. 'Normal' fillers such as limestone or slate dust produce the least effect; fillers with plate-like particles, such as talc, are intermediate and fibrous fillers, such as asbestos, show the greatest effect for a given concentration.

Figures 7.3, 7.4 and 7.5 show the effect of the volume percent of the filler in mastic mixture on the softening point, penetration value and stiffness properties. It can be clearly seen that hydrated lime has a much greater effect than limestone dust. The volume percentage must be calculated from the weight and density of the material and not estimated from the volume of filler added. A comparison of mass percentage and volume percentage is shown in table 7.4 for limestone filler.

For 'normal' fillers, the effect of the filler on penetration and softening point is approximately proportional to the filler concentration up to about 40 per cent by volume of the mixture. For fibrous fillers the effect is much greater and hence the proportional limit is lower.

7.2.2.1 Powders

This class of material is the most widely used additive with bitumen, being used in both the road construction and roofing industries. Of the many materials available, limestone filler is the most commonly used particuarly in the UK because of its availability and cheapness. It is added to roofing felt, carpet tiles, pipe enamels, clay pigeons, mastic, jointing compounds and many other materials except where very thin coatings, eg paints, are required. As well as altering the rheological properties of the bitumen, the filler also increases the specific gravity of the mixture by virtue of its greater relative density, eg 2.7 for filler compared with 1.0 for bitumen. Hence addition of 30 per cent by mass of limestone filler increases the density from 1.0 to 1.5 g/cm^3. This is important in applications such as roofing felt and carpet tiles where heavier materials give better lay-flat properties. However, for applications which require resistance to corrosive environments, limestone filler is unsuitable because of its vunerability to attack by even weakly acidic materials.

7.2.2.2 Fibres

Fibres have been used for the modification of bitumens for many years and are often used in applications where either a very thick coating or a coating which is resistant to cracking is required. The types of fibres commonly encountered in bitumen modification include:

- glass fibre;
- cellulose fibres;
- mineral fibres;
    - rockwool,
    - asbestos,
    - anionic amorphous fibres (aluminium magnesium silicates);
- hydrocarbon polymer fibres;
    - polyester,
    - polypropylene,
    - polyethylene,
    - polyvinyl chloride.

The effect of the fibres on the bitumen is not to chemically modify it, but to reinforce and stiffen the binder by a physical effect. The net effect of the addition of fibres to a bitumen is to improve the cohesion and tensile strength of the binder by producing a uniformly distributed three dimensional fibre structure which toughens the resultant composition. In mixtures of bitumen with mineral aggregates, such as mastic asphalt, the presence of fibres enables a higher bitumen content to be achieved, thus improving the flexibility and fatigue resistance of the material without the risk of deformation. In mixtures of bitumen and aggregate, such as an asphalt, the presence of fibres tends to thicken up the bitumen thus preventing it from running off the aggregate during mixing and transportation.

In roofing and industrial waterproofing, asbestos fibres have traditionally been used. However, due to the health hazards associated with this material, manufactured or man-made fibres have been replacing the use of asbestos. In the roofing industry fibres have long been used as a reinforcement and stiffener for conventional bitumen.

Fibres are normally added to the bitumen at the manufacturing plant rather than by the bitumen supplier. As the fibres tend to be small and finely divided, typically 0.2 to 2 mm in length, the material can be difficult to handle in bulk and special handling equipment may be necessary. Fibres are often supplied in pre-weighed quantities in easily melted plastic bags for ease of handling, the bags simply being added to the mixer. Once added to the bituminous mix the product appears to handle similarly to conventional material except that additional cohesiveness and toughness may be noted. It has been observed that materials such as mastic asphalt may be more difficult to work by hand.

The use of fibres in a product will generally require an increased amount of bitumen to ensure normal coating of the mixture as the fibres present a high surface area per unit weight in much the same way as a powdered filler. In an asphalt mix an additional 0.25 per cent of bitumen is normally required to ensure adequate coating of the fibres which normally amount to some 0.3 per cent of the mix. The use of fibres and the additional bitumen required will present an increased cost which must be balanced against the perceived benefit of this modification and the overall economics of the process.

The Monoform roofing system is an example of the use of a fibrous reinforcement which employs a clay stabilised bitumen emulsion sprayed onto a roof deck simultaneously with the application of chopped glass strands to form a tough, seamless, waterproofing membrane.

7.2.2.3 Choice of filler

In considering the selection of suitable fillers the following factors should be addressed:

- Asbestos fibres are not always suitable for applications in which the mixture is used as a sealant or protective coating in continuous contact with a liquid, because asbestos fibre can act as a wick and so transport liquid through the bitumen.
- The use of asbestos fibres has declined markedly over the last few years because of associated health problems. Whilst it is an excellent filler, it has largely been replaced by cellulose fibres which are much safer but are considered by some users to be inferior to asbestos. Acrylic, glass and 'rockwool' fibres may also be used.
- Fillers which absorb water such as clay and gypsum should not be used for applications in contact with water.
- Where the bitumen is used as an acid resistant coating, then acid-resistant fillers such as silica or slate dust must be used.
- The use of hydrated lime improves the adhesion of bitumen to mineral surfaces in the presence of water.
- Fibrous fillers invariably protrude through the bitumen producing a rough surface finish.

Table 7.5[2] shows the effect of some fillers on the flow properties of an oxidised bitumen, R85/40.

Filler type	Filler % by mass	Flow at 75°C, mm
Micro asbestos	15	220
	30	100
Asbestos fibre	15	10
Slag wool	15	10
Slate filler	15	250
Minatitlan clay	15	160
Diatomaceous earth	15	120

5 mm thick layer on a steel plate at 45° incline

Table 7.5 — Influence of some fillers on the flow properties of R85/40 bitumen

7.2.2.4 Manufacture

Fillers should be blended into the bitumen at a temperature such that the viscosity is about 200 cSt (0.2 Pa.s), which for a penetration grade is approximately 100°C above its softening point. The filler should be completely dry to prevent frothing and added slowly so as not to cool the bitumen. The mixture should be stirred thoroughly to an even consistency and to remove entrained air and should also be stirred immediately prior to use to prevent sedimentation.

7.2.2.5 Mouldable fillers

This group of fillers includes materials which are dissolved in hot bitumen and modify its properties in some way on cooling. Included in this category are bitumens, naturally occurring bitumens, sulphur and wax. Although certain polymers fit into this category, they are discussed in section 7.2.3.

7.2.2.5.1 Paraffin wax

Wax is the generic name given to generally straight-chain saturated hydrocarbons. Wax is found in all crude oils to a greater or lesser extent and is present in bitumen at up to about five per cent. Waxes are crystalline in nature, have precise melting points, form very low viscosity liquids above their melting point, have very low PIs, are greasy to the touch and are non-sticky. By its very nature wax is generally deleterious to many bitumen properties, particularly adhesion. There are occasions, however, when paraffin wax is added to bitumen:

- to reduce the viscosity when hot while leaving the low temperature properties largely unchanged (see figure 5.8, BTDC, line W);
- to reduce surface stickiness (tackiness) when cold.

Paraffin wax with a melting point of 50-60°C, which is about the highest melting point grade available, is usually used at concentrations of 5-10 per cent by mass. Concentrations above 20 per cent by mass may upset the colloidal stability of the bitumen and cause precipitation of the asphaltenes. During blending the wax should be added either hot or as lumps to the bitumen and not vice versa to avoid high local concentrations of wax.

7.2.3 Polymers

7.2.3.1 Rubbers

Modification of bitumen with rubbers has been conducted since the earliest times. The first patent on the addition of rubber to bitumen was taken out in 1843 by Henry Austin(3) who specified a glue for fixing wooden pavement blocks comprising "pitch or lae and caoutchouc dissolved in naphtha and poured in." Also in 1843, Thomas Hancock(4) was granted a patent for "Preparing caoutchouc in combination with other substances", including asphalt (sic).

Many types of naturally occurring and man-made rubbers have been used for the modification of bitumens including polybutadiene, polyisoprene, natural rubber, butyl rubber, chloroprene and styrene-butadiene rubber. The principal effect of these materials is to increase the viscosity of the bitumen.

Reclaimed powdered tyre rubber has been used in both its vulcanised state and after degradation. In its vulcanised state, tyre rubber is difficult to disperse in bitumen, requiring high temperatures and long digestion times and usually results in a heterogeneous binder with the rubber acting as a flexible filler. It is claimed that degradation of the tyre rubber by heat and chemical treatment in a bitumen digester will devulcanise the rubber forming a homogeneous binder. There is some doubt that these processes successfully result in devulcanisation. What is clear is that these processes almost invariably require long digestion times at high process temperatures and produce unpleasant and toxic by-products such as sulphur dioxide and hydrogen sulphide. In addition, the digestion and decomposition of the rubber tyres invariably releases into the bitumen substances which may be harmful to humans such as PCAs from distillate aromatic extracts, a common constituent of tyres, and carbon black, a substance which is increasingly being viewed as a risk to health.

Rubber tyres(5) are made up of pigments, chemicals, and some thirty different materials including various rubbers, cord fabric, steel wire fabric and bead wire. The basic rubbers are processed with oils, carbon black, pigments, antioxidants, accelerators and other additives. The synthetic tyre rubber is made up from two basic monomers - butadiene and styrene - which are combined to form the rubber polymer. Typical composition of tyre rubber is shown in table 7.6.

Car tyre rubber has been used in conjunction with bitumen for the manufacture of:

crack and joint sealants;

surface dressing for asphalt pavements (sometimes known as Stress Absorbing Membranes - SAMs);

Stress Absorbing Membrane Interlayers (SAMIs) between the layers of asphalt pavements;

bitumen/rubber hot mix asphalt applications;

sub-grade seals, used to keep water in or out of a constructed system, often used in ponds, lagoons and lakes;

bitumen/rubber roofing membranes.

Type of tyre	% of rubber	
	Natural	Synthetic
Car tyres		
Radial	35	65
Crossply	15	85
Truck tyres		
Radial	65	35
Crossply	30	70

Table 7.6 — Typical composition of car tyre rubber

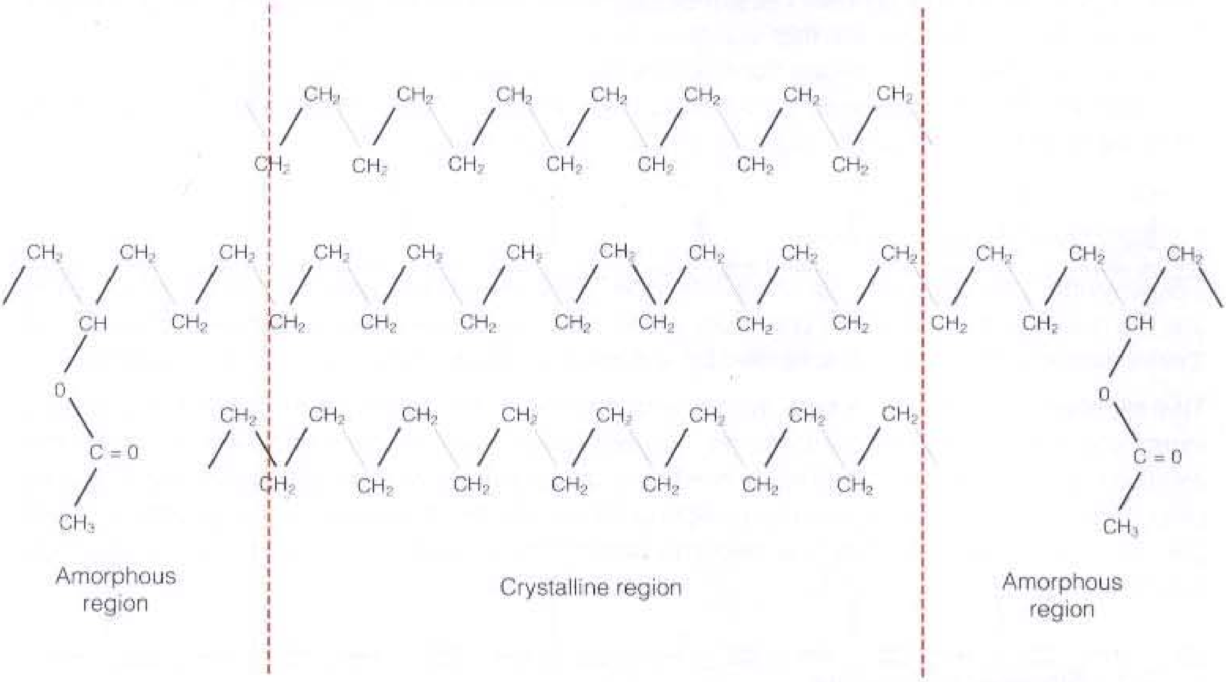


Figure 7.6 — Packing of the polyethylene regions in EVA

The disposal of used tyres, world-wide, is becoming a problem of immense proportions. In the USA alone approximately 285,000,000 used tyres require disposal per annum. Of this total, 33 million are retreaded, 22 million are resold and 42 million are used in various alternative manners(6). The remainder are considered scrap and are added to stock piles which are estimated in 1993 to contain some 2 to 3 billion tyres.

Landfill sites are increasingly reluctant to accept used tyres for disposal because they take up a disproportionate amount of space, they resist compaction, trap gases and become buoyant, penetrating the covering membrane of the landfill. The presence of huge stockpiles of tyres is undesirable for a number of reasons including the potential for an ecological disaster if a stockpile catches fire and the health risks associated with the encouragement of vermin and insect vectors for disease, especially in warmer climatic areas.

In Europe the situation is little better, with some 1 510 000 tonnes of used tyres being generated each year, see table 7.7.

Country	Tonnes
France	400,000
Germany	450,000
UK	300,000
Italy	250,000
Netherlands	65,000
Austria	45,000
Total	1,510,000

Table 7.7 — Estimated annual volume of scrap tyres generated in Europe (1993)

Given the scale of the problem, it is not surprising that much attention is being given to potential alternative uses for this waste material. Legislation is already in effect in some states in the USA which obliges contractors to utilise a proportion of reclaimed tyre rubber into asphalt. This trend is likely to continue throughout the USA and will probably spread to other parts of the world as the disposal problem becomes worse.

7.2.3.2 Thermoplastic polymers

Polyethylene, polypropylene, polyvinyl chloride, polystyrene and ethylene vinyl acetate (EVA) are the principal thermoplastic polymers which have been examined in modified binders. As thermoplastics, they are characterised by softening on heating and hardening on cooling.

Thermoplastic polymers, when mixed with bitumen, associate at ambient temperature increasing the viscosity of the bitumen. Unfortunately they do not significantly increase the elasticity of the bitumen and when heated they can separate which may give rise to a coarse dispersion on cooling(7). However, accepting these limitations, EVA at a concentration of five per cent in 70 pen bitumen has become commonly utilised in the UK road construction industry.

7.2.3.2.1 Ethylene vinyl acetate

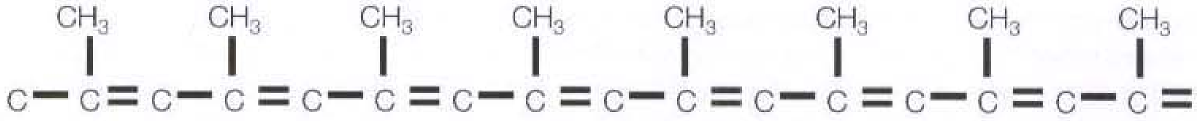
EVA copolymers are thermoplastic materials with a random structure produced by the copolymerisation of ethylene with vinyl acetate. Copolymers with low vinyl acetate content possess properties similar to low density polyethylene. As the level of vinyl acetate increases so the copolymer properties change(8). The properties of EVA copolymers are controlled by molecular weight and vinyl acetate content:

- molecular weight; the molecular weights of many polymers, are defined in terms of an alternative property; standard practice for EVAs is to measure melt flow index (MFI) in g/10 minutes, a viscosity test that is inversely related to molecular weight; the higher the MFI, the lower the molecular weight and viscosity; this is analogous to the penetration test for bitumen - the higher the penetration the lower the average molecular weight and viscosity of the bitumen;
- vinyl acetate content; in order to appreciate the main effects of vinyl acetate on the properties of the modified binder it is useful to consider a simple illustration of its structure, as shown in figure 7.6; this shows how the regular polyethylene segments of the chain can pack closely together and form what are known as crystalline regions; it also shows how the bulky vinyl acetate groups disrupt this closely packed arrangement to give non-crystalline or amorphous rubbery regions; the crystalline regions are relatively stiff and give considerable reinforcing effect, whereas the amorphous regions are rubbery; quite obviously the more vinyl acetate groups (or the higher the vinyl acetate content), the higher the proportion of rubbery regions, and conversely, the lower the proportion of crystalline regions.

There is a wide range of EVA copolymers available which are specified by MFI and vinyl acetate content. For example EVA with an MFI of 150 and a vinyl acetate content of 19 per cent is the 150/19 grade. From the wide range available the 150/19 and to a lesser extent

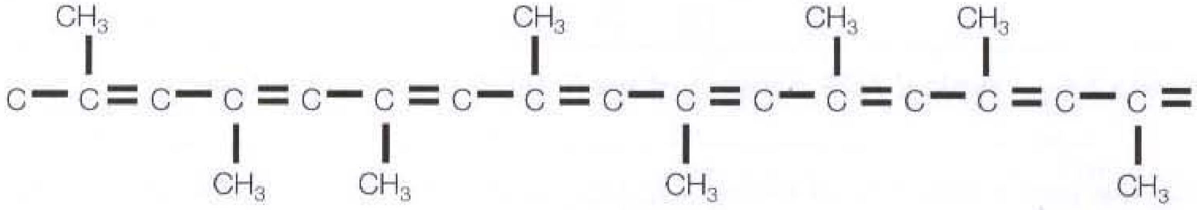
Figure 7.7 — Structure of polypropylene isomers

a) Isotactic polypropylene



CH_3 groups all the same side

b) Atactic polypropylene



CH_3 groups orientate randomly

the 45/33 grades are usually blended in 70 pen bitumen. EVA copolymers are easily dispersed in, and have relatively good compatibility with bitumen. They are thermally stable at normal bitumen temperatures. However, during static storage some separation may occur and it is therefore recommended that the blended product should be thoroughly circulated before use. In some countries workers have reported fumes of acetic acid partially caused by thermal degradation of the EVA.

7.2.3.2.2 Atactic polypropylene

Atactic polypropylene (APP) was originally a by-product of the manufacture of isotactic polypropylene, see figure 7.7, the disposal of which was a problem. The production of large quantities of low grade APP resulted in great stockpiles of unwanted material which were often dumped in landfill sites. Early experimentation with its incorporation into bitumen demonstrated that it could be blended with penetration grades and would give a significant increase in softening point.

The introduction of bitumens modified by APP in Italy resulted from an historical fortuity - the availability of scrap, locally produced APP, a by-product of the manufacture of polypropylene, and the discovery that bitumen modified by APP could achieve the same properties as blown bitumen at a lower cost. The consequent substitution of blown bitumen by blends of penetration bitumen modified by APP resulted in the closure of most bitumen blowing facilities in Italy. This trend was accelerated by subsequent oil shocks which caused bitumen prices to increase dramatically. Although the price of APP subsequently exceeded that of blown bitumen, the situation, once established, did not change and the great bulk of bitumen used for roofing in Italy is still APP modified.

The introduction of more efficient catalysts in the 1970s with higher yields and improved stereo-specificity ended the production of scrap APP in Western Europe. Today, APP derives either from Eastern European or Asian/Pacific countries, where it is still a by-product, or it is manufactured specifically for the bitumen market. The result is that the price is much higher, although the quality from specific manufacture is much more consistent.

Three qualities of APP-modified roofing felts are produced in Italy; table 7.8 shows their relative production volumes.

APP Content, % by mass	Filler, % by mass	Production volume, %
30	0	5
20	15	40
10	25	55

Table 7.8 — Typical APP content of roofing felt produced in Italy

The low level modification of bitumen by APP (ca 10 per cent) is not the same as that generally encountered in modified bitumens outside Italy and these materials are discounted from further discussion on modification as their performance approximates to that of normal blown bitumen. Those bitumens containing greater than 20 per cent of APP may be regarded as truly modified bitumens in the sense of having premium properties.

Bitumen/APP blends exhibit a different set of characteristic properties from blends of bitumen with thermoplastic rubber (TR). The polymer, which is a plastomer, modifies the bitumen by changing its viscous properties rather than by making it more elastic. The result is a stiffer binder. The amorphous nature of the additive and the weak rubbery character lead to high softening points and excellent flow resistance. Cold bend test results are adequate to good if sufficient APP is used (up to 30 per cent). Elongations which are slightly greater than those of an oxidised grade having a similar softening point can be obtained in tensile testing, but the permanent set is considerable. Generally, larger concentrations of APP are required to obtain the desired modification of bitumen properties than are necessary with TR compounds. However, as the cost of APP is considerably less than that of TR, the two types of modified binders tend to be competitive with one another.

Modifier		APP	SBS	Blown bitumen
Concentration	% mass	10 - 30	10 - 12	—
Softening point, (R & B)	°C	100 - 150	100 -140	100
Viscosity @ 180°C	Pa.s	0.3 - 2.5	0.9 - 4.0	1.5
Elongation at break,	%	200 - 400	1500 - 2000	140
Breaking stress	kPa	2 - 3	10 - 15	0.5
Cold bend temperature, pass,	°C	-10 to -20	-20 to -40	-10

Table 7.9 — Typical properties of bitumen modified with APP and SBS

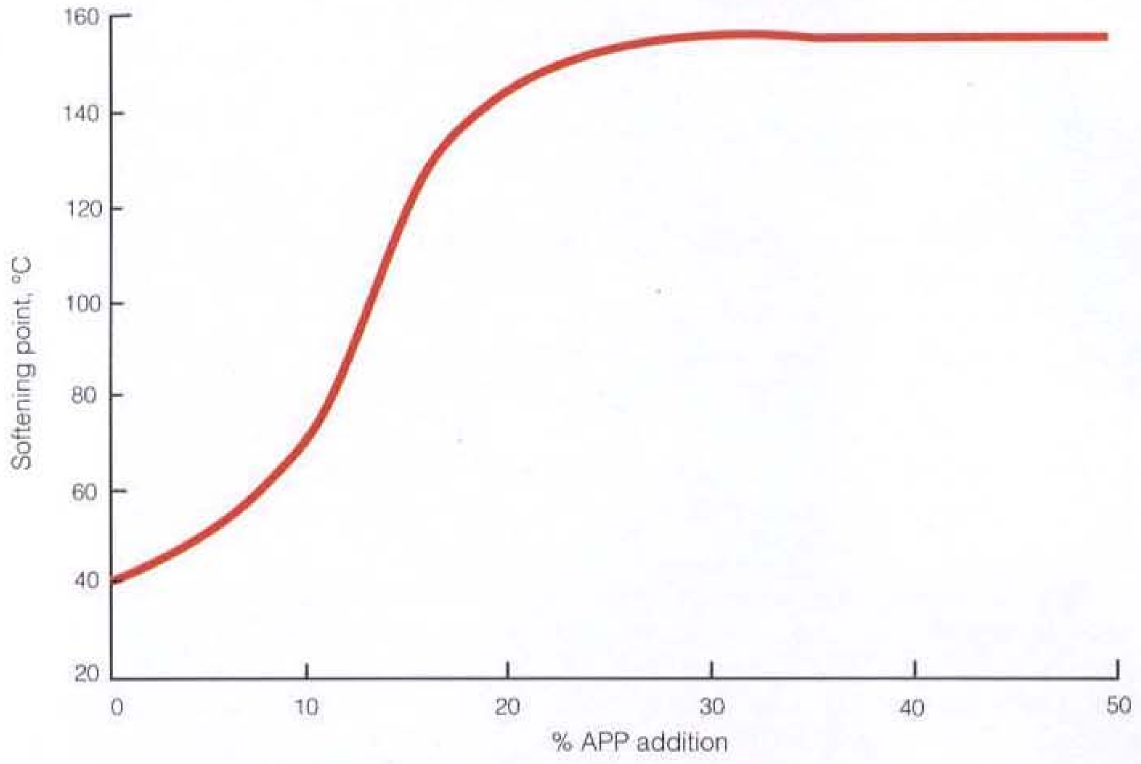


Figure 7.8 — Effect of APP addition on the softening point of 200 pen bitumen

The temperature susceptibility of bitumen is improved by the addition of APP and can be further improved by substituting some homopolymer by copolymer. However, this also softens the blend and consequently a small amount of isotactic polypropylene (IPP) may be used to compensate. Figure 7.8 shows the effect of APP addition to 200 penetration bitumen and table 7.9 shows typical properties of bitumens modified with APP and SBS compared to a blown bitumen.

APP is produced as the commonly available homo-polymer in a number of grades and purities. APP may also be produced as a blend with an alpha-olefin co-polymer (commonly called co-polymer APP) in order to achieve specific polymer properties. It is, therefore, often difficult to determine clearly the distinctions between these two types of APP.

As a thermoplastic material APP readily melts at high temperatures and is easily dissolved into hot bitumen. Whilst it is not necessary to mill APP into the bitumen, in practice this is often done to speed up the dissolution process. APP is, however, not completely compatible with bitumen and care needs to be taken on prolonged hot storage to avoid phase separation effects.

7.2.3.3 Thermoplastic rubbers

Bitumens have been used in roofing and waterproofing with satisfactory performance for many years(9). In the course of these years the number of bitumen types and grades has increased to cope with more severe demands, in particular with respect to resistance to flow

	Straight run bitumen	Blown bitumen
Softening point °C	35 to 55	85 to 110
Fraass breaking point °C	-22 to -16	-26 to -16

Table 7.10 — Effect of blowing on flow properties

and low temperature flexibility. Until the late 1960s bitumens used in roofing applications were mainly of the straight run types in mastics and emulsions, and of the air-blown types in roofing felts, built up roofings (BURs) and shingles. The improvements to bitumen by air blowing are now believed to have reached the limits with grades such as 105/35. In any case, blowing improves flow resistance at high temperature without affecting low temperature properties, see table 7.10.

Improvements in flexibility can be achieved only by using suitable polymers and since 1970 two polymers, thermoplastic rubber (TR) and atactic polypropylene (APP) have been used extensively.

Styrenic block copolymers, commonly called thermoplastic rubbers (TR), may be produced by a sequential operation of successive polymerisation of styrene-butadiene-styrene (SBS) or styrene-isoprene-styrene (SIS). Alternatively, a di-block precursor can be produced by successive polymerisation of styrene and mid-block monomer, followed by a reaction with a coupling agent. Thus, not only linear copolymers but also multi-armed co-polymers can be produced; these are often referred to as star-shaped, radial or branched copolymers (see figure 7.9)(10).

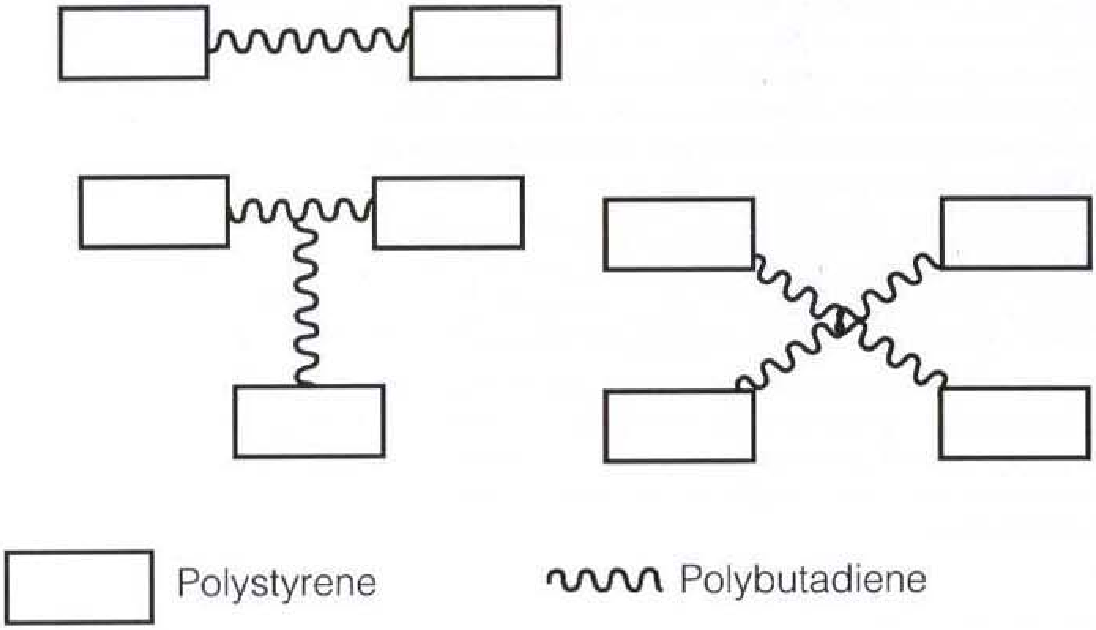


Figure 7.9 — Linear and branched thermoplastic rubbers

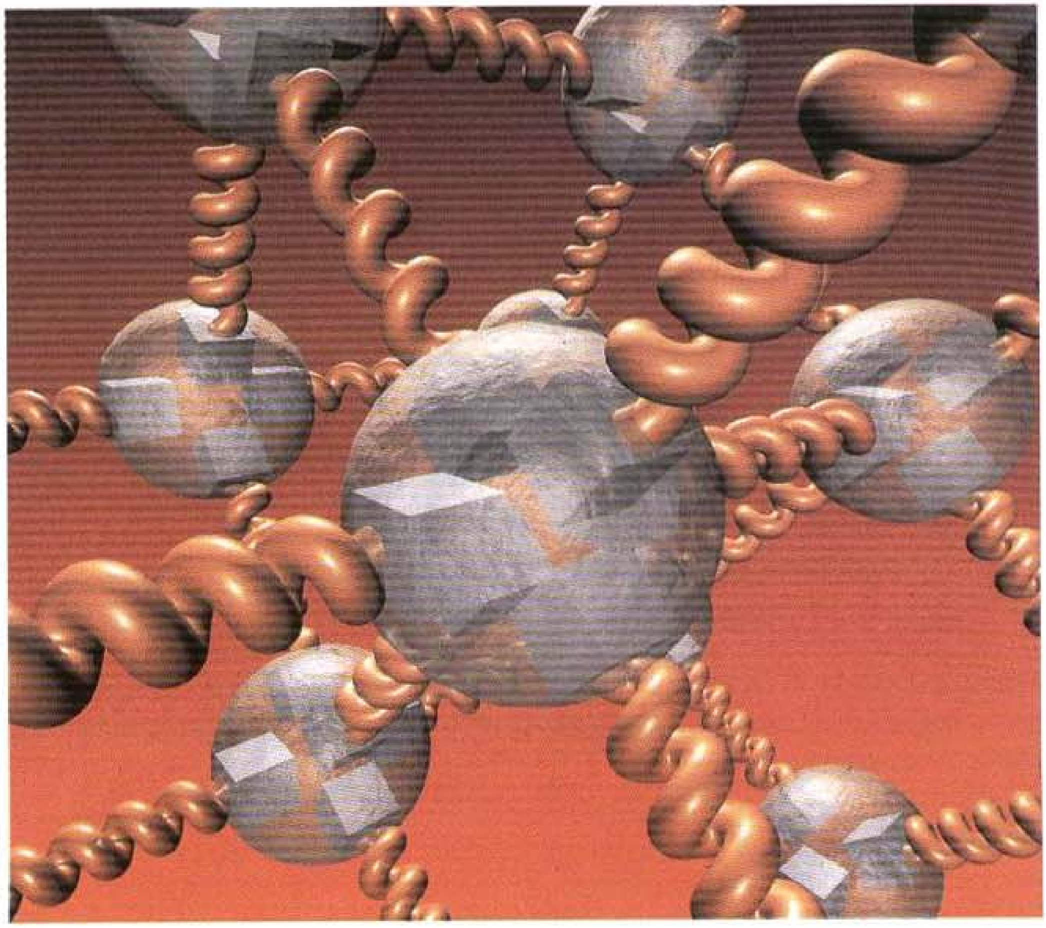


Figure 7.10 — Schematic of the three dimensional SBS network

These polymers comprise long chains of monomer building blocks (styrene, butadiene or isoprene) sometimes a few hundred in number but more frequently between 10,000 and 100,000. The polymer blocks are large enough to have their own separate identity and the relative sizes of the different polymer blocks determine the particular properties of the grade of TR.

Thermoplastic rubbers derive their name from their behaviour at ambient temperature, where they possess high strength and elasticity, but melt at high temperature and behave as viscous liquids. They obtain their strength and elasticity from a physical, rather than chemical, cross-linking of the molecules into a three-dimensional network. The physical cross-links result from the inherent incompatibility between the mid blocks and the styrene end blocks. The different blocks tend to separate into discrete phases, but are chemically linked, as shown in figure 7.10, providing a three-dimensional rubbery matrix. It is the polystyrene end-blocks which impart strength to the polymer and the mid-block which gives the material its exceptional elasticity(11).

At temperatures above the glass transition point of polystyrene (100°C) the polystyrene softens and the domains weaken and will even dissociate under stress, thus allowing easy processing. Upon cooling, the domains reassociate and the strength and elasticity is restored, ie the material is thermoplastic.

7.2.3.3.1 The influence of thermoplastic rubber type on bitumen/TR blends

Thermoplastic rubbers when added to bitumen produce dramatic improvements in its properties, a benefit which has found wide applicability in roofing and sealing compositions. The TRs most commonly used in the building industry from the Shell Chemicals range of products include:

Kraton D 1101	Cariflex TR 1101	linear, SBS* copolymer
Kraton D 1102	Cariflex TR 1102	linear, SBS copolymer
Kraton D 1107	Cariflex TR 1107	linear, SIS** copolymer
Kraton D 1184	Cariflex TR 1184	radial, SBS copolymer
Kraton D 1186	Cariflex TR 1186	radial, SBS copolymer
Kraton G		linear, SEBS*** copolymer

* SBS Styrene-butadiene-styrene block copolymer

** SIS Styrene-isoprene-styrene block copolymer

*** SEBS Styrene-ethylene-butylene-styrene block copolymer.

Before December 1994, Shell Chemical's TRs were marketed under the trade marks Cariflex and Kraton. In the Americas, TR grades were designated Kraton D, whilst in most of the rest of the world they were known as Cariflex TR.

Since December 1994, all Shell Chemical's TRs (or TPEs) have been re-designated as Kraton D. Each Kraton grade is identified by a number, such as 1101,1107, etc, and those materials manufactured outside the USA are distinguished by the use of a suffix C (eg Kraton D-1101 C). The equivalent US grade would be Kraton D-1101.

In this book Shell thermoplastic rubbers are referred to by their old Cariflex designation. However, this should be taken to refer also to the equivalent new Kraton grade.

The chemical composition of the TR is very important in determining the properties of bitumen/TR formulations(12). The amount of polymer, the nature of the mid-block, the polystyrene content and the molecular weight of the polymer have a profound influence on the performance properties of bitumen/TR compositions.

Polymer content. The influence of TR content on bitumen properties is described in detail in section 7.2.3.3. On addition of a TR to bitumen, oily maltenes are absorbed by the polymer which results in swelling and extension of the polymer. The polymer swells to about 6 to 9 times its initial volume. In a two phase system this is referred to as the polymer-rich phase, and if this phase is sufficiently extended it will become macroscopically continuous throughout the total blend(13). This normally happens when the TR content is between 4 and 8 per cent by mass. The formation of the continuous network is usually evidenced by the S-shaped softening point versus polymer content curve, see figure 7.11. A minimum of twelve per cent of TR is usually required to maximise softening point whilst cold bend performance is improved with lower levels of TR addition, see figures 7.11 and 7.12.

Polymer mid-block. The nature of the TR mid-block has a strong influence on the properties of bitumen/TR blends such as low temperature flexibility, thermal stability and tack. Low temperature flexibility, as demonstrated by cold bend temperature, is related to the glass transition temperature (T_g) of the polymer mid-block. The difference between the T_g of a butadiene mid-block (-90°C) in an SBS and that of an ethylene-butylene mid-block

Polymer properties	TR 1101	Kraton G
Polymer type	linear SBS	linear SEBS
Molecular weight	medium	low
Mid-block	butadiene	ethylene butylene
Polystyrene content	29	30
Mid-block glass transition temperature (Tg) °C	-90	-60
Polymer-bitumen properties		
Softening point, (R & B),°C	100	106
Penetration at 25°C, dmm	81	48
Viscosity at 180°C, Pa.s	1.1	1.3
DIN flow, pass, °C	80	80
DIN cold bend. pass, °C	-35	-10
Service temperature range, ΔT. °C	115	90

12 per cent TR in low asphaltene 200 penetration bitumen

Table 7.11 — Influence of mid-block character on bitumen blend

(-60°C) in an SEBS is clearly illustrated by the difference in cold bend performance, see table 7.11. The saturated mid-block of the Kraton G polymer is highly resistant to thermal degradation and imparts very good high temperature stability to bitumen/TR blends.

The isoprene mid-block of the SIS polymer gives it a high degree of tack which makes it particularly suitable for adhesive formulations - such as are found in self adhesive roofing membranes.

Molecular weight. The molecular weight of the TR can be used to influence the softening point of the bitumen/TR blend. In storage stable systems softening point is an indicator of flow resistance (about 20 to 25°C below the softening point) according to DIN 52123(14). A high softening point can be achieved by the use of a high molecular weight TR; however, this is usually at the expense of viscosity, see figure 7.13. This illustrates that for a fixed styrene content (30 per cent), there is a linear logarithmic relationship between softening point and viscosity as the molecular weight of the polymer increases for SBS thermoplastic rubbers. This is essentially the result of the linear logarithmic relationship between molecular weight, softening point and viscosity as illustrated in figure 7.14 for a series of bitumen/TR blends containing linear SBS polymers in storage stable systems. The same relationship exists for radial SBS systems. Cold bend and penetration value change very little because these properties are influenced primarily by the rubber content of the blend rather than molecular weight of the TR.

Polystyrene content. Figure 7.15 shows that for different styrene contents a series of lines exists relating softening point and viscosity. This series of lines can be used for the selection of TRs to give a blend with specific end properties. Softening points of 135°C of bitumen/TR compositions can be achieved using styrene contents of 35 per cent or higher. However, the use of such TRs is restricted by their limited compatibility in bituminous blends.

For high asphaltene bitumens the relationship between softening point and DIN flow resistance is more tenuous and hence the flow resistance measurements must be verified experimentally.

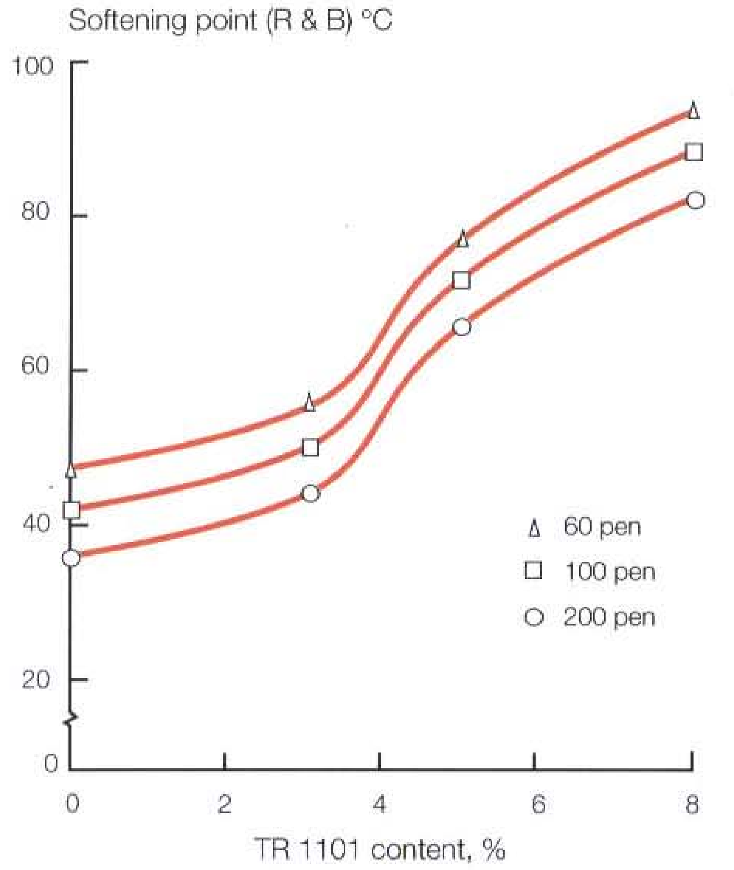


Figure 7.11 — Effect of Cariflex TR 1101 content on softening point

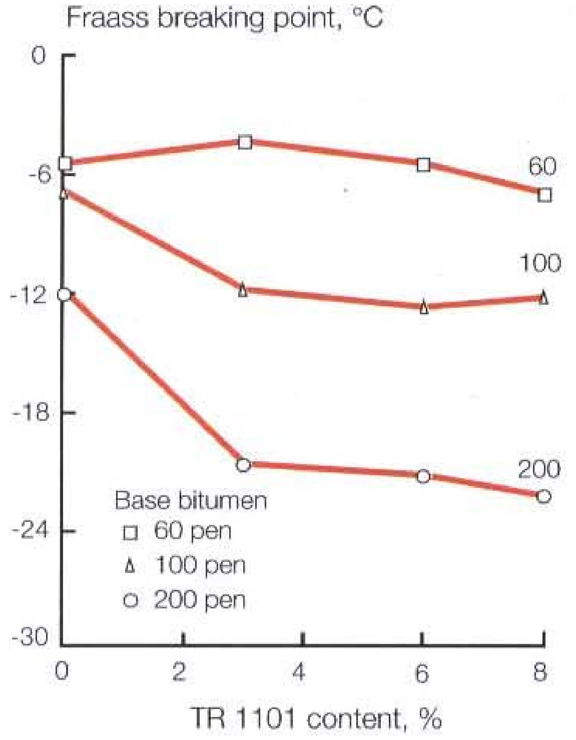


Figure 7.12 — Effect of Cariflex TR 1101 content on the Fraass breaking point

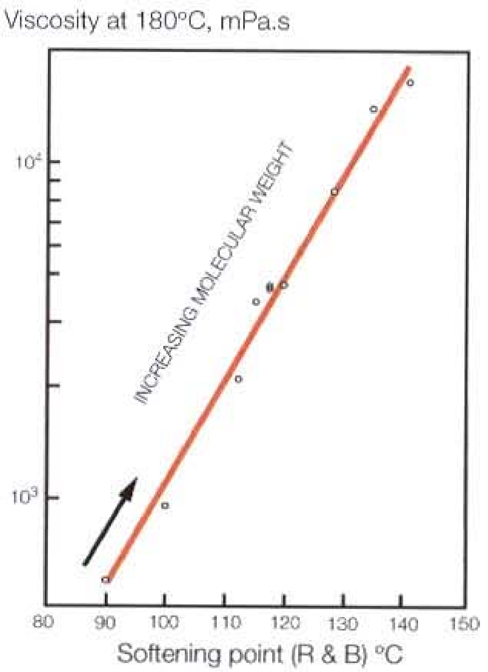


Figure 7.13 — Relationship between the viscosity at 180°C and the softening point of blends of 12% linear or radial SBS elastomers (styrene content 30%) in a low asphaltene 200 pen bitumen

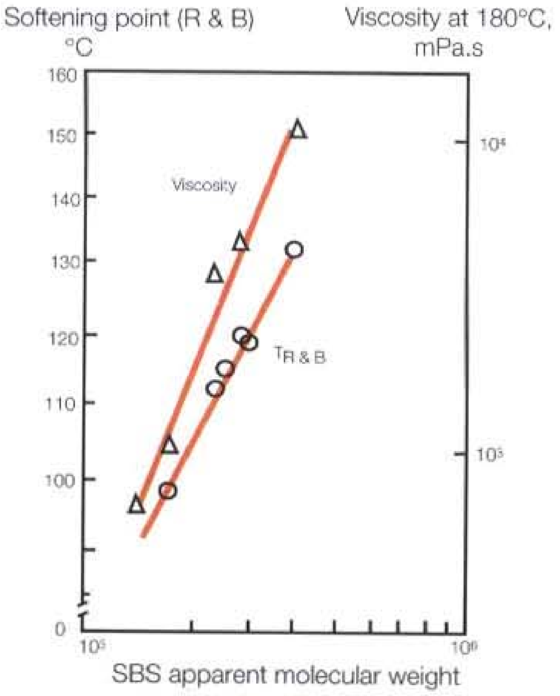


Figure 7.14 — The viscosity at 180°C and the softening point of a blend of 12% linear SBS (styrene content 30%) in a low asphaltene 200 pen bitumen as functions of the "apparent" molecular weight of the SBS

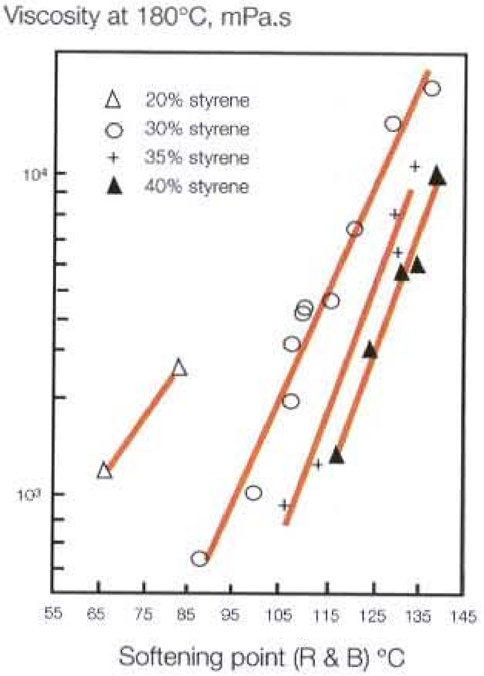


Figure 7.15 — Relationship between the viscosity at 180°C and the softening point of blends of 12% linear or radial SBS of differing styrene content in a low asphaltene 200 pen bitumen

	Polystyrene content increasing	Molecular weight increasing
Viscosity	↔	↑
Mixability	↓	↓
Incompatibility	↑	↑
Penetration	↔	↔
Softening point (R & B)	↑↑	↑
Elongation	↓	↓
Permanent set	↑	↔
DIN Cold Bend	↑	↑
DIN Flow	↑	↑

Key	↑	Increases
	↔	No change
	↓	Decreases

Table 7.12 — Effect of molecular parameters of the TR on the properties of bitumen/TR blends (12% TR in 200 pen compatible bitumen)

Table 7.12 summarises the effects of increasing either the polystyrene content of the TR, or increasing the molecular weight of the TR (at constant styrene content of 30 per cent) on the properties of a bitumen/TR blend containing a twelve per cent concentration of TR in a 200 pen compatible bitumen.

Polymer form. The physical shape of the polymer particles is important for the efficient blending and dispersion of the TR in the bitumen. Three physical forms of the polymers are possible, powder, fluffy and pellets, and the grades may be dusted with silica to prevent agglomeration. For details of the effect of polymer form on blending see section 7.2.3.3.3.

Cariflex TR 1101 is a linear, medium molecular weight, SBS copolymer containing 31 per cent of styrene. TR 1102 is a low molecular weight version of TR 1101 with 29 per cent of styrene and is commonly used when a lower blend viscosity is required. TR 1102 is unusual in as much as it has a combination of very high permanent set and low cold bend temperature. This behaviour results from the low molecular weight of the polystyrene domains, making them susceptible to softening by the maltenes fraction of the bitumen and reducing the high temperature flow resistance.

Cariflex TR 1184 is a radial, high molecular weight, SBS copolymer characterised by much higher viscosity than TR 1101 or TR 1102. It is commonly used in roofing felt coating formulations. TR 1186 has a slightly higher viscosity than TR 1184 and tends to produce a higher softening point product with bitumen than TR 1184.

Cariflex TR 1107 is a linear, low molecular weight, SIS copolymer, generally used in applications where a high tack is required. The polymer has a similar viscosity to TR 1102 and contains about fifteen per cent of styrene. The lower styrene content and the isoprene mid-block result in a considerably softer polymer than its SBS counterparts.

SBS copolymers are generally more stable than their SIS homologues at normal mixing temperatures (165 to 185°C). On prolonged heating, SBS types will be more prone to cross link or gel, especially at higher polymer concentrations, while the SIS copolymers will be more prone to chain scission under the same conditions.

Kraton G is a block copolymer with polystyrene end-blocks, but the butadiene or isoprene mid-block has been substituted by a saturated poly(ethylene-butylene) rubber. The saturated mid-block gives the Kraton G rubber a high resistance to outdoor weathering and it is especially resistant to high temperatures. Its resistance to high temperature degradation makes it particularly useful in formulations for mopping adhesives where temperatures well in excess of 200°C may be encountered. It is also ideal for use in environments which are particularly harsh such as desert conditions where both high and low temperatures may be encountered. Kraton G polymer maintains its low temperature flexibility down to -40°C.

The most important properties of the Cariflex polymers commonly used in the building industry are given in table 7.13.

7.2.3.3.2 The influence of bitumen constitution on bitumen/TR blends

As discussed in chapter 4, bitumens are complex mixtures which can, to a limited extent, be subdivided into groups of molecules with common chemical structures:

- saturates,
- aromatics,
- resins, and
- asphaltenes.

The saturates and aromatics can be viewed as carriers for the polar aromatics, ie the resins and asphaltenes. The polar aromatics are responsible for the visco-elastic properties of the bitumen at ambient temperatures due to association of the polar molecules which leads to large structures and in some cases even to three-dimensional networks, ie the so-called 'gel' type bitumen. The degree to which this association takes place depends on the temperature, molecular weight distribution, the concentration of the polar aromatics and on the solvency power of the saturates and aromatics in the maltenes phase. If the concentration and molecular weight of the asphaltenes is relatively low, the result will be a 'sol' type bitumen.

Studies by Vonk and Bull(13) have shown that when a thermoplastic rubber copolymer is in contact with bitumen, the elastomer copolymer absorbs, almost proportionately, all the bitumen components, with the exception of the asphaltenes. Independently of the bitumen composition and the asphaltenes content, a certain amount of the maltenes is taken up. Consequently, the elastomer rich phase is a fairly fixed fraction of the blend, determined by the elastomer content. The asphaltenes, however, require support from the presence of the maltenes to avoid their being precipitated. Thus, if the asphaltene content of the bitumen is too high, addition of TR can result in asphaltene precipitation or gellation and the blend becomes unworkable. Conversely, if the asphaltene content is low the polymer is able to absorb more maltenes after which even a single phase blend may be obtained.

Thus, addition of TR having a molecular weight similar to or greater than that of asphaltenes disturbs the phase equilibrium of the bitumen, causing competition between the polymer and the asphaltenes for the solvency power of the maltenes phase. Depending upon the available solvency power and the required amount of maltenes, phase separation may occur.

When phase separation occurs in a bitumen/TR material, the TR phase rises to the surface of the bitumen and the asphaltene phase falls to the bottom. The top section of the mixture thus becomes soft and elastic while the bottom becomes hard and brittle. The ratio of pen_{top}/pen_{bottom} quantifies the extent to which any separation of the binder has taken place, see figure 7.16. The extent to which a stable system is formed when the bitumen is modified by the addition of TR is dependent upon a number of factors which include:

- the amount and size of the asphaltenes,
- the amount and size of the polymer molecules,
- the aromaticity of the maltenes phase.

The softening points of bitumen/TR blends are largely governed by the aromaticity and average molecular weight of the base bitumen(15), see figure 7.17 and tend to be little influenced by the hardness of the base bitumen. The viscosity of blends at 180°C is predominantly affected by the average molecular weight of the base bitumen(13), see figure 7.18.

The complexity of the inter-relationships between these factors can be seen in figure 7.19(15). Although the axes in this diagram are unscaled, it can be deduced that too high an aromaticity should be avoided as this leads to a weakening of the polystyrene domains causing low softening points and low flow resistance. At low aromaticity levels, however, insufficient polymer will be incorporated into the bitumen which also leads to low flow resistance and furthermore to a low degree of upgrading of the bitumen.

The asphaltene content of the bitumen/TR blend must also be carefully balanced as, at low concentrations, the asphaltenes interact with the TR molecules forming beneficial associations which result in higher flow resistance and higher softening points. Conversely, too high an asphaltene content will result in phase separation leading to a lower proportion of the TR being available in the continuous phase. The permissible level of the asphaltene concentration is dependent upon:

- polymer content,
- polymer molecular weight,
- asphaltene molecular weight,
- aromaticity.

Figure 7.19 shows the role of the asphaltenes and aromatics in a qualitative sense. The range of bitumens suitable at low polymer modification levels is illustrated by the whole of the hatched area, whilst at high TR levels only those bitumens that fall within the cross-hatched area are suitable.

Careful balancing of the aromatic content and the aromaticity in relation to polymer content is necessary in order to produce a bitumen/TR blend which is stable and in which the TR is present as a continuous phase to the maximum extent possible, in order to achieve the maximum possible benefit from the polymer. Such blends are termed "compatible" blends.

Physical form							
Dusted porous pellet		TR-1101S	TR-1102S	TR-1107S	TR-1184S	TR-1186S	KRATON G G-1650
Dusted powder		TR-1101M			TR-1184M	TR-1186M	
Porous pellet		TR-1101	TR-1102	TR-1107	TR-1184		
Fluffy		TR-1101F				TR-1186F	
Typical properties							
Molecular Weight		Medium	Low	Low	High	High	Medium
Structure		linear S-B-S	linear S-B-S	linear S-I-S	radial (S-B)$_n$	radial (S-B)$_n$	linear SEBS
Styrene content	% by mass	31	29	15	30	30	29
Volatile matter	% by mass	0.3	0.3	0.3	0.3	0.3	0.3
Total extractables	% by mass	1.0	1.0	1.0	1.0	1.0	1.0
Viscosity, Pa.s., 25%mass toluene solution		4.0	1.2	1.6	20.0	21.0	1.5 (20%)
Melt flow rate (200°C/5kg)	g/10 min	<1	6	9	<1	<1	—
Density,	Mg/m^3	0.94	0.94	0.92	0.94	0.94	0.91
Hardness (Shore A, 30s)		72	70	30	75	74	75
Tensile strength,	MPa	33	33	28	27	24	—
Modulus 300%	MPa	2.9	2.9	0.9	2.5	3.0	—
Elongation at break,	%	880	880	1300	820	800	500

Table 7.13 — Shell Cariflex TR range of thermoplastic rubber polymers

Polymer type		TR-1101	TR-1101	TR-1102	TR-1102	TR-1184	TR-1184	Bitumen R100/40
Concentration in unfilled binder	% by mass	8	12	8	12	8	12	—
Softening point (R & B)	°C	90	100	76	80	105	117	100
Penetration @ 25 °C	dmm	95	81	84	73	89	72	—
Viscosity @ 180°C	mPa.s.	350	1100	250	650	1100	4000	1400
Fraass temperature	°c	-25	<-38	ND*	ND*	-25	-38	—
Flow temperature DIN, pass	°C	+65	+80	+50	+55	+70	+90	—
Cold bend temperature DIN, pass	°C	-10	-35	-20	-40	-10	-30	-4
Elongation at break	%	2400	1940	1860	1830	2000	1700	>100
Permanent set	%	8	9	29	32	5	3	>100

* Fraass temperature was not determined since cold bend test indicated it would be well below the limits of the test.

Table 7.14 — Properties of compatible 200 pen bitumen/TR blends

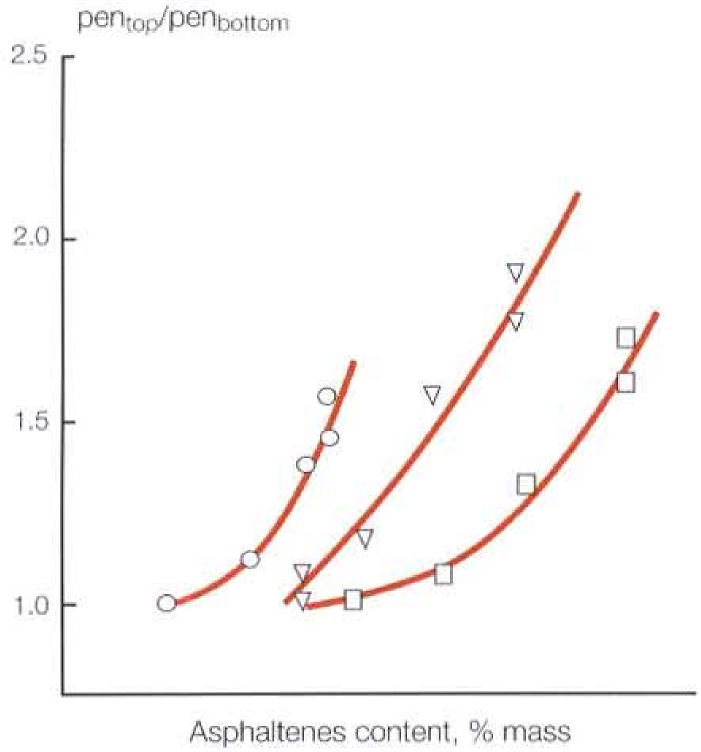


Figure 7.16 — **Effect of asphaltene content on the pen_{top}/pen_{bottom} ratio after hot storage of bitumen/TR blends. Bitumens blended from three base bitumens and non-volatile flux oil**

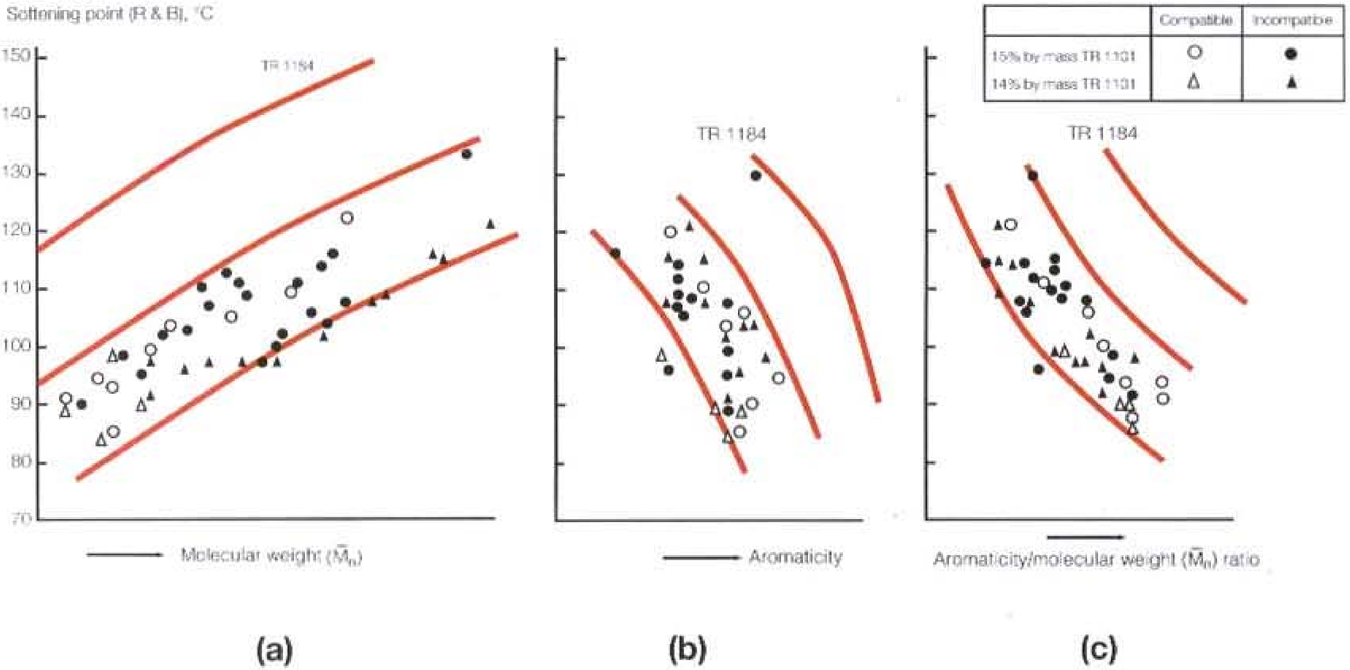


Figure 7.17 — **Correlation between softening point (R & B) of bitumen/TR blends and different constitution parameters of the bituminous base**

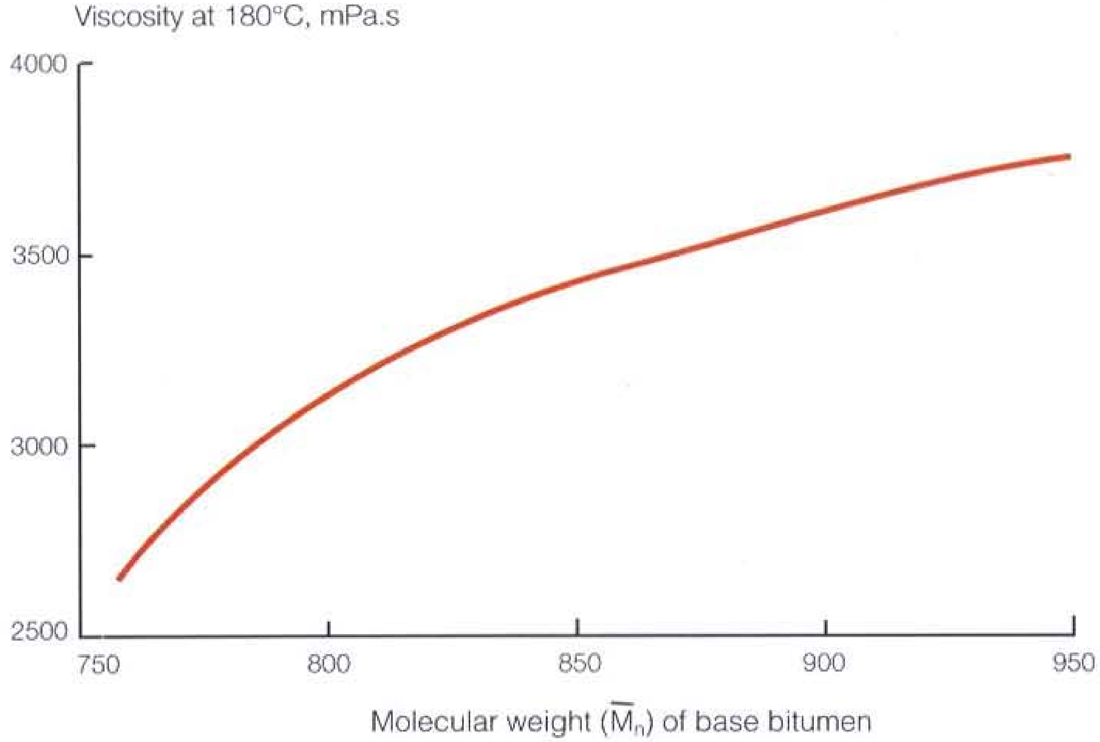


Figure 7.18 — Effect of base bitumen average molecular weight $\overline{M}_n$ on the viscosity of a blend with 14% Cariflex TR 1101

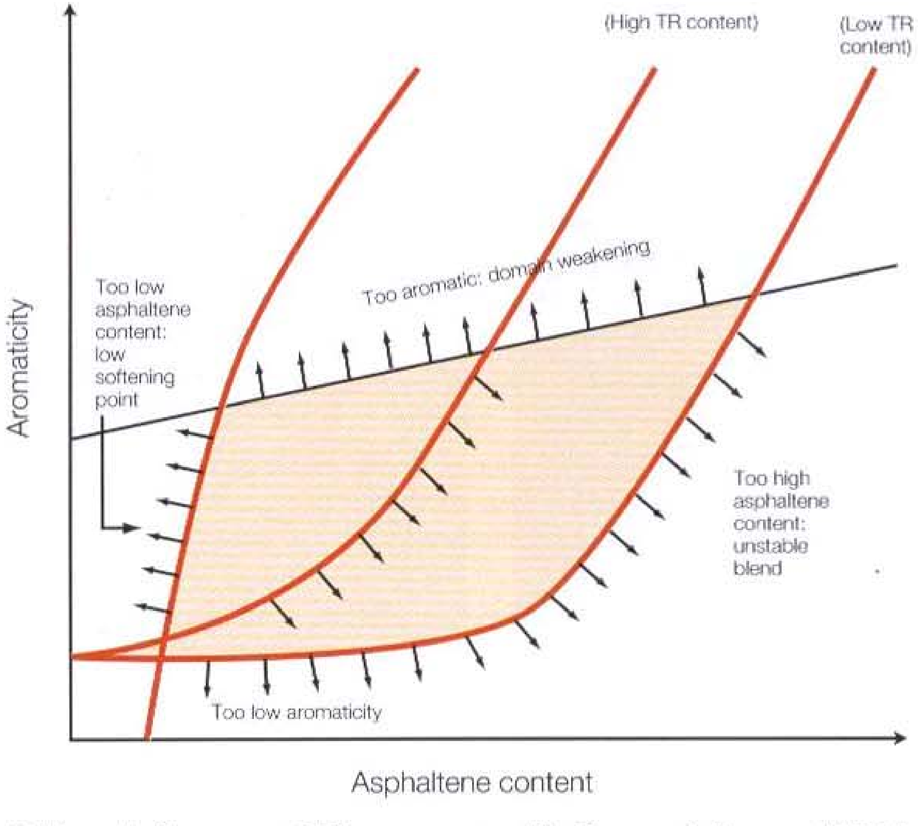


Figure 7.19 — Influence of bitumen constitution on bitumen/TR blends[15]

7.2.3.3.2.1 Definition of compatibility

A bitumen/polymer blend is defined as 'compatible' if the mixture is stable on hot storage without stirring to such an extent that phase separation does not occur to any appreciable extent and that the properties of the binder are not significantly changed.

Photograph 7.1 shows the microscopic structures of 'compatible' and 'incompatible' bitumen/polymer systems. The compatible system has a smooth, homogeneous, 'sponge-like' structure whereas that of the incompatible system is coarse and discontinuous.

The use of compatible bitumens offers a number of advantages in bitumen/TR technology, including:

● during compounding	shorter blending times, lower viscosity,
● during storage	storage stability,
● during service	better elasticity, improved durability, longer fatigue life.

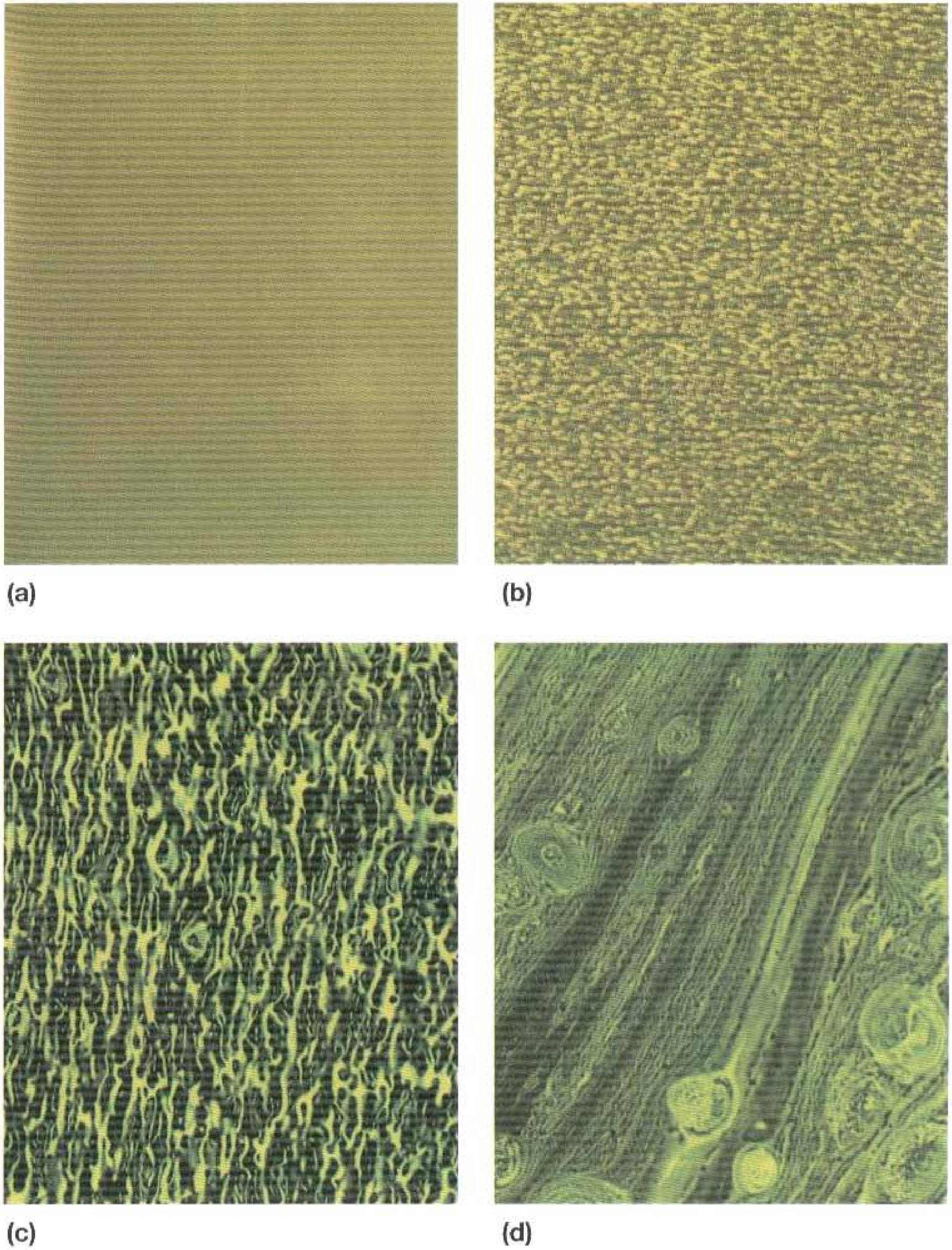
Incompatible bitumens generally give higher softening points and lead to somewhat higher flow resistance because of the increased interaction with the asphaltenes. However, they tend to have inferior long term performance and elasticity as less efficient use is made of the polymer. Polymer efficiency and softening point levels are illustrated in figure 7.20, and it can be seen that at low asphaltene content the polymer is more readily incorporated as demonstrated by the higher rise in softening point at low TR concentration.

Storage stability of bitumen/TR blends is not important where blends are manufactured and used immediately. However, this property acquires greater significance when blends are required to be stored for extended periods of time, such as over a weekend or during a holiday period. The effects of instability in storage can be lessened by the use of continuous stirring or recirculation to maintain the homogeneity of the mixture.

The first observable effect of compatibility manifests itself during blending. Since a compatible bitumen is constitutionally a better 'solvent' for the TR the blending time may be considerably reduced, see figure 7.21.

The second effect manifests itself as a difference in softening point and viscosity of the bitumen/TR blend. Incompatible systems give higher softening points and may also lead to higher flow resistance because of the interaction between the TR and the asphaltenes in the bitumen.

There is much evidence to indicate that fully compatible systems achieve the optimum performance and make the best use of the polymer present in terms of elasticity, fatigue resistance and ageing. However, most manufacturers of industrial products such as roofing felts have chosen not to follow this route but have instead utilised a semi-compatible system based on 200 pen bitumen with around twelve per cent by mass of a linear or radial TR depending upon the end performance required. Perfectly satisfactory products can be made this way if storage times between preparation and use are closely controlled.



Photograph 7.1 — Photomicrographs of bitumen/TR blends: (a) compatible; (b) and (c) semi-compatible; (d) incompatible

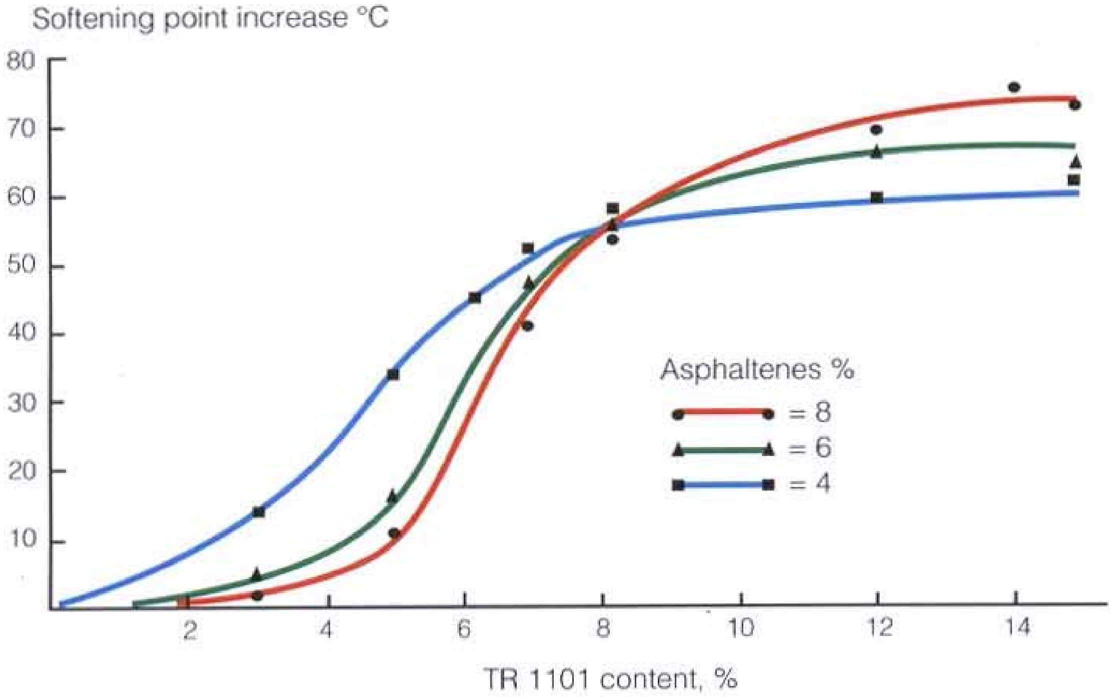


Figure 7.20 — Softening point increase as a result of TR 1101 content in relation to the asphaltene content of the base bitumen

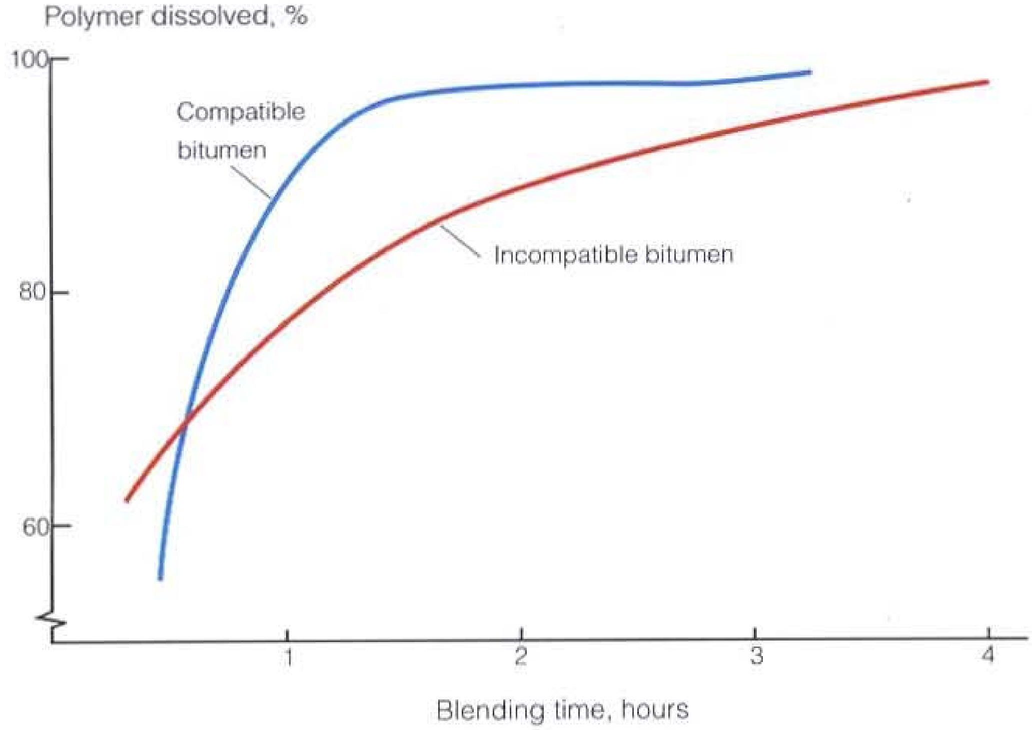


Figure 7.21 — Low shear blending with 12 per cent TR 1184(16)(17)

There is a considerable difference of opinion as to whether naphthenic or paraffinic bitumens are more compatible with TR as is evidenced by the number of users specifying one or the other type. One reason for this is that many manufacturers do not carry out storage tests but instead control their process on final test properties such as softening point, flow and cold bend properties. Bitumen constitution is subject to periodic small variations because crude oil from a single well is subject to natural variations. For polymer systems which are only semi-compatible this variation may have a large impact on final product properties even though the bitumen properties (penetration and softening point) remain constant. In these circumstances the polymer/bitumen manufacturer may observe differences in processing time, microscopic dispersion, softening point, etc, depending on whether the system is becoming more or less compatible.

7.2.3.3.2.2 Blends with compatible bitumen

The performance properties of blends of various thermoplastic rubbers with 200 penetration compatible bitumen are detailed in table 7.14. From this data, it can be seen that the softening point, viscosity and flow temperature increase, while penetration, elongation at break and Fraass temperature decrease. The radial polymer, TR-1184, gives the highest improvement in softening point and flow temperatures but gives viscosities which are much higher than the linear polymer, TR-1101.

In order to achieve a Fraass temperature of -38°C and a cold bend temperature of -25°C the concentration of thermoplastic rubber in the bitumen should be greater than 12 per cent.

The properties of bitumen/TR blends are contrasted in table 7.14 with those of standard R100/40 oxidised bitumen which is commonly used in the roofing industry. The high elongation at break and low permanent set of the modified bitumens clearly demonstrate the superior elasticity of these materials. The viscosity of the R100/40 bitumen is of the same order as that of 200 penetration bitumen containing about twelve per cent of Cariflex TR-1101, ensuring that handling and coating is conducted efficiently on conventional equipment.

The Cariflex TR-1102 polymer combines low melt viscosity and ease of blending with excellent cold flexibility but has poor flow resistance and permanent set and is more suitable for end use applications in colder environments.

In order to meet the requirement for a bitumen/TR compound for roofing with specified minimum softening point, flow and cold bend properties, table 7.15 gives a guide to the polymer concentrations which will be needed in a 200 pen compatible bitumen.

Cariflex grade		Softening point (R & B) °C		DIN Flow temperature pass °C		DIN Cold bend temperature °C	
		110	120	>80	>100	-10	-20
TR 1101	%	16	20	12	17	9.5	11
TR 1184	%	10	13	10	14	9	10

Table 7.15 — The amount of TR required in a 200 pen compatible bitumen to obtain softening point, flow and cold bend performance

Cariflex grade	Molecular weight	TR type	Service temperature range, ΔT
TR 1101	Medium	SBS	115
TR 1102	Low	SBS	95
TR 1184	High	SBS	120
TR 1186	High	SBS	130

Table 7.16 — Service temperature range of bitumen/TR blends

The absolute values for flow and cold bend temperature of a bitumen/TR blend indicate the service temperature range ΔT (flow temperature - cold bend temperature) for each system. Typically this is illustrated in table 7.16. In general, the best service temperature range is achieved by the radial SBS polymer Cariflex TR-1186, see section 8.1.3.10.3.

Compatible bitumen/TR blends have the advantage of superior resistance to ageing on prolonged hot storage and in-service(15, 16). In addition, the bitumen is a good solvent for the TR and the composition forms a homogeneous, storage stable material. This latter attribute of compatible blends is particularly important where transport at elevated temperatures between manufacturing installations is required. A homogeneous bitumen/TR material will not separate on transport and hot storage eliminating the risk of creaming. However, most roofing felt manufacturers produce and use the bitumen/TR coating on-site and are prepared to accept the lower resistance to ageing resulting from the cheaper, but more readily available, penetration grade bitumen.

7.2.3.3.2.3 Blends with penetration grade bitumens

Conventional penetration grade bitumens, in general, are not totally compatible with thermoplastic rubber. The TR does not dissolve in the bitumen to the same extent as the compatible bitumens discussed earlier. The bitumen and TR exist as two discrete phases, except perhaps at very high temperatures (greater than 170°C) when the TR may become totally soluble, but on cooling the two phases reappear. This can be seen in photograph 7.1 which shows photomicrographs of the two types of bitumen/TR systems(16). The consequence of this incompatibility is that blends of penetration grade bitumen with TR are often not storage stable and may separate on long term hot storage. It is usually necessary to maintain constant agitation, stirring or recirculation to ensure homogeneity of the dispersion of TR in the bitumen. This physical difference makes for some profound differences in the performance of the two types of materials, particularly in ageing resistance. It is possible to determine whether a bitumen-polymer blend is compatible by the use of the storage stability test which is described in section 5.6.1.

In general, substitution of an incompatible bitumen for a compatible bitumen will result in an increase in the apparent service temperature range of the blend (the difference between the cold bend and DIN flow resistance) by about 10°C, see table 7.17, which compares the properties of a twelve per cent addition of TR-1184 in both an incompatible and a compatible bitumen.

As with the compatible bitumen, the radial polymer TR-1186 gives the best working temperature range when blended with a conventional bitumen. The addition of filler to the bitumen/TR blend reduces its penetration but has little effect on its other properties within the normal range of filler concentration, see table 7.18.

Bitumen type		Compatible	Incompatible
Softening point (R & B)	°C	120	129
Viscosity at 180°C	Pa.s	4.3	2.4
DIN flow temperature, pass	°C	90	95
DIN Cold bend temperature, pass	°C	-20	-25
Service temperature range,ΔT	°C	110	120
Elongation at break	%	1750	1750
Permanent set after 1500%, 24 hours	%	2	4

Table 7.17 — Properties of 12% Cariflex TR-1184 blends in 200 pen bitumens

Polymer type		TR 1101	TR 1184	TR 1184	TR 1184	TR 1184
Concentration in binder	%w	15	15	15	12	10
Slate dust (per hundred binder)		—	—	20	20	20
Softening point, (R & B)	°C	109	127	128	117	112
Penetration @ 25°C	dmm	52	56	44	53	61
DIN Cold bend temperature, pass	°c	<-35	-35	-35	-30	-15
Elongation at break	%	1520	1720	1620	1840	1700

Table 7.18 — Properties of 200 pen bitumen with Cariflex TR

7.2.3.3.3 Manufacture and handling of TR/blends

7.2.3.3.3.1 Manufacture

When thermoplastic rubber polymer is added to hot bitumen, the bitumen maltene components immediately start to penetrate into the polymer particles, causing the styrene domains of the polymer to become solvated and swollen. The form of the polymer is important at this stage as the rate of dissolution of the polymer is dependant to a very great extent on the surface area of the polymer. The greater the surface area, the faster the dissolution process proceeds. If the polymer is in a finely divided form, such as a powder, dissolution may be adequately achieved by low shear stirring in a suitable mixing tank. However, if the polymer is in the form of dense 3 mm pellets it is essential that it is reduced in particle size as quickly as possible. This is normally achieved by the use of a high shear disintegrator. The slurry of bitumen and TR pellets from the mixing tank is passed through the high shear disintegrator as soon as possible after addition to the mixer to prevent the pellets becoming too soft to process. It is normal for this to be achieved between 20 and 30 minutes after addition of the TR to the bitumen. Once the TR pellets become soft, due to the heat absorbed from the bitumen, they are difficult to comminute and may pass through the disintegrator unchanged. Utilising a high shear disintegrator with TR pellets it is usually possible to complete the dissolution process within two to three hours.

The uptake of the maltenes by the TR generally amounts to some six to nine times the mass of the polymer and is termed the "polymer rich phase". Blends of bitumen and TR are not always homogeneous and single phase, and on cooling a two phase system may become apparent. The second phase is composed of asphaltenes and the balance of the maltenes .

The parameters influencing the mixing process include:

- Nature (grade) of Cariflex TR
- Physical form of Cariflex TR
- Nature and grade of bitumen
- Type of equipment
- Time-temperature profile during mixing

The last of these is not strictly an independent variable, but its importance in the context of subsequent performance of the blend warrants its inclusion here.

Nature (grade) of Cariflex TR. For a given set of mixing conditions on a given plant, the time required to achieve a homogeneous blend of TR and bitumen will vary with the molecular weight of the Cariflex TR, which is reflected to some extent in the final viscosity of the TR, and the styrene content of the TR. Both higher molecular weight (or viscosity) and higher styrene content will give rise to longer blending times, and vice versa. The isoprene based TR-1107 (containing 15 per cent by mass of styrene) will produce the shortest blend time.

Physical form of Cariflex TR. The physical form of the TR influences the blending process in two ways. The smaller the particle size of the polymer, the less reduction is required in any disintegration step in the process. In addition, since smaller particle size means larger surface area per unit mass of TR, penetration of the bitumen and swelling of the TR is facilitated and thus more rapid dissolution is achieved. Powdered TR grades will therefore disperse and dissolve more rapidly than porous pellets. Indeed, it may be possible to blend powdered TR with bitumen employing only low shear equipment and without any disintegration stage. Whether this is cost effective depends on the equipment available; if this is already high shear, then the extra cost of powdered TR may not be justified.

Nature and grade of bitumen. Bitumen plays a complex role in the mixing process as both its composition and viscosity affect the blending process in more than one way. High maltenes content and high aromatics content in a bitumen will encourage swelling of the TR to a greater extent than those with a high asphaltene content. Rapid and excessive initial swelling of the TR will reduce the milling effect on the TR as it passes through a high shear disintegrator, whilst for a powdered TR with low shear mixing rapid swelling is a considerable benefit.

Low viscosity bitumen is beneficial in aiding predispersion of the polymer in the bitumen and will subsequently speed the penetration and swelling of the TR particles. A low bitumen viscosity at the blending temperature will improve the disintegration of the polymer at the mill and result in a more rapid particle size reduction.

It is most unlikely that a bitumen for use in bitumen/TR compositions will be selected on the basis of its temperature/viscosity characteristics in order to aid penetration and swelling of the TR. The performance criteria of the finished products will generally be the dominating influence, the mixing process then being tailored to the availability of the components.

Mixing equipment. Two principal methods exist for the dissolution of the TR in the bitumen, high shear and low shear mixing. For low shear mixing a simple mixing tank with a paddle stirrer can be utilised with powdered TR, the action being confined to the swelling and dissolving by the bitumen. The mixer serves to maintain homogeneity of composition and uniformity of temperature, proving little or no heat input itself.

In high shear mixing the TR particles are physically reduced in size by mechanical/hydrodynamic shear in a rotor-stator combination accompanied by significant input of heat energy to the mix. This type of equipment, whilst functioning as a grinding stage, also provides rapid and effective dispersion and mixing of the TR in the bitumen. The most effective form of high shear disintegration is accomplished by a single pass through a disintegrator mounted in-line between two mixing vessels. Experience has shown that this type of equipment, which ensures that all the mixture passes through the rotor-stator gap, gives more rapid disintegration and dissolution of the TR than other types of mixer.

Time-temperature profile during mixing. Ideally the mixing process would be undertaken at the lowest possible temperature for the shortest possible time, commensurate with the complete incorporation of the TR into the bitumen both from an economic standpoint and to minimise any thermal effects on the polymer. In practical terms however, the temperature/time profile will be a function of the bitumen chosen and its requirement to achieve mobility and initial swelling of the TR. Empirically, for the penetration grades of bitumen normally used in combination with TR an operating temperature of 170 to 190°C is generally satisfactory. Higher temperatures should be avoided to minimise thermal effects on the polymer.

7.2.3.3.3.2 The mixing process

The choice of mixing process is determined initially by the physical form of the TR. If only low shear equipment is available to the processor, then a powdered TR should be selected. However, high shear equipment will provide much faster dispersion and solution even of powdered grades and is therefore recommended as providing much greater flexibility in operation and choice of materials.

All high shear equipment operates on a similar principle in that particles suspended in a liquid pass through a gap between one or more annular stator(s) and high speed rotor(s). The particle disintegration achieved in this type of equipment is dependent upon the rotor-stator combination and gap width, and will be by a combination of mechanical and hydrodynamic shear. Smaller gap widths give the highest shear whilst also increasing the temperature and power consumption by a greater amount. Larger gap widths give a higher throughput.

The blending operation is usually conducted in three stages:

- a pre-dispersion stage,
- a disintegration stage,
- a soaking or swelling stage.

In the first stage the bitumen is preheated to the required temperature - normally about 180°C - and the TR is added as quickly as possible without causing agglomeration, and stirred to distribute it throughout the hot bitumen. The length of this stage is dependent upon the requirements of the mill. For mills which require a hard particle to operate effectively, a short pre-mix stage is advised. A pre-mix time of about 30 minutes for a ten tonne batch is fairly normal, although the pre-mix time may be dictated by other plant conditions such as the TR charging rate.

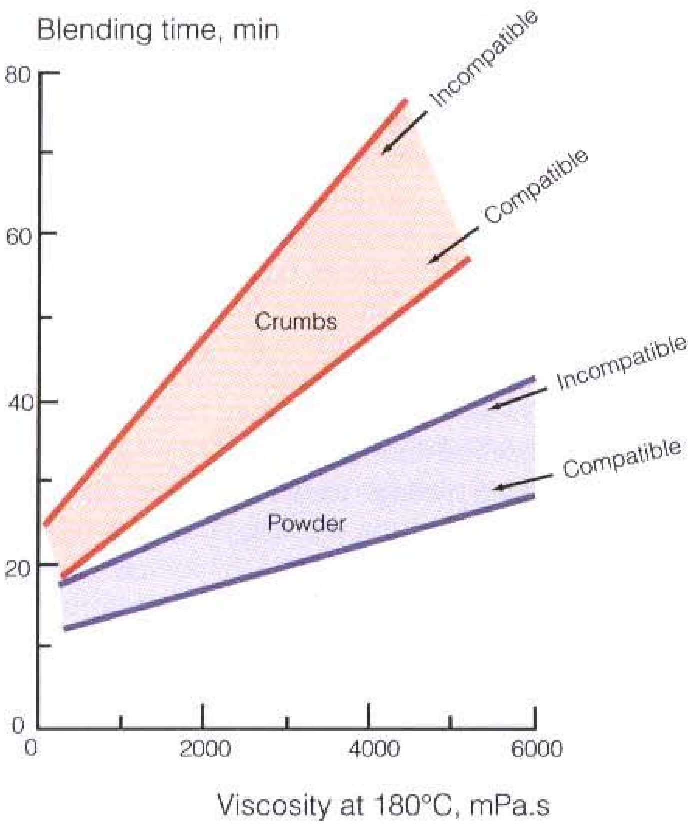


Figure 7.22 — Bitumen/TR blending times using high-shear, high-energy laboratory mixers

The pre-mixed batch is passed through the milling stage to disintegrate the TR particles. The rate at which this can be conducted is dependent upon the maximum power consumption of the mill, which is dependent upon the mill gap. The milling stage may be conducted in a single pass, as described above, or may be achieved by recirculation through the mill. The temperature rises as a result of energy dissipation into the mix.

The final swelling stage of the process may be carried out under low shear stirring whilst maintaining the blend at a temperature of about 180°C until there are no visible particles of TR present. The time taken in this final stage is independent of batch size but is influenced by the efficiency of the milling stage and on the nature of the bitumen.

The dissolution process is often monitored by dispersion and viscosity. A sample of the bitumen/TR blend is taken at intervals and spread into a thin film on a plastic sheet. When cold the bitumen/TR sample is stretched against the light and examined for undissolved TR. If no specks of undissolved TR are visible in the stretched film it is assumed that dispersion is complete. Viscosity is checked for compliance with internal specifications.

Figures 7.21 and 7.22(15,17) show the effect on processing time of compatible and incompatible bitumens. Figure 7.23(18) shows the effect of stirring time on viscosity at different temperatures. It is clear that viscosity increase occurs at higher temperature because of polymer cross-linking as well as dissolution. It is essential that close control of process temperature is maintained during manufacture to avoid degrading the polymer and to obviate the risk of initiating gelation. This is especially relevant to high polymer content blends of bitumen with TR and particularly when high asphaltene content bitumens are used.

Cariflex TR grade	TR 1101					
Content % mass		12			14	
Penetration of bitumen dmm	100	200	300	100	200	300
Viscosity @ 180°C, mPa.s	1870	1100	800	2700	2000	1600
TR grade	TR 1184					
Content % mass		12			14	
Penetration of bitumen dmm	100	200	300	100	200	300
Viscosity @ 180°C mPa.s	3700	2900	2300	7000	6000	5200

Table 7.19 — Penetration/viscosity relationship for bitumen TR blends

7.2.3.3.3.3 Handling criteria for bitumen/TR blends

The properties which are most relevant in respect of the handling of bitumen/TR compounds are viscosity and storage stability. The viscosity of the material determines the efficiency of mixing, pumping and coating whilst storage stability dictates the need for stirring or recirculation during storage of the binder to prevent separation.

Roofing felt coating plants are sometimes subject to limitations on the viscosity of the bitumen/TR compounds that can be handled due to restrictions on equipment power rating, production rates, or the type of carrier in use.

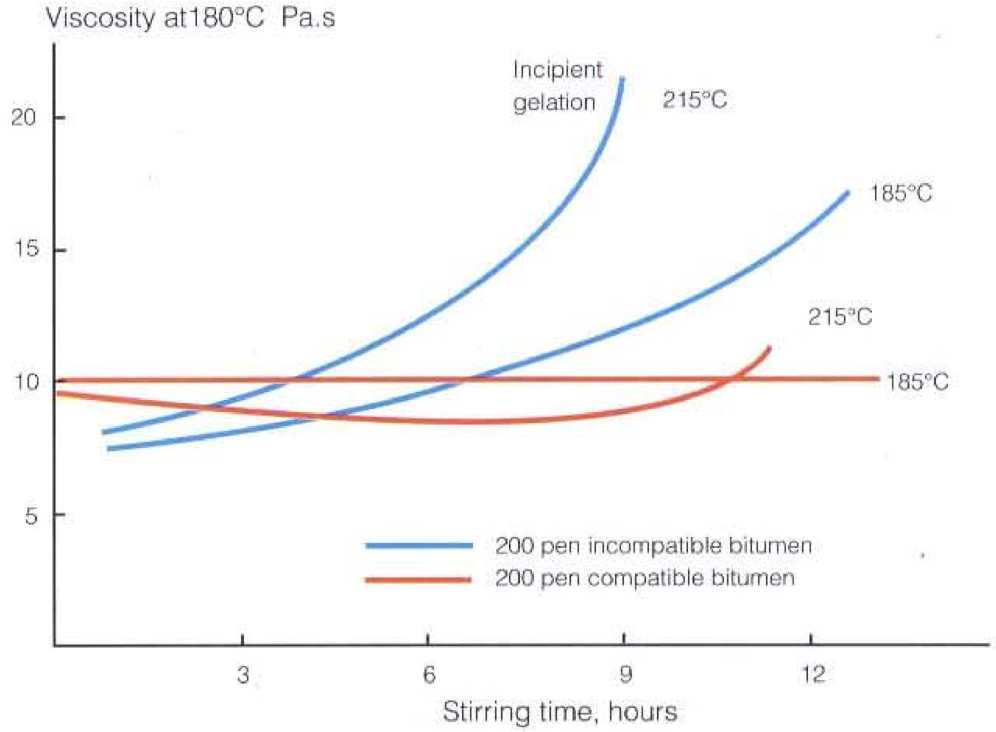


Figure 7.23 — Viscosities of bitumen/polymer blends (15% TR 1184/200 pen bitumen) after prolonged stirring at high temperature[18]

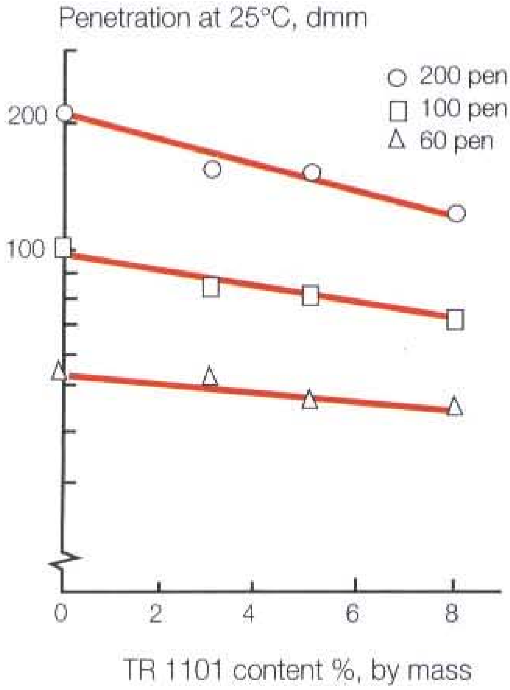


Figure 7.24 — Effect of Cariflex TR1101 on the penetration of bitumens

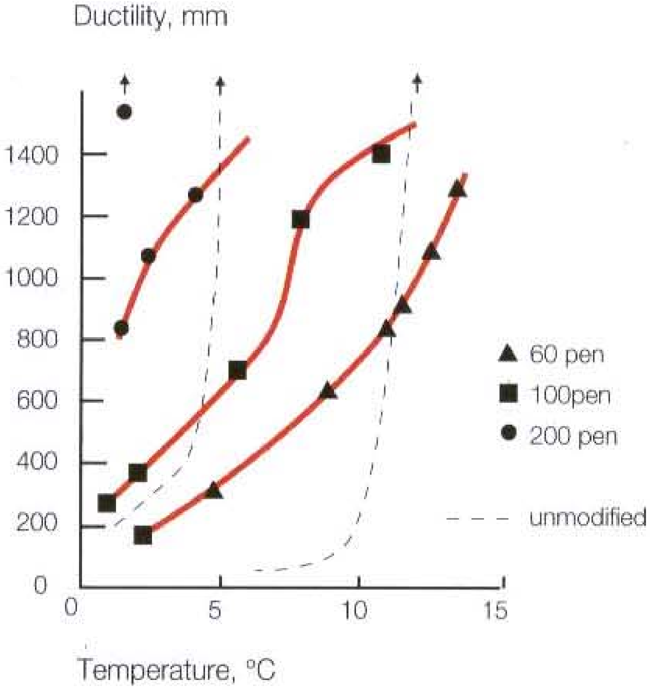


Figure 7.25 — Effect of test temperature on the ductility of bitumens modified with 5% of Cariflex TR 1101

At the maximum temperatures at which bitumen/TR blends can be handled without risk of degradation of the polymer, bitumen/TR 1101 blends have appreciably lower viscosities than the blends with TR 1184. This can be seen in table 7.19. In the case of a constraint on maximum allowable viscosity it may be possible to obtain a suitable TR grade giving the required viscosity. A lower blend viscosity should be adopted if mineral fillers are also to be incorporated.

However, in general, bitumen/TR blends have high temperature viscosities similar to those of the R-grades, enabling felt manufacture to be undertaken on standard roofing felt lines.

Storage stability considerations are also of importance and depend very much on the individual circumstances at a roofing felt manufacturing facility. Storage stability is associated with product homogeneity which in turn depends upon the compatibility between polymer and bitumen. Compatibility is dependent upon the composition of the bitumen; softer bitumens tending to give compatible blends more readily. However, this is not universally the case, see section 7.2.3.3.1. The handling criteria should therefore be considered on an individual basis by compounders, the use of softer bitumens and linear TR 1101 being less constraining.

7.2.3.3.4 Properties of thermoplastic rubber/bitumen blends

7.2.3.3.4.1 General properties

The addition of TR to bitumen makes a significant change to its properties even at fairly low concentrations.

The properties of the bitumen/TR blend are related to the elastomer grade (molecular weight, styrene content, mid-block type), but its increased elasticity is less dependent upon these parameters.

7.2.3.3.4.2 Softening point

Figure 7.11 shows the increase in softening point as a function of TR content for different penetration grades of bitumen. It can be seen that a significant increase in softening point takes place at between three and five per cent addition of TR. In this concentration range it is believed that a continuous three dimensional network of polymer begins to be formed. It can be seen that at low polymer addition levels the highest efficiency is obtained with the softest bitumen. It should be noted that the softening point increase and the absolute level of softening points varies with the nature and composition of the base bitumen. For example, figure 7.20 shows the effect on the softening point of differences in the asphaltene content of various bitumens. The efficiency of the polymer is very much influenced by the concentration of asphaltenes in the bitumen.

Softening point correlates with viscosity although the softening point of TR modified bitumen does not represent the same viscosity level as that of unmodified bitumen with the same softening point. However, it can still be regarded as an indication of the contribution of the binder to resistance to creep deformation. In more sophisticated rheological studies, blends of TR and bitumen have proved to be more affected by shear rate than by loading time when compared to unmodified bitumens.

7.2.3.3.4.3 Penetration

Penetration also correlates with viscosity, but at a very much higher stress level than softening point. Here too it is clear that even at low polymer contents the TR is effective and that the highest efficiency is again obtained in the softer bitumens, as shown in figure 7.24.

7.2.3.3.4.4 Fraass breaking point

The same conclusion as above may be derived for the Fraass breaking point test. Figure 7.12 shows how the low temperature flexibility is improved even by small additions of TR to the softer base bitumens.

It should be noted that increasing the TR content to concentrations of ten per cent leads to the Fraass breaking point falling below the test limit of -38°C.

7.2.3.3.4.5 Ductility

Ductility is a property of bitumen which is partly related to its ability to flow. It is therefore not surprising that TR modification of the bitumen does not necessarily lead to higher ductility values. Figure 7.25 shows that the ductility of TR modified bitumen at the higher end of the temperature range, where the extension of the base bitumen cannot be followed by the SBS polymer network, may not necessarily be improved by the polymer addition. However, at lower temperatures, where the base bitumen cannot sustain large extensions, the TR modification enhances the flexibility of the binder and the ductility increases with increasing polymer content. It should be noted that the behaviour of a polymer modified bitumen in the ductility test is very different from that of a conventional bitumen, and therefore a straight comparison of the test data can be misleading.

7.2.3.3.4.6 Elastic recovery

Today, the ductility test equipment is frequently used to demonstrate the more elastic nature of the TR modified binders. The recovery of the deformation after release of the loading is a measure of the elastic behaviour of the binder. Various test methods may be employed, but the one which is gaining popularity in Europe is the ductility recovery test, which utilises the existing bitumen ductility apparatus, see photograph 7.2. Given the nature of the TR, it is to be expected that the elasticity of a bitumen/TR binder will be very high. Table 7.20 shows how the TR content and the hardness of the base bitumen affects the elastic recovery of the ductility test specimen.

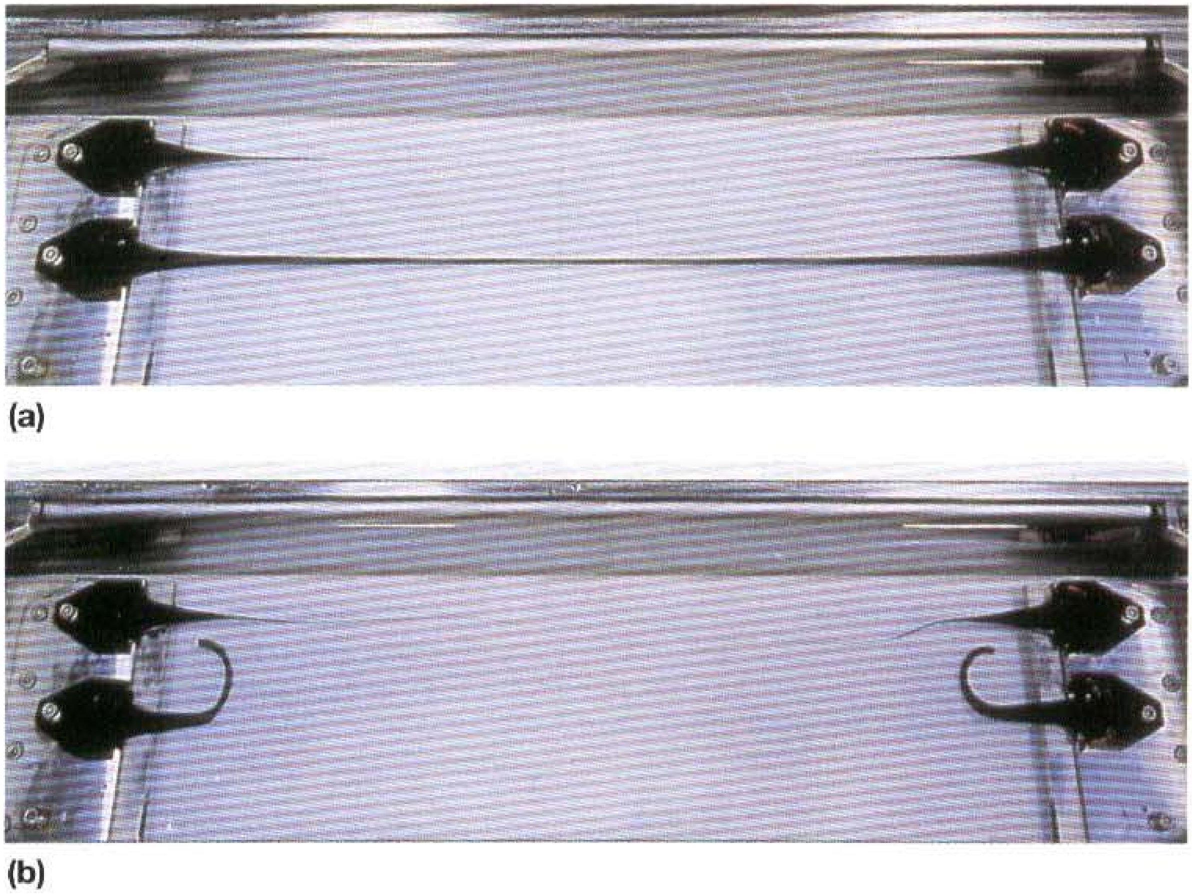
Base bitumen	Cariflex TR1101	
	3% by mass	7% by mass
60 pen	77	93
200 pen	88	100

Table 7.20 — Elastic recovery (%) after 50 cm ductility strain

In this test a specimen is elongated up to specified length (20 or 50 cm) at a specified temperature (10, 13 or 25°C) and then cut into two halves. After one hour of recovery, during which time the elastic memory of the specimen causes it to return more or less to its original length, the length of the specimen is measured and the result expressed as a percentage of the applied strain. Generally, this test is carried out at a fairly low temperature, thus compliance with a minimum ductility specification is established at the same time.

7.2.3.3.4.7 Adhesion/cohesion

When used in an asphalt mix, for example mastic asphalt, bitumen binds together the aggregate, sand and filler that comprises the mix and which carries the heavy stresses imposed by traffic loading. The binder should have sufficient cohesive and adhesive strength to ensure the minimum loss of aggregate. Under the effects of intense traffic the binder may



Photograph 7.2 — Elastic recovery specimens of bitumen and bitumen/SBS:
(a) Specimens extended to 50 cm

(b) Specimens after one hour

bitumen upper specimen, bitumen/SBS lower specimen

not be sufficiently strong to achieve this. One of the purposes of adding a polymer to the bitumen is to improve the net effect of the cohesive and adhesive properties of the binder and to enable the binder to withstand higher stresses.

Measurement of adhesion is notoriously difficult to achieve in a reproducible manner and many methods have been employed to measure the combined forces of adhesion and cohesion (known as adhesive strength). A butt test was selected to measure the peak force required to separate two pieces of aggregate bound by 0.1 mm of binder, see figure 7.26.

Comparison of different grades of conventional bitumen shows a correlation between increasing bitumen hardness and increasing adhesive strength together with decreasing strain at failure.

Figure 7.27 shows that bitumens modified with low concentrations of TR (three per cent) have a similar strength to that of unmodified binders at the same penetration value. This implies that the improvement in adhesive strength is marginally greater than the reduction in penetration when small amounts of TR are added.

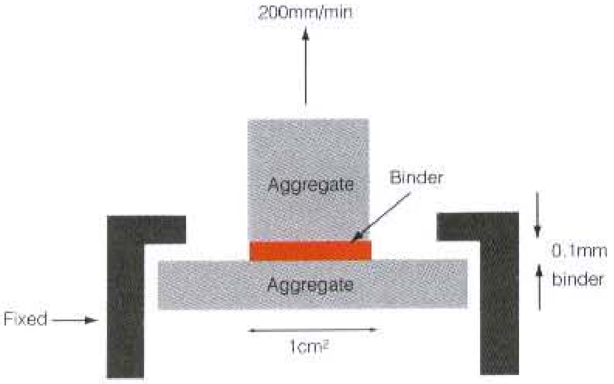
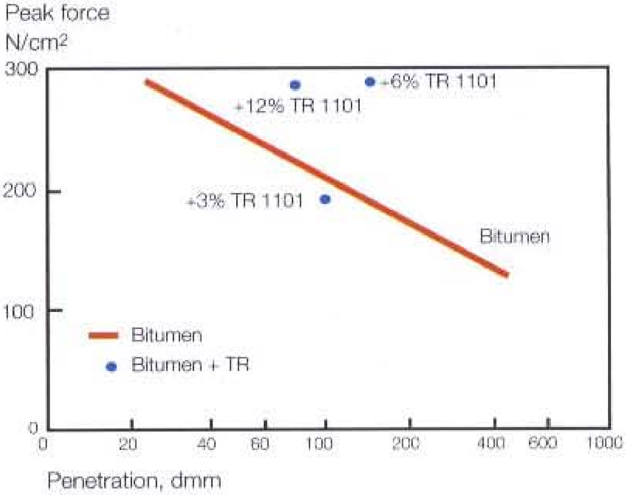


Figure 7.26 — Butt jointing test specimen



Test temperature: 20°C; test speed: 200 mm/min

Figure 7.27 — Effect of binder penetration on adhesive strength in butt joint test

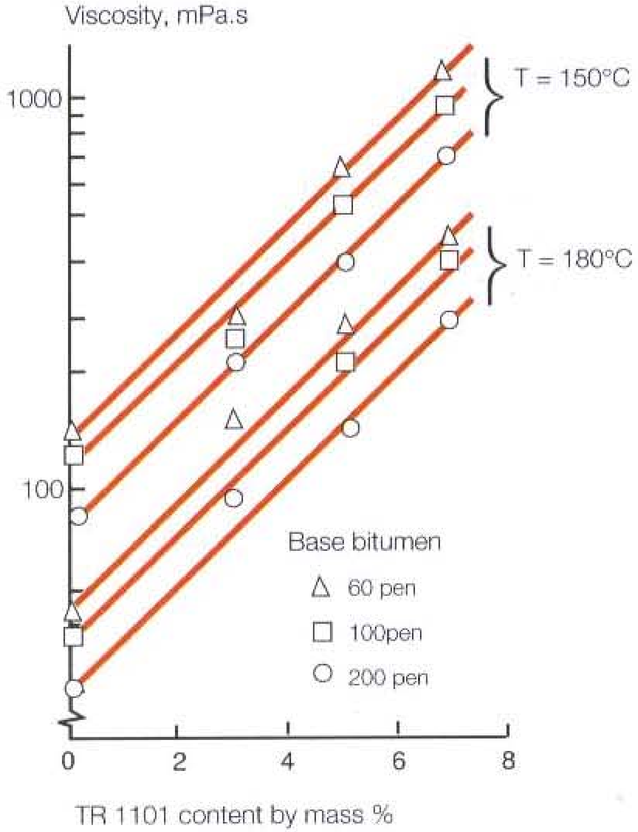


Figure 7.28 — Effect of Cariflex TR 1101 on blend viscosity.

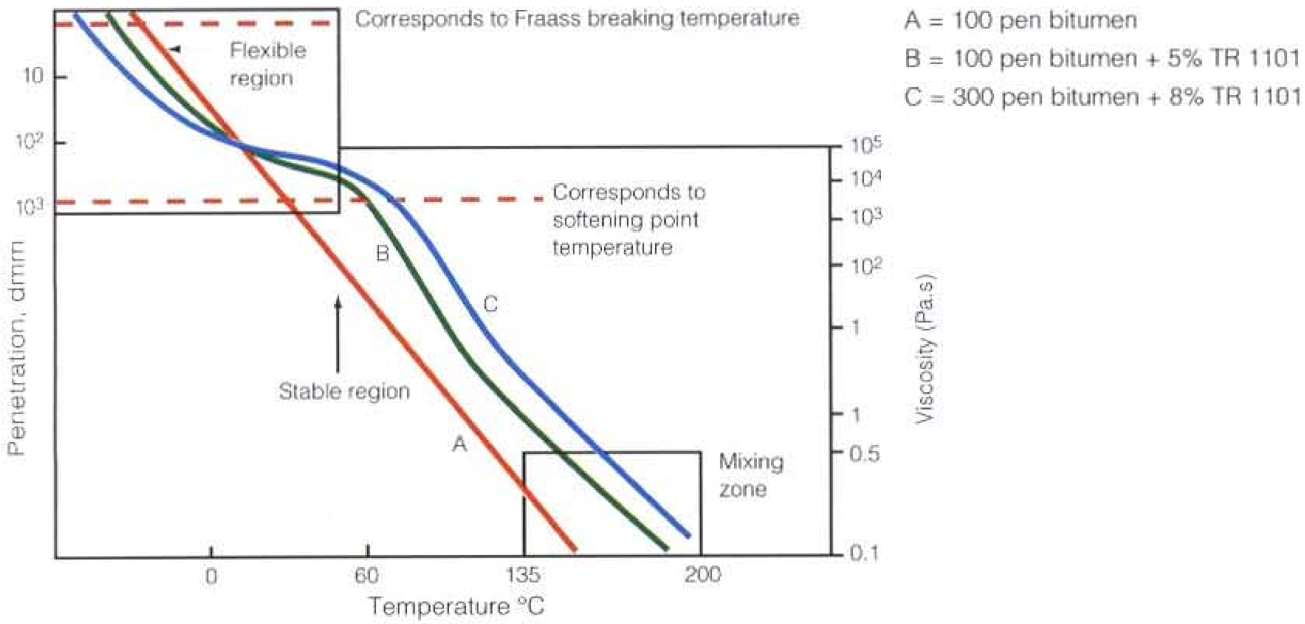


Figure 7.29 — Heukelom Test Data Chart, bitumen compared with TR modified bitumen

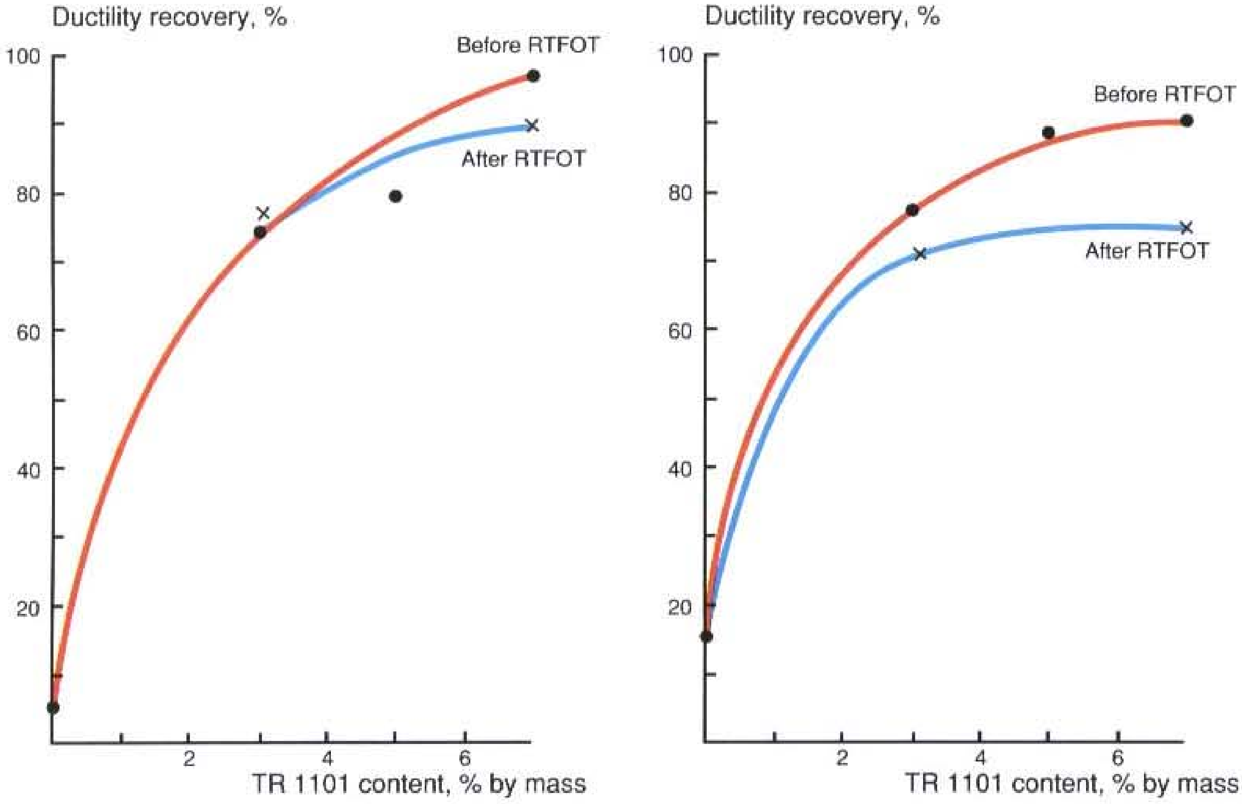
If, however, the TR content is high enough for a continuous network to be formed (around five to seven per cent), the results obtained are far better than might be expected on the basis of the penetration. Addition of TR up to twelve per cent does not further increase the force required to separate the aggregate.

To obtain a binder of about 100 pen with three per cent of TR requires a base bitumen of about 130 pen and for six per cent TR the base is about 180 pen. In contrast to the unmodified bitumens, the TR modified binders combine higher adhesive strength with a higher maximum allowable strain.

7.2.3.3.4.8 Viscosity

Modification of bitumen by a TR leads to a viscosity increase which is related to the polymer content, see figure 7.28. Assuming that a viscosity of 200 mPa.s is the upper viscosity limit for efficient mixing/coating and 180°C the maximum temperature for mixing, the number of potential binder formulations becomes limited. However, experience in practice with asphalt mixes manufactured using modified binders with higher than normal viscosities has shown that the asphalt compaction was not inferior to that of conventional mixes produced at the normal viscosity. This effect is now attributed to shear thinning of the binder, a not uncommon phenomenon in polymer technology.

The rheology of SBS bitumen binders at service temperature is rather complex, the behaviour of the binder being more elastic than normal bitumen especially at longer loading times and higher temperatures. The viscosity/temperature characteristics of a TR modified bitumen are compared with a conventional bitumen on a Heukelom bitumen test data chart shown in figure 7.29.



Compatible bitumen

Incompatible bitumen

Figure 7.30 — Ductility recovery after 200 mm elongation at 13°C before and after RTFOT

It is clear that at very low temperatures (measured by the Fraass test) the modified binder is more flexible and therefore more resistant to low temperature cracking, see figure 7.12. At higher service temperatures it is stiffer and more elastic and should therefore be more resistant to permanent deformation.

7.2.3.3.4.9 Ageing

The properties of the binder in a formulated mixture are of more relevance to the engineer than those of the fresh unaged binder. It is known that the binder is exposed to ageing (oxidative hardening) in many manufacturing processes which can reduce the penetration by some 20 to 40 per cent and increase the softening point temperature by about five degrees Celcius.

It is generally accepted that TR modified binders tend to age at a lower rate than normal bitumens. This is considered to be due to the fact that, in a TR modified system, the hardening process of the bitumen is to some extent counteracted by some loss of effectiveness of the SBS polymer. However, in practical terms, it is not penetration and softening point which relate to performance but the elastic properties of the binder such as elastic recovery. This has been measured after ageing in the rolling thin film oven test (RTFOT) to ascertain the degree of the loss of effectiveness of the polymer, see table 7.21 and figure 7.30.

Ductility elongation	RTFOT	TR content	
		3% by mass	7% by mass
20 cm	Before	74	96
20 cm	After	75	90
50 cm	Before	82	97
50 cm	After	82	93

Table 7.21 — Elastic recovery (%) of TR modified bitumen after RTFOT

Figure 7.30 shows that the changes in the RTFOT are affected by bitumen type. The use of special compatible bitumen gives better results than a normal penetration type of bitumen, see table 7.22. The elastic recovery of TR bitumen blends tends to be high after RTFOT (typically greater than 70 per cent).

These results are in agreement with overheating trials and practical experience in Germany in 1990 on TR modified Gussasphalt(19), where despite very severe overheating at temperatures in excess of 230°C, the elastic recovery of the binder was affected to a surprisingly small extent.

Further experiments conducted by Vonk, Phillips and Roele(16) on the ageing resistance of bituminous road binders modified by TR polymer have shown that, despite the apparent total degradation of the TR in the binder after ageing in the RTFOT for 72 hours, the level of performance of the binder, especially in the elastic recovery test, was very much better than might have been expected on the basis of polymer analysis.

Figures 7.31, 7.32, 7.33 and 7.34 show the effect of ageing in the RTFOT on penetration, softening point, Fraass temperature and viscosity for periods of time up to 72 hours. Some of the observations from this study were as follows:

Property	Compatible bitumen		Incompatible bitumen	
	Fresh	1 year @ 60°C	Fresh	1 year @ 60°C
Elongation at break %	1950	1650	1700	550
Permanent set %	9	90	12	*
Fatigue: cycle to failure	> 10,000	> 10,000	6,500	1,600
Flow temperature, DIN pass °C	80	70	80	70
Cold bend temp, DIN pass °C	-20	-10	-15	-5

*Could not be measured; minimum elongation required is 1500%

Table 7.22 — Ageing behaviour of bitumen/TR blends(12)

- The penetration value of the TR bitumen binder changes at a relatively slower rate than the bitumen control.
- The softening point of the TR binder remained fairly constant while that of the normal bitumen increased considerably.
- The Fraass breaking temperature showed a remarkable improvement from -15°C to -30°C.
- The GPC pattern of the SBS modified system changed during exposure in the RTFOT indicating that the polymer had degraded. GPC chromatograms, figure 7.35, show the gradual disappearance of the SBS peaks in a sample of TR modified bitumen during the ageing test.
- The TR modified systems became more homogeneous on prolonged storage to the extent that incompatible blends changed to a one phase morphology.

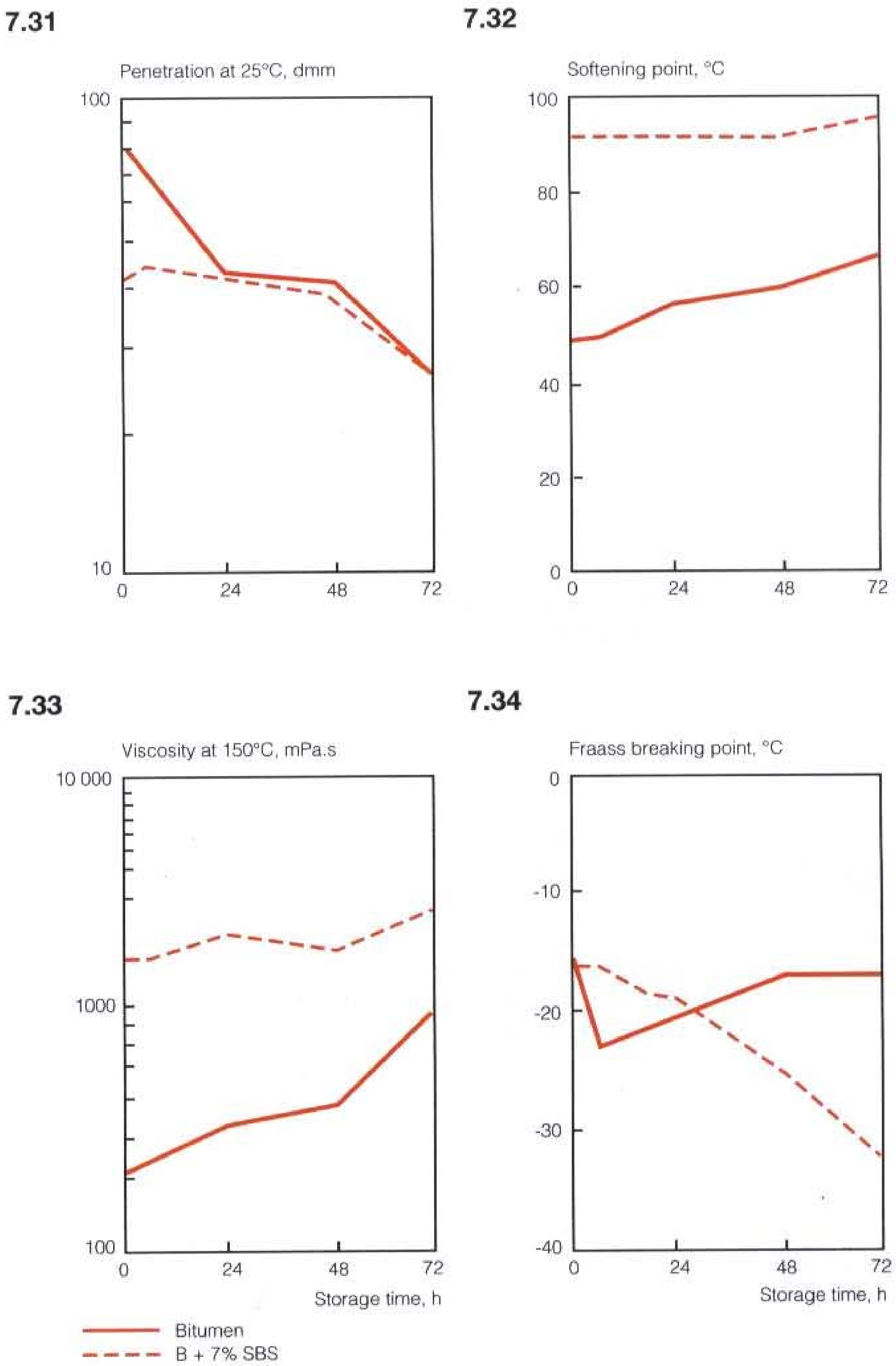
This remarkable behaviour of the TR modified binders on ageing can be explained by changes in the polymer. One of the important factors determining the compatibility of the bitumen/TR system is the molecular weight of the polymer. If the polymer breaks down, ie its molecular weight is reduced, the compatibility is bound to improve. The GPC data suggests that such a mechanism is at work. The SBS tri-block peak disappears while more material is in evidence at molecular weights intermediate to those of the polymer and bitumen.

Breakdown of the SBS polymer results in the formation of SB di-blocks which are known to have little influence on bitumen properties as they do not develop a network. The enhanced properties of the degraded modified binder (softening point, viscosity, elastic recovery) strongly suggest that another mechanism must be at work.

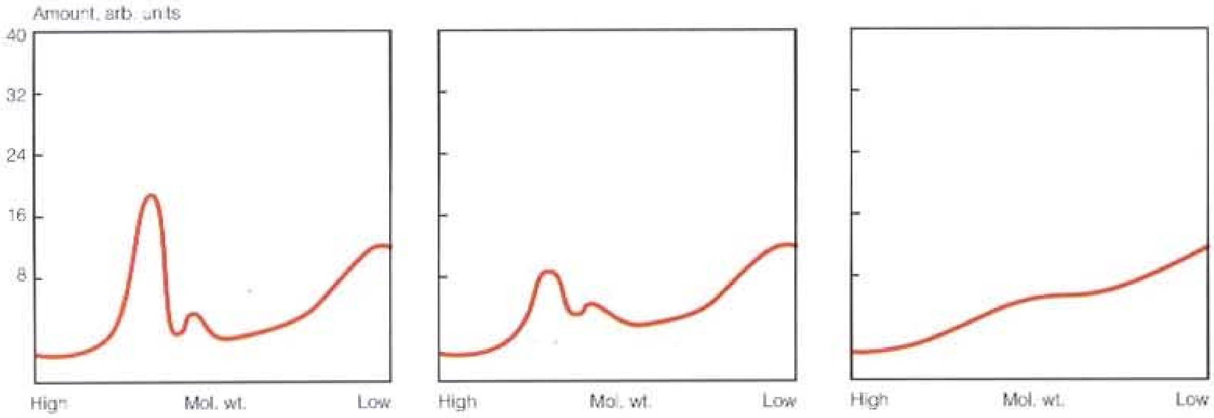
It would appear that even as oxidative degradation of the binder is taking place, the polymer fragments released may reunite or react with species in the bitumen developing a network which includes the more reactive asphaltenes. Such a recombination mechanism would explain both the better than expected properties of the degraded binder and the improved compatibility of the TR/bitumen blends.

7.2.3.3.10 Influence of filler

Fillers are often added to bitumen/TR blends where they result in some reduction in elongation, increase in permanent set and improvement in penetration. This is illustrated in table 7.23(20). However, all fillers do not behave the same, as shown by table 7.24(20). The reasons are not clear but it is known that some fillers promote polymer degradation more readily than others and those fillers which contain heavy metal complexes should be avoided. Whatever the reason, choice of fillers is important for the performance of materials in service.



Figures 7.31 to 7.34 — Properties of bitumen vs storage time in the RTFOT



Fresh

After 24 h storage

After 72 h storage

Figures 7.35 — GPC chromatograms showing polymer degradation during ageing in the RTFOT

7.2.4 Active chemicals

7.2.4.1 Adhesion agents

Adhesion or wetting agents can generally be classified into two categories: passive or active. Passive wetting agents improve the adhesion characteristics of bitumen and provide a long-term resistance to detachment caused by water attack. Active agents modify the surface tension of the binder and allow preferential wetting in the presence of water. Their effectiveness is short term and they are not generally heat-stable. Most adhesion agents contain highly polar groups such as amines and amides. Their major use is in binders for surface dressing of roads where they are incorporated at a level of 0.1 - 0.5 per cent but they are also used in adhesives and self adhesive membranes.

Wetting by the binder is opposed by viscous forces. The time t, taken to wet a given surface whose dimensions constitute a constant, Z, is given by:

$$t = \frac{ZV}{S \text{ Cos } A}$$

where V = binder viscosity

S = binder surface tension

A = contact angle of the binder to the surface.

Thus, if A is less than 90 degrees, the time to wet the surface will be finite and spontaneous spreading can occur but if A is 90 degrees or greater the time will be infinite. The effect of

Property		No filler	10 % limestone filler
Penetration at 25°C	dmm	77	60
Softening point, (R & B)	°C	100	102
Viscosity at 180°C,	mPa.S	1200	1800
DIN Flow temperature, pass	°C	80	80
DIN Cold bend temperature, pass,	°C	-25	-25
Elongation at break	%	2300	2000
Permanent set	%	8	15

Table 7.23 — Influence of filler on a bitumen/TR blend(20)

Filler	Softening point °C	Penetration at 25°C dmm	Flow temp, pass °C		Max. stress 10^5 N/m		Elongation at break, %	
			Initial	3 month	Initial	3 month	Initial	3 month
Talc	108	44	0	90	16.6	6.5	1700	860
Chalk	106	52.5	85	80	17.5	5.4	1740	1350
Limestone	109	50.5	0	90	18.9	5,6	1600	1120
Slate dust	109	47	85	80	18.8	ductile	1600	850
Fly-ash	105	49	5	80	16.7	ductile	1600	620

3 Months at 70°C, 14% Cariflex TR1101/86% 200 pen bitumen, 30% filler

Table 7.24 — Effect of ageing on filled bitumen/TR compositions(20)

using a primer can also be explained by this relationship. The primer has lower contact angle, high surface tension and lower viscosity. Once 'cured' or dry, subsequent application of bitumen has a contact angle of virtually zero (bitumen contact to itself) and hence time is much reduced and adhesion improved.

7.2.4.2 Silicone oil

Silicone oil is sometimes added to hot bitumen where there is a danger of frothing caused by the presence of water, eg where bitumen is put into a tank which has been out of service or which may have previously contained an emulsion. The oil works by simply breaking down any bubbles formed at the bitumen surface and so prevents the tank from frothing over. Usually a few millilitres of virtually any grade will suffice to treat a full tank. A solution of the oil in kerosene helps to disperse it rapidly in the bitumen.

7.2.4.3 Curing agents

There has been much interest in the past in the chemical modifier 'Chemcrete' for use in road mixes. The additive, an organometallic compound of manganese, also containing other metals, is added to the bitumen during mixing. After paving the additive reacts with the bitumen and oxygen causing it to harden over a period of months. It was intended to improve workability of the asphalt by allowing the use of a softer than normal grade of bitumen. This would allow improved compaction of the asphalt in cold weather or with stiff mixes. The major disadvantage of this additive is that it is not easy to control the rate of 'cure'.

7.3 References

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Chapter 8 - Bitumens used in the building industry

8.1 Roofing applications

8.1.1 Market situation

There are three main types of bituminous roofing in common usage around the world. These are:

- mastic asphalt
- built up roofing (BUR)
- liquid based roofing.

Country	Roofing felt installed 10^6 m^2	Bitumen %	Bitumen/SBS %	Bitumen/APP %
France	24.5	17.5	74.7	7.7
Switzerland	3.5	22.8	45.7	31.4
Germany	35.4	27.7	46.9	25.4
Belgium	11.5	14.8	17.4	67.8
Italy	35.8	10.3	26.8	62.8
UK	18.5	17.8	65.9	16.2
Spain	14.4	9.7	18.0	72.2
Netherlands	16.4	10.4	22.6	67.1
Sweden	6.7	70.0	—	29.9
Austria	3.3	36.4	51.5	12.1
Total	170	24.0	37.0	39.0

Total roofing felt production about 606 million m^2
Total area of roofing felt installed > 170 million m^2

Table 8.1 — European roofing market 1989

Built up roofing is commonly found in the USA, Canada and Europe, while liquid systems predominate in the Far East and Asia. Both mastic asphalt and liquid bitumen systems are losing ground to built up roofing systems which can be applied more quickly and effectively.

Type of coating	% of market
Bitumen	41
EPDM	26
Bitumen APP	10
Bitumen SBS	5
Liquid systems	9
Others	9

Total roofing felt production about 12.7 million m^2

Table 8.2 — USA roofing market 1988

Accurate published statistics on roofing systems are difficult to find but the data in table 8.1 and 8.2 show clearly the size of the industry in Europe and the USA and the extent to which conventional bitumens are being displaced by high performance modified bitumens.

The trend in all areas of the roofing industry is for high performance materials to substitute for bitumen. BUR is commonly modified with either Thermoplastic Rubber (TR) or Atactic Polypropylene (APP), while liquid bituminous roofing systems may be modified using TR or natural rubber. Mastic asphalt has benefited by TR in Germany for many years for bridge deck waterproofing, whilst in the UK these materials are finding increasing use in buildings due to their greater flexibility.

8.1.2 Mastic asphalt

Although mastic asphalt is used for roofing, flooring and tanking, it is discussed for convenience here under a single subject heading. The traditional uses of mastic asphalt are for flooring, roofing, tanking and as a damp-proof course.

The use of mastic asphalt for roofing is common in the UK, particularly in older buildings and can be found extensively in France, particularly on footways and pedestrian areas. In Germany a particular type of mastic asphalt called Gussasphalt is used extensively as an impermeable surface for bridge decks.

Mastic asphalt is one of the oldest known building materials containing bitumen. Naturally occurring bitumen from the many seepages in the oil-rich Middle East region has been used as a water-proofing medium for over five thousand years. Rock asphalt, which usually contains less than twenty per cent of bitumen, was melted down to extract the binder. In this process large mineral particles would settle out and leave the finer particles in suspension. Hence mastic asphalt was born. Many examples of early work, particularly where it was used for brickwork mortar, embankment waterproofing and wells, etc., remain intact today as a testament to the excellent durability of mastic asphalt. One good example is the embankment at Assur on the Tigris built by King Adad Nirari I over three thousand years ago.

Mastic asphalt is a mixture of fine aggregate, filler and a bituminous binder which can be petroleum bitumen, lake asphalt, asphaltite or blends of these with each other or with flux oils. The fine aggregate may comprise crushed rock and the filler may be finely graded material such as limestone or slate dust. It is laid hot and, unlike other types of asphalt, does not require compaction after laying. For large flat areas it can be laid by machine but for most work it is laid by hand with a wooden trowel. It can be laid on flat, curved, horizontal or vertical surfaces, on wood, insulation board, brick and concrete. Mastic asphalt is binder rich and is, consequently, impermeable to water.

Flooring mastic is finished to a smooth surface by a sanding machine when it is almost cool. Conventional mastic itself cannot easily be pigmented but can be finished to virtually any desired colour using an epoxy paint which is applied after laying is complete. Mastic asphalt manufactured from the clear binder Mexphalte C can be produced in a great variety of colours and is commonly used in France.

8.1.2.1 Specifications

Many standards exist for mastic asphalt but for convenience only the British Standard will be discussed here.

British Standards exist for mastic asphalt for use in roads and pathways and for use in buildings. There are two standards covering mastic for buildings:

- BS 6925 : 1988 Specification for mastic asphalt for building and civil engineering (limestone aggregate), and,
- BS 6577 : 1985 Specification for mastic asphalt for building (natural rock asphalt aggregate)

Since the two standards are very similar and because there is little or no mastic produced using natural rock aggregate this latter standard is not discussed here.

There are four types of mastic asphalt classified as follows:

- R 988 for roofing
- F1076 for flooring
- T1097 for tanking and damp-proof courses
- F1451 for coloured flooring

The flooring mastics are further sub-divided according to usage:

- Grade I : special hard flooring
- Grade II : light duty flooring
- Grade III : medium duty flooring
- Grade IV : heavy duty flooring

The binder for mastic asphalt is termed asphaltic cement (or sometimes AC) as it can be based on either bitumen, type B, or a mixture of bitumen and lake asphalt, type T. The binder requirements for the various grades of mastic are shown in tables 8.3 and 8.4 and the aggregate gradings and compositions in tables 8.5, 8.6, and 8.7.

The bitumen binder requirement for roofing and tanking grades of mastic asphalt may not easily be satisfied by bitumen grades produced to normal bitumen specifications, such as BS 3690. Many manufacturers prefer to blend their own binders from a combination of a penetration grade of bitumen such as Mexphalte 50 pen and a hard grade such as Mexphalte H80/90. This also allows direct use of Mexphalte H80/90 in grades II, III and IV flooring mastics.

8.1.2.2 Requirements

Mastic asphalt, or mastic as it is known in the industry, is a type of asphalt composed of suitably graded mineral matter and bitumen in such proportions that it forms a cohesive, voidless, impermeable mass, solid or semi-solid under normal temperature conditions, but is

Property	Test method	Type of asphaltic cement		
	BS 2000	B (bitumen)	T25 (25±5% rla**)	T50 (R988 only) (50±5% rla**)
Penetration at 25°C, dmm	Part 49	40±10	40±10	40±10
Softening point (R & B) °C	Part 58	60±10	60±10	60±10
Loss on heating for 5 h at 163°C % by mass max	Part 45	2.0	2.0	2.0
Solubility in trichloroethylene % by mass min max	Part 47	95* 99	86 91	75 79
Ash (mineral matter) % by mass min max	Part 223	— 4.0	7.5 11.0	16.5 20.0

* This allows for the presence of any small residual amout of Trinidad Lake Asphalt in the tank.

** Refined lake asphalt

Table 8.3 — BS6925 : 1988 Properties of asphaltic cement for types R988 and T1097 mastic

Property	Test method BS 2000	F1076 F1451,I	F1076 F1451, I & II		F1076 F1451, IV	
		Bitumen + rla* (15±5% rla*)	B (bitumen)	T25 (25±5% rla*)	B (bitumen)	T25 (25±5% rla*)
Penetration at 25°C, dmm	Part 49	—	8±4	8±4	10±5	10±5
Penetration at 35°C, dmm	Part 49	10±5	—	—	—	—
Softening point,°C max	Part 58	105	100	100	100	100
Loss on heating for 5 h at 163°C % by mass max	Part 45	2.0	2.0	2.0	2.0	2.0
Solubility in trichloroethylene % by mass min max	Part 47	60 —	95 99	86 91	95 99	86 91
Ash (mineral matter) % by mass min max	Part 223	— 30	— 4	7.5 11	— 4	7.5 11

* Refined lake asphalt

Table 8.4 — BS6925 : 1988 Properties of asphaltic cement for types F1076 and F1451 mastic

Grading/composition	% by mass of mastic asphalt			
	R988		T1097	
	min	max	min	max
Retained on 3.35mm mesh	0	3.0	0	2.0
Passing 3.35mm mesh and retained on 600 μm mesh	12.0	23.0	4.0	17.0
Passing 600 μm mesh and retained on 212 μm mesh	8.0	22.0	8.0	26.0
Passing 212 μm mesh and retained on 75 μm mesh	8.0	22.0	8.0	26.0
Passing 75 μm mesh	35.0	45.0	38.0	50.0
Soluble bitumen	11.0	13.5	12.0	15.0

Table 8.5 — BS6925 : 1988 Composition of R988 (roofing) and T1097 (tanking) mastic

Grading/composition	% by mass of mastic asphalt	
	min	max
Passing 600 μm mesh and retained on 212 μm mesh	8.0	32.0
Passing 212 μm mesh and retained on 75 μm mesh	8.0	25.0
Passing 75 μm mesh	40.0	56.0
Soluble bitumen	12.0	18.0*

* If the fine aggregate is Irish or Scottish limestone, a maximum soluble bitumen content of 19% shall be permitted

Table 8.6 — BS6925 : 1988 Composition of F1076 and F1451 (flooring) mastics excluding coarse aggregate

Grading	% by mass	
	min	max
Retained on 2.36 mm mesh	—	3.0
Passing 2.36 mm mesh and retained on 600 μm mesh	5	25
Passing 600 μm mesh and retained on 212 μm mesh	10	30
Passing 212 μm mesh and retained on 75 μm mesh	10	30
Passing 75 μm mesh	45	55

Table 8.7a — Fine aggregate grading

Grading	% by mass	
	min	max
Passing 5.0 mm mesh	100	—
Passing 5.0 mm mesh and retained on 3.35 mm mesh	0	15
Passing 3.35 mm mesh and retained on 600 μm mesh	70	100
Passing 600 μm mesh	0	15
If coarse aggregate is incorporated, the quantity added shall be such that the mass of the combined coarse and fine aggregate retained on a 600 μm sieve, expressed as a percentage by mass of mastic asphalt on analysis, shall comply with the limilts given in table 8.3 of BS 6925		

Table 8.7b — Coarse aggregate grading for roofing and tanking mastic

Grade	Grading of added coarse aggregate		Coarse aggregate content
		% by mass	retained on 600 μm mesh % by mass of the total mix
I and II	Passing 5.0 mm mesh Retained on 600 μm mesh	100 85 min	15-25
III	Passing 5.0 mm mesh Retained on 600 μm mesh	100 85 min	25-35
IV	Passing 10 mm mesh Passing 6.3 mm mesh Retained on 600 μm mesh	100 85 min 98 min	30-50

Table 8.7c — Coarse aggregate grading for flooring mastic

sufficiently fluid when brought to application temperature to be spread by means of a hand float, without the need for compaction.

Mastic asphalts generally have the following typical characteristics:

- a high binder content, typically ten to eighteen per cent by mass,
- a fine aggregate with 50 per cent passing 75 μm and a maximum stone size of two millimetres,
- low penetration binder to ensure resistance to deformation at service temperatures (the mineral content of the mix makes virtually no contribution to deformation resistance).

In the UK, the most commonly used filler is limestone and the normal binder is 50 pen bitumen although 35 pen bitumen may also be used. Where high resistance to indentation is required (mainly in flooring applications) coarse aggregate is added, amounting to between 15 and 45 per cent depending on the floor thickness. The formulation is a balance between application temperature, workability and indentation resistance.

8.1.2.3 Manufacture

Mastic asphalt comprises a mixture of materials which include:

- asphaltic cement which comprises either bitumen or lake asphalt or blends of these two,
- fine aggregate: normally limestone filler which is crushed to less than 75 μm,
- coarse aggregate: usually crushed stone (eg granite or limestone) or naturally occurring siliceous material (eg grit).

Mastic grade		Hardness number	
		At manufacture	At laying
R988		45-90 @ 25°C	> 30 @ 25°C
T1097		55-120 @ 25°C	> 40 @ 25°C
F1076 and F1451	Type 1	< 15 @ 45°C	2-12 @ 45°C
	Type II & III	< 12 @ 35°C	2-12 @ 35°C
	Type IV*	< 40 @ 35°C	By agreement

* Before addition of coarse aggregate

Table 8.8 — Hardness number requirement for mastic asphalt

The mastic is manufactured by mixing the aggregate, filler and bitumen in a special mastic digester at about 170 - 230°C for around five hours. This period of digestion is needed because of the high fines content which produces a very viscous mix. The mixer blades resemble the action of a paddle steamer and turn over slowly at about twenty revolutions per minute. After digestion the mastic can be transported hot to site in special transporters equipped with heating and stirring facilities, or can be cast into blocks in wooden or steel moulds. The moulds may be square or round and require to be coated with limestone filler, talc or soap prior to filling to aid release from the mould after cooling. When coarse aggregate is to be included in the mastic asphalt formulation, it is usually added on site during remelting.

Application	Grade			
	I	II	III	IV
Recommended thickness, mm	15-20	15-20	20-30	30-50
Underlays for other floor coverings	X	X		
Hospital wards	X			
Hospital corridors (according to traffic)		X	X	
Schools	X			
Shops (floors to take moveable racks)	X			
Shops (floors to take fixed racks)		X		
Offices	X			
Factory floors : light		X		
Factory floors : medium			X	
Factory floors : heavy				X
Loading sheds				X
Breweries				X
Railway platforms (covered)				X
Domestic floors (either as a finished floor or an underlay)	X	X		
Floors or passageways subject to heavy foot traffic			X	

Table 8.9 — Recommended grades of mastic for various applications

8.1.2.4 *Workability*

Workability is a very important property of any materials which are hand-laid. Mastic asphalt with poor workability will lead to a reduced work rate as the laying gang take longer to achieve the required finish. Workability cannot be measured directly but can be assessed only by the operative laying the mix and is, therefore, extremely subjective. Workability increases with increasing bitumen content and increasing binder penetration. Workability is also believed to be dependent on the extent to which the binder 'peptises' the filler, ie keeps it dispersed. Bitumens with high acid content (acid value) are said to have good peptising properties and give mastics with good workability characteristics.

Low acid number bitumens are reputed to give mastics with poorer workability (but satisfactory in all other respects) although the reasons for this are not known. Low acid number bitumens can be acid 'doped' to improve their peptising power but the workability of the mastic produced is always said to be inferior to bitumens with naturally high acid content.

8.1.2.5 *Indentation or hardness number*

The hardness number test is used in quality control for measuring the consistency of freshly manufactured mastic asphalt. The definition[1] of hardness number given by the Mastic Asphalt Producers Association of the UK is as follows:

> The hardness number is the figure denoting the depth in tenths of a millimetre to which a flat ended indentor pin in the form of a steel rod 6.35 mm in diameter will indent the mastic asphalt under a load of 311 N, applied for 60 seconds at the specified temperature. This force is equivalent to an applied stress of 9.8 N/mm^2. The standard test temperatures are maintained as follows:

Mastic asphalt for roofing and tanking	25°C
Mastic asphalt flooring	35/45°C.

Indentation or hardness number is of primary importance in flooring applications and is often specified in contracts. Typical values for hardness numbers of mastic asphalt are given in table 8.8. Its value can be reduced by lowering the binder content or by using harder bitumen but this has direct consequences on workability. The usual way to harden the mastic asphalt is to use a more angular rock.

It is well known that bitumens increase their resistance to deformation on storage at room temperature due to a slow stabilisation of the structure in the bitumen[2,3,4,5]. It has been shown that mastic asphalt also hardens with time resulting in a reduction of about 40 per cent in hardness number over a period of one year followed by a further reduction of about 20 per cent after another year, see figure 5.4. A mastic asphalt with a hardness number of 30 at the time of laying would therefore harden to give a value of about 20 after the first year and eventually reduce to about 10-15.

Mastic asphalt samples taken from roofs which have performed perfectly satisfactorily for over forty years[1] support the above observations. This serves to illustrate that the test is meaningless as a measure of the physical properties of mastic asphalt and gives no indication of the potential performance and durability of the mastic asphalt.

8.1.2.6 Problems associated with mastic asphalt

- Tearing under the trowel is usually a sign that more peptising acids are required or that the temperature or binder content is low.

- Mastic is often applied at temperatures far in excess of those considered safe for bitumen and kettle fires are not uncommon. It cannot be emphasised too strongly that overheating or fiercely heating bitumen will cause a degradation in its properties and may, in extreme cases, make the mastic unsuitable for use. Reheating must be slow and gentle and bitumen should not be heated above 230°C. It is recommended that workers should not be exposed to fumes produced at these very high temperatures.

- Mastic floors may be made resistant to many chemicals by using suitable aggregates and filler. Table 8.10 shows some of the chemicals to which mastic is resistant.

Inorganic acids		20°C	40°C
Oleum		X	X
Sulphuric acid	95%	X	X
Sulphuric acid	4%	✓✓✓	✓✓✓
Hydrochloric acid	35%	✓✓✓	✓✓
Hydrochloric acid	4%	✓✓✓	✓✓✓
Nitric acid	65%	X	X
Nitric acid	4%	✓✓✓	✓✓✓
Phosphoric acid conc		✓✓	✓
Phosphoric acid	25%	✓✓✓	✓✓✓
Organic acids			
Formic acid	40%	✓✓✓	✓✓✓
Acetic acid	95%	✓✓✓	✓✓
Acetic acid	5%	✓✓✓	✓✓✓
Butyric acid		X	X
Oleic acid		X	X
Oxalic acid		✓✓✓	✓✓✓
Citric acid		✓✓✓	✓✓✓
Lactic acid		✓✓	X
Benzoic acid		✓✓✓	✓✓✓
Phthalic acid		✓✓✓	✓✓✓
Phenols		X	X
Solvents			
Methyl alcohol		X	X
Ethyl alcohol		✓✓✓	✓✓✓
Methylated spirit		✓✓	✓✓

Inorganic alkalis		20°C	40°C
Caustic soda		✓✓✓	✓✓✓
Ammonium hydroxide		✓✓✓	✓✓✓
Soap solution		✓✓✓	✓✓✓
Industrial detergent		✓✓✓	✓✓
Organic alkalis			
Triethanolamine		✓✓✓	✓✓✓
Aniline		X	X
Pyridine and homologues		X	X
Salts			
Common salt		✓✓✓	✓✓✓
Sea water		✓✓✓	✓✓✓
Ammonium chloride		✓✓✓	✓✓✓
Sodium sulphate		✓✓✓	✓✓✓
Ammonium sulphate		✓✓✓	✓✓✓
Sodium nitrate		✓✓✓	✓✓✓
Calcium nitrate		✓✓✓	✓✓✓
Calcium ammonium nitrate		✓✓✓	✓✓✓
'Superphosphate'		✓✓✓	✓✓✓
Sodium cyanide		✓✓✓	✓✓✓
Sodium carbonate		✓✓✓	✓✓✓
Miscellaneous			
Hydrogen peroxide	30%	✓✓	X
Formalin		✓✓✓	✓✓✓
Glycol		✓✓✓	✓✓✓
Glycerine		✓✓✓	✓✓✓

X	— not suitable	✓✓	— moderate resistance
✓	— poor resistance	✓✓✓	— good resistance

Table 8.10 — Resistance of mastic asphalt floors made with fillers resistant to attack by acids and chemicals

8.1.2.7 Application of mastic asphalt[6]

Black sheathing felt is normally used, laid loose, under horizontal applications of mastic asphalt roofing. When keying to vertical or sloping timber surfaces, bitumen coated plain expanded metal lathing is used over a layer of sheathing felt. For vertical or sloping concrete surfaces which are very smooth, surface treatment is necessary to provide a satisfactory key for the mastic asphalt. One of the following treatments may be adopted:

- removal of laitance by wire brushing,
- application of proprietary sand cement plastic emulsion in accordance with the manufacturer's recommendations,
- a light application of a bitumen/rubber emulsion composition,
- fixing of expanded metal lathing.

Mastic asphalt cannot be applied directly to lightweight concrete, which should be rendered with a suitable sand cement facing, treated with a proprietary sand cement plastic emulsion or have expanded metal lathing fixed at suitable intervals.

Mastic asphalt is commonly supplied to site in the form of precast blocks which must be remelted before use. Remelting is undertaken in a suitable bitumen boiler fitted with a stirrer. During remelting it is recommended that the temperature of the mastic asphalt does not exceed 230°C to avoid excessive thermal degradation of the bitumen binder. Buckets used to carry the mastic asphalt should be lined with fine inert dust. Ashes or oil should not be used.

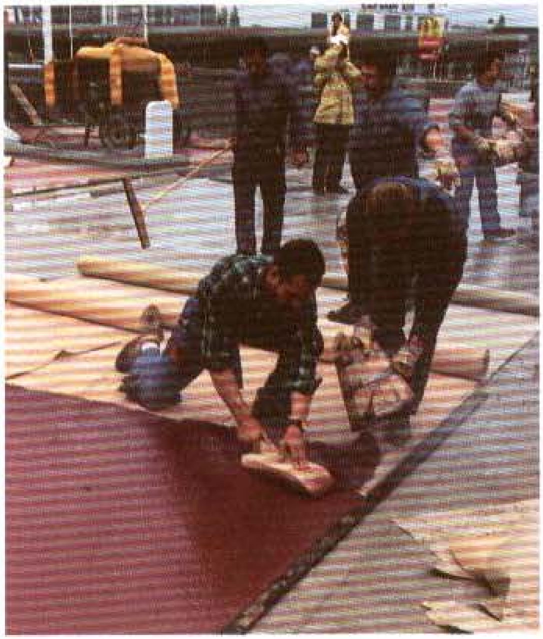
During laying each coat of mastic should be applied as evenly as possible using a hand float and undue delays between coats should be avoided to obviate contamination. Any bubbles (commonly called blows) should be pierced and made good whilst the mastic is still warm. The final coat should be rubbed with coarse sharp sand using a wooden float to present a smooth even appearance.

It is recommended[7] that in situations where mastic asphalt is exposed to solar radiation, and is not protected by an inverted roof covering, a solar protective coating should be applied.

This may take the form of either:

- solar reflective chippings nine to fourteen millimetres in size bedded in a suitable compound, or
- large chippings exceeding fifteen millimetres in size (depending upon site conditions), loose laid, but secured around rainwater outlets, or
- a suitable white solar reflective paint.

The application of loose laid solar reflective chippings has the added advantage of easy removal for maintenance and inspection and affords some protection to the mastic against the effects of thermal shock. All vertical exposed surfaces should be protected by an application of white solar reflective paint.



Photograph 8.1

Photograph 8.2

Photograph 8.1 — Application of coloured mastic asphalt in France (note use of Kraft paper as interlayer and the use of wooden buckets and floats)

Photograph 8.2 — Mastic asphalt on garage forecourt (note special stirred mastic asphalt transporter)

8.1.2.8 Mastic asphalt properties(6)

8.1.2.8.1 Mass

The mass of mastic asphalt is dependent upon a number of factors such as the proportions of the different constituents utilised in its manufacture and the nature and quantity of coarse aggregate incorporated. For the purpose of load calculations, however, the mass of mastic asphalt can be taken to be 2.4 kg/m^2 per mm of thickness.

8.1.2.8.2 Compressive strength

When mastic asphalt is fully confined it has the same compressive strength as the containing material. When unconfined its compressive strength is dependent upon a number of factors including the in-service temperature to which it may be exposed.

8.1.2.8.3 Vapour properties

The vapour resistivity of mastic asphalt is very high and is normally assumed to be not less than 100,000 MN s/g m.

The vapour diffusion resistance factor (μ), the ratio of the vapour resistivity of the material to that of still air, is usually taken to be a factor of 20,000 for condensation control calculations.

8.1.2.8.4 Thermal properties

- Thermal conductivity:

  Mastic asphalt has a thermal conductivity value (k) of between 0.43 and 1.15 W/m°C and consequently provides little contribution to the overall thermal insulation of a roof structure. For design purposes it is normal to assume a k value of 0.50 W/m°C.

- Thermal expansion:

  The thermoplastic nature of mastic asphalt means that it is capable of accommodating the normal movement encountered in a well-designed building structure.

- Coefficient of cubic expansion:

  Mastic asphalt has a coefficient of cubic expansion of 15 x 10^{-5}/°C.

8.1.3 Felt roofing

8.1.3.1 British Standard specifications

In the UK the only national or industry standard for roofing felts is British Standard BS 747 which was first issued in 1937 and last updated in 1994, although it is recognised that the forthcoming European specification will replace it. The standard specifies minimum weights per unit area of carrier and bitumen and for the first time includes performance requirements for the finished felt (eg break strength, rupture, low temperature flexibility and shrinkage). Class 2 felt (asbestos based) has been deleted from the standard. There are four types of felt specified largely by the type of carrier used:

- Class 1 - fibre based
- Class 3 - glass fibre based
- Class 4 - sheathing and hair felts
- Class 5 - polyester with oxidised bitumen coating.

For Class 1 felts the saturant grade is a penetration grade bitumen within the range 60 - 230 dmm which equates to bitumen grades from BS 3690 of 70, 100 or 200 pen. 200 pen grade is frequently used. Class 5 felts use a saturant grade with a penetration within the range 20 - 120 dmm which allows a choice of a hard penetration grade or, more likely, an oxidised grade such as 95/25. Saturant grades are not used in Class 3 & 4 felts. A coating grade is specified for Class 1, 3 & 5 felts with a softening point in the range 80 - 120°C which allows a number of grades from BS 3690 : Part 2 including R85/25, R95/40, R95/25, R105/35 and R115/15 and hard bitumens H80/90 and H100/120.

Whilst H80/90 and H100/120 are allowed according to the standard, it should be noted that their higher viscosities would make it very difficult to achieve adequate coating and their low penetrations would make them too brittle in service. Also, the standard allows for the inclusion of up to 40 per cent mineral filler which, if added, would exclude R115/15 as the specification refers to the coating grade (ie bitumen plus any filler). A summary of the standard is given in table 8.11.

Class	Mass per unit area by analysis			Mass per unit area	Type of felt	Typical use
	Base g/m^2	Bitumen, g/m^2	Surfacing, g/m^2			
1F	9	59	23	15	Hessian reinforced	Underslating
1F	140	550	250	13	Aluminium faced	Underslating
3B	55	780	4550	18	Fine granule surface	BUR base layer
3E	55	690	1350	28	Mineral surfaced	BUR top layer*
3G	55	690	1350+	26	Venting base	BUR base layer*
4A				17	Sheathing felt	Underlayer for mastic asphalt
4A				41	Sheathing felt	Underlayer for mastic asphalt
5B	330	2200	450	42	Fine granule surface	BUR top layer*
5E	330	2200	100+	47	Mineral surfaced	BUR capsheet
5U	118	700	450	18	Fine granule surface	BUR underlayer

* Top layer felts require protection from atmospheric degradation; + plus 250 sand

Table 8.11 — Summary of British Standard 747, Specification for roofing felts

Class 4 felts are sheathing felts and are specified only loosely. The fibre types can be either:

- sheathing felts: flax, jute and/or other suitable fibres, or
- hair felts: cow hair and/or other suitable animal hair.

The coating material can be either bitumen or wood-based tars and pitches. No limits are given for binder penetration or softening point. Although manufactured in different sized rolls to other roofing felts, the nominal roll weights vary from eight to twenty kilograms for a roll twenty square metres in area. The standard does not specify minimum weights for fibre or coating material.

8.1.3.2 General

Roofing felt comprises a sheet of matted fibre, generally called the carrier, which is rendered partially or completely impervious to water by treatment with bitumen, which is known as the coating. According to the type of roofing felt which is being produced, the carrier may comprise one of a number of different types of fibrous materials and fabrics including:

● vegetable fibres	eg cotton, jute, flax, wood pulp,
● animal fibres	eg hair or wool,
● mineral fibres	eg glass fibre,
● synthetic fibre fabrics	eg polyester,
● combinations of these materials.	

Depending upon the nature of the carrier and its weight, it may be treated with a saturant bitumen (usually a penetration grade) and a coating bitumen (normally an oxidised grade). The finished thickness of the roofing felt is governed by the density of the carrier and the thickness of the applied coating both of which are determined by the end use application of the felt. When the carrier has been coated its two surfaces may be lightly coated with sand (or similar) to prevent sticking when the felt is rolled. Sometimes, a polymer film is added to one side of the felt while the other is sanded or coated with a decorative aggregate.

Roofing felts can be laid on most types of buildings giving the most versatile type of weatherproofing. The inherent flexibility of the felt makes it possible to weatherproof all types of roof whether horizontal, sloping or curved. Roofing felts are rarely, if ever, applied as a single layer to buildings of any consequence but are usually laid as several layers bonded by bitumen adhesive. This technique has given rise to the term built-up roofing (BUR).

Felt roofing is suitable for application onto many types of substrate including wood, concrete, chipboard and plywood, asbestos board and metal. It is common practice today to incorporate an insulation layer in the roof construction. Such layers can also be included in the BUR system. Some of the commonest insulation materials used are rigid polymer foams such as polyurethane (PUR), expanded polystyrene, mineral fibre, cork slabs and aerated concrete.

Photograph 8.3 — Manchester Airport terminal building with built-up roofing (reproduced by kind permission of D Anderson & Son Ltd)

Bituminous BUR systems have advantages for traditional buildings of:

- low cost,
- long service life,
- minimal maintenance,
- versatility.

8.1.3.3 Early development

The felt roofing industry started in the early nineteenth century when it was used to waterproof timber 'barrel' roofs of large buildings and houses, in place of lead sheeting, and on railway carriage roofs before the advent of aluminium. Felt sheets were not used, but rather the waterproof membrane was made in-situ by applying alternate layers of tar or pitch and hessian. By today's standards the finished membranes would be considered to be very thick but many have survived intact for over a century.

In about 1870 Callenders of Erith began importing Trinidad Lake Asphalt (TLA) and used it in preference to tar. It was 'refined' to reduce the filler content by settling in hot storage tanks. Later, TLA was refined prior to shipment and was used right up until the 1970s. The first true roofing felts were made in the late 1800s by hand. Large sheets of hessian were dipped into a vat of molten TLA and drawn out over a roller. The completeness of the coating was judged by the operator and the thickness of the coating controlled by the rate of withdrawal from the vat. The sheets, 6 feet (2 metres) wide by 18 feet (6 metres) long, were immediately cooled either by immersion in water or by drawing over a wet sand bed. The whole process was manual but consistently high quality sheets were produced this way up until about 1970. The sheets were mainly used for roofing but also for tanking and damp courses. One of the best known tanking applications is the Tower Bridge in London where the hydraulic machine room was waterproofed with bitumen felt in 1880. For damp courses the large roofing sheets were cut into strips by hand using heavy scissors. Bitumen damp courses made this way were in common usage in 1890.

Whilst TLA was commonly used, bitumen could also be used and was obtained from naturally occurring deposits in Europe, eg Limmer in Germany, Neuchatel in Switzerland, and several other sources. These materials were routinely fluxed with oil to produce softer grades. When the industry was in its infancy, bitumen was supplied solid in blocks or bags, a practice which continued right into the 1980s.

8.1.3.4 Built up roof construction

The waterproof membrane is rarely a single layer but usually a multi-layer system. One or more layers of sand-finished felt are bonded with an oxidised grade such as R85/25. Traditionally this is applied hot and is poured from a bucket immediately in front of the felt as it is unrolled. The final layer is usually a mineral-surfaced felt. The whole roof can then be left as it is or (if flat) can be covered in a layer of stone chippings to protect the felt from the effects of heat and UV light. The chippings are applied in a layer typically 25 mm deep and are usually bonded to the felt with a soft bitumen which is applied as a cutback or sometimes as emulsion.

The application rate of mopping adhesive used to glue the roofing felt to the substrate is normally 1 - 1.5 kg m^{-2} but can be higher. The weight of a roofing felt can be as high as 1.5 kg /m^2 and may even be as high as 6.0 kg/m^2 for some high performance polymer modified bitumen systems.

Where a polymer modified bitumen roofing felt is used, it is normal practice to use polymer modified felts for all layers of the built up roof. When TR modified bitumen roofing felts are used, felt adhesives utilising the same modified bitumen may also be used for the bonding layers, although few problems have been reported using normal oxidised bitumen. APP modified felts require to be applied by the use of a propane torch and do not normally employ a mopping adhesive.

A schematic diagram of a BUR system is shown in figure 8.1 and various types of roof construction are shown in figure 8.2.

Where chippings are not used and a decorative mineral finish is not required (eg industrial and public buildings and concealed roofs) solar reflective paints can be applied. These are usually based on a white pigment (eg titanium dioxide) or aluminium paste. Applied by brush or roller, they can lower the roof temperature by 20 - 30°C.

It is of interest to contrast roofing practice in the USA with that in Europe. In the USA most houses and many factories are of light construction with a life expectation of considerably less than one hundred years. Most roofs are waterproofed with bitumen felt (or shingles) and it is normal for the roof to be replaced after twenty years or less. Factories are built on a scale which is unknown in Europe with flat roofs covering hectares. These factories are

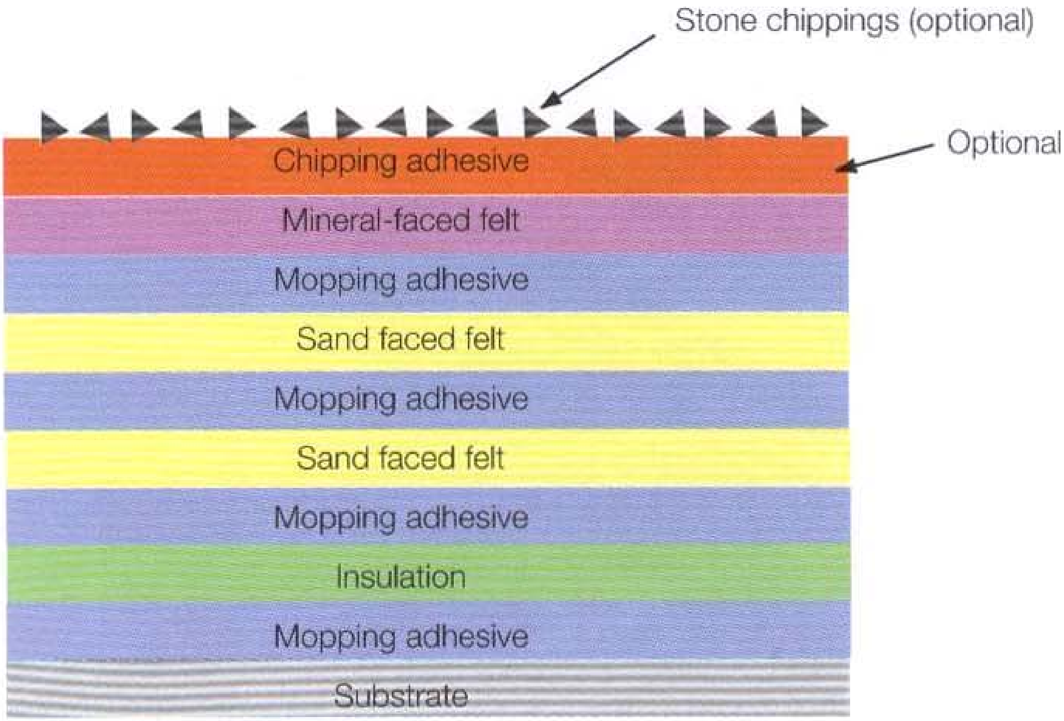


Figure 8.1 — Schematic of a traditional-built up roofing system

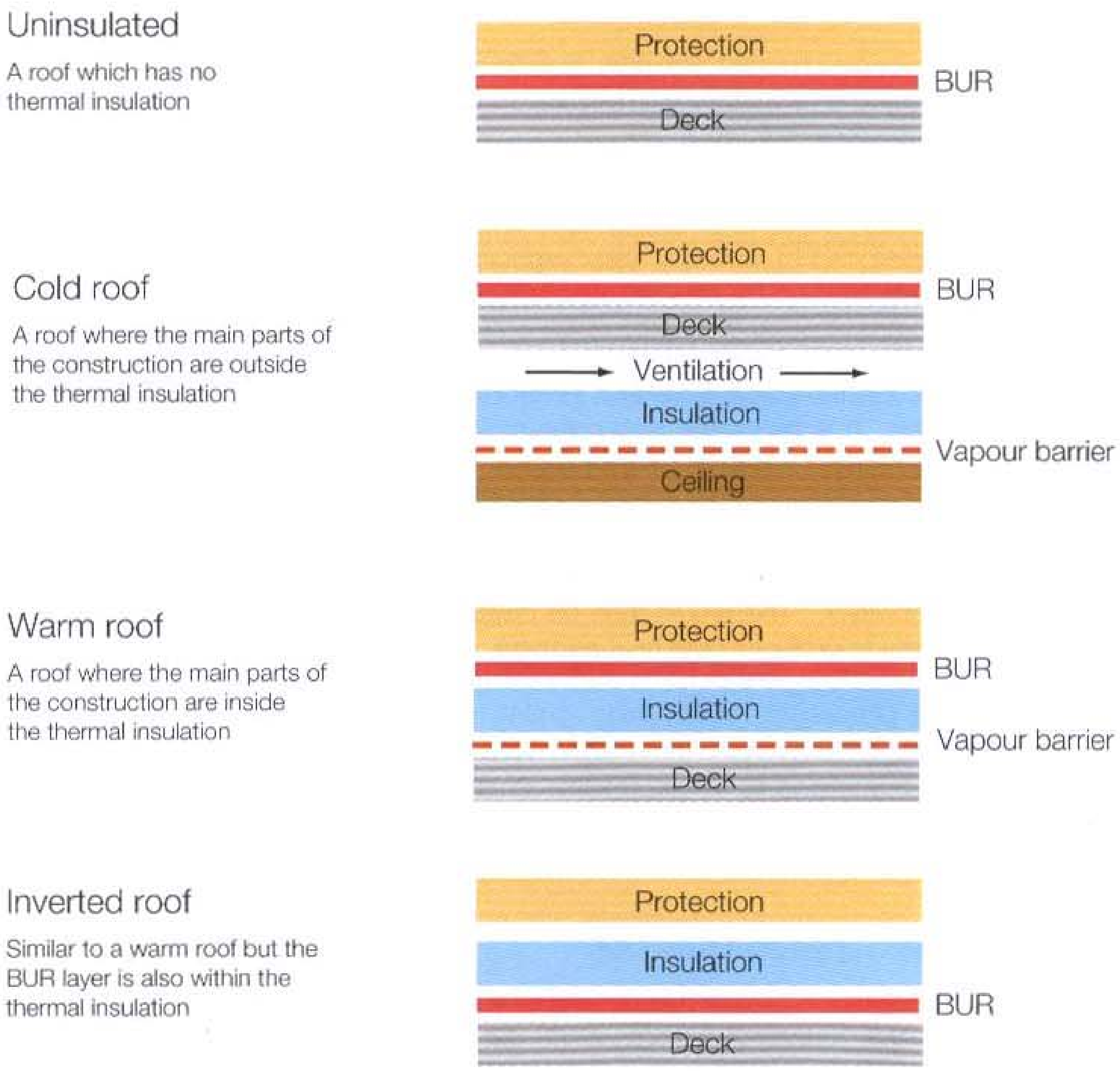


Figure 8.2 — Types of roof construction

refurbished normally after only a short period, typically twenty years or less, at which time they would be completely re-roofed. Normal practice is to machine-lay felt made from 25 pen bitumen and it is commonly put down in five layers. Sand-finished felt covered by a deep layer of ballast is used in preference to mineral finished felt.

In Europe there are millions of properties built over a century ago still in everyday use which have received no major maintenance apart from upgrading (eg plumbing, sanitation and electrical). Consequently, felt roofing is only used on flat roof constructions for lightweight factories and public buildings and in low-cost domestic extensions.

8.1.3.5 Types of roofing felts

Felt roofing is almost always applied in several layers with the different layers performing different functions. Some types of bituminous felt membranes are used in applications other than roofing and their uses are described here for convenience.

8.1.3.5.1 Base layer (sand finished, fine granule surfaced or underlay)

This is the first layer of a built up roof which may be nailed or bonded to the substrate. If nailed to a timber substrate a polyester based underlay (eg BS type 5U, see section 8.1.3.1) would be used and is termed a bonding layer. It is usually sand finished on both sides but could also be manufactured with a venting layer incorporated.

A venting layer is designed to allow any water vapour to flow to the edge of a roof where it is vented to atmosphere thereby preventing blistering. It can be made from a layer of compressed fibres (approx. 0.5 mm thick) which is perforated to allow partial bonding to the substrate. A venting felt can be applied as a layer on its own in which case it is made from a glass carrier and is finished with fine sand on its upper surface and mineral (eg slate) granules on its lower surface. It is perforated with holes throughout its length. It is loose laid and bonded with hot bitumen which is poured on top and bonds through the holes to the substrate to create a partial bonding system allowing any vapour to disperse through the mineral layer.

In applications on flat roofs where a mineral finish is not required a heavy base layer will often be used as the top layer. This would then be covered with stone chippings or insulating board and flagstones to protect it from heat and cold.

8.1.3.5.2 Top layer mineral finished (also called capsheet)

This is the final layer applied to a horizontal or sloping roof where visual appearance and weather resistance are required. The felt is normally coated with a layer of decorative mineral granules but may be metal finished to protect the bitumen from the effects of solar radiation.

8.1.3.5.3 Underslating (also called slaters felt)

As the name implies this felt is used under slates and roof tiles where it is nailed onto the rafters. Its purpose is to protect the roof members in the event of updraughts which can blow rain or snow up beneath the tiles and to prevent draughts in the loft area. It is considered as a last-ditch defensive measure and is not intended to keep weather out for any length of time. In fact underslating felt contains many pinholes which allow vapour out of the loft thereby preventing condensation and as a consequence of this it is not recommended for external use. It is made from a base consisting of animal or vegetable fibres made into a close textured absorbent sheet which is impregnated with bitumen and immediately reinforced with a layer of jute hessian embedded in a filled oxidised coating, surfaced with fine sand to prevent sticking in the roll. The bitumen layer is quite thin leaving the hessian clearly visible. The hessian prevents sag and rupture in the loft space where the felt hangs between rafters. The felt may be faced with a bitumen saturated paper or merely dusted with sand. Sometimes a layer of thermal insulation (eg glass wool) is incorporated into the felt. Such a layer is normally limited to 25 mm thickness because of the need to nail battens through the felt. Underslating felt is used extensively in the UK as a consequence of building regulations where it accounts for nearly a quarter of all roofing felt sales. It is not used elsewhere to any extent.

8.1.3.5.4 Sheathing felt (also called hair felts)

Sheathing felts are used as underlays for mastic asphalt and some metal roof coverings. For mastic asphalt the felt is used to allow movement of the substrate, thereby preventing damage caused by differential expansion, and water vapour beneath the mastic layer. When laid on top of concrete the surface is first 'blinded' with filler or fine sand and felt laid over this. This prevents the mastic sticking to the concrete and creates a venting layer which reduces the likelihood of blistering.

Sheathing felts consist of an open layer of comparatively long fibres which are formed as a loose open batt on a machine. This is immediately impregnated with hot bitumen and compressed between rollers to final thickness. The felt is then 'dusted', 'haired' or 'shined' to prevent sticking on the roll.

Sheathing felts have excellent dimensional stability, that is, they do not buckle or shrink and have good lay flat properties. This is attributable to their loose fibre carrier which does not transmit stress readily.

8.1.3.5.5 Shingles

Shingles are roof tiles made from a thick felt which is cut to shape. They can be supplied on rolls of about 10 metres in length or, more usually, singly measuring approximately 0.9 metres by 0.35 metres. They are nailed onto a wooden substrate having, normally, a minimum fall of 30 degrees and are also glued and/or slotted together. The adhesive used can be either hot or cold applied or may be incorporated into a self adhesive shingle at the time of manufacture. Typical hot applied adhesives would be R105/35 and R85/25 containing up to 50 per cent of filler.

Shingles have a number of advantages over traditional tiles including:

- ease of manufacture
- ease of application and maintenance, as they can be easily trimmed on site, are flexible and are nailed into place
- lightweight, typically 10 kg/m^2 compared to 55 kg/m^2 for roof tiles.

Because flexibility is not required, a hard penetration grade such as Mexphalte 50 or even Mexphalte 35 is used as a saturating grade. A hard oxidised grade such as R115/15 is used as a coating grade. Tiles are finished with mineral granules which are available in almost any colour.

Although produced in the UK in the 1950s shingles were never popular enough to establish a foothold in the market place and at the peak in 1970 only accounted for about ten per cent of the felt roofing market. They are still produced in France but account for only about five per cent of the market. This is in marked contrast to the USA where they are used extensively and account for over 50 per cent of the market. Development in the USA has reached a high level where shingles are available in almost any colour and can be laid on slopes with falls as little as ten degrees.

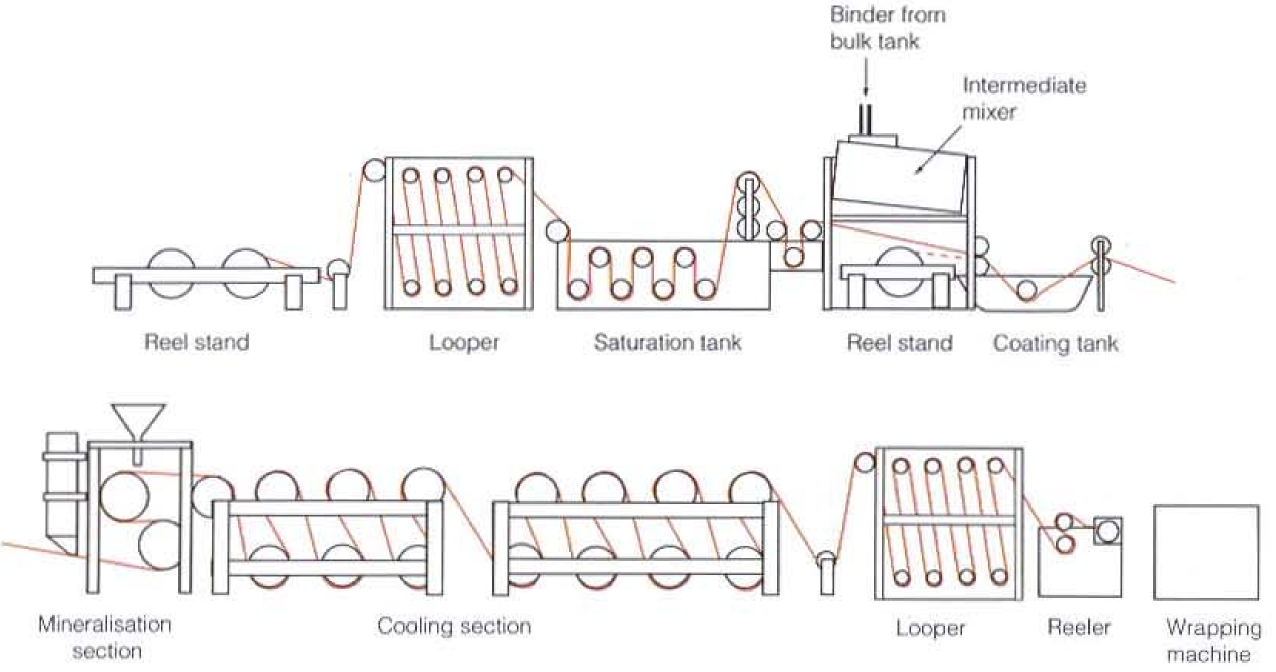


Figure 8.3 — Schematic of a roofing felt plant

8.1.3.6 Roofing felt manufacture

Roofing felt is made in a continuous process from raw materials to packaged and labelled rolls of product on a machine around 50 metres long in a single run (see figure 8.3). A roofing felt coating line consists essentially of seven stages:

1. Reel stand and looper
2. Saturation stage
3. Coating stage
4. Mineralisation stage
5. Cooling stage
6. Looper and reeler
7. Weighing and packing stage

The carrier, which is fed from the reel stand at the start of the process, is slowly unwound and when necessary is passed between rollers into the saturant tank. The bitumen in the saturant tank is usually a non-filled penetration grade (often 200 pen) at a temperature of about 170°C.

On leaving the saturant tank, the bitumen impregnated carrier passes between rollers which squeeze out any excess bitumen. The impregnated carrier then passes into the coating tank which may contain either an oxidised bitumen or a polymer modified bitumen normally containing limestone filler or a similar material.

After immersion the felt is passed between rollers to gauge coating thickness and to achieve an even coverage. Finishing is done by doctor blades which control the final coating layer thickness. This step is usually crucial as the felt thickness is tightly specified in the final product.

After coating with bitumen, the felt receives one of a number of alternative treatments designed either to aid packing and handling or to improve the aesthetics of the finished product including:

- a light coating of sand applied to one or both sides of the felt to prevent sticking during storage
- for torch applied materials a thin film of polyethylene or polypropylene is applied to the base of the felt as sand does not aid bonding
- a layer of release paper on the bottom of self-adhesive felts which can be easily peeled off during laying
- a layer of decorative mineral particles applied to the upper felt surface whilst warm.

The felt is cooled by passing over a series of rollers which are water or air cooled. Following cooling the felt is cut into standard lengths, reeled, weighed, wrapped and stacked on standard pallets. Out-of-specification rolls are rejected and the batch number and other details are usually printed on the label.

At the beginning and end of the process, there is usually a looper around which the felt passes. This device, which stores about 50 metres of material, acts as a reservoir for the process allowing the machinery to be operated continuously. The looper enables rolls of carrier to be changed at the beginning of the operation without stopping the machinery, and allows the reeling process at the end of the operation to continue uninterrupted in the event of a short breakdown.

8.1.3.7 Materials used in felt manufacture

8.1.3.7.1 Carrier materials

When the roofing felt industry was in its infancy, carriers were manufactured from little more than waste or by-products. Although widely referred to as 'wool felts' and even though they contained high proportions of wool fibre early carriers required other fibres to give the necessary strength, flexibility and absorbency properties. Roofing felts became more generally known as 'rag felts' because for a long time they were prepared from the fibres of rags and similar materials. As new techniques developed, and the industry looked for higher performance, other materials such as wood fibres, bark fibre, cotton-seed-hull fibre and paper were all used. Some felts contained no rag-fibre at all. Being based on vegetable matter all of these early materials suffered from a tendency to rot and also from a lack of strength. Today these materials are still used but are being replaced by glass fibre and synthetic fibres such as polyester. The advantages of these modern materials are:

- resistance to rupture caused by roof movement;
- low moisture absorbency during manufacture;
- rot proof;
- stable over a wide temperature range;
- resistance to puncture;
- consistent quality.

Types of carrier material	Typical product
loose fibre	sheathing felt
fibre/hessian	underslating felt
glass fleece	BUR
polyester	BUR
polypropylene	BUR

Table 8.12 — Types of carrier used in roofing felt

Carriers are produced in a variety of thicknesses, strengths, textures or weights depending on the fibre type and application, see table 8.12.

The base for underslating and hair felts is not pre-formed but is made from a loose open batt of long staple fibres which is immediately treated with bitumen to bind the fibres together. Underslating felt is further reinforced with an open hessian carrier.

8.1.3.7.2 Saturant materials

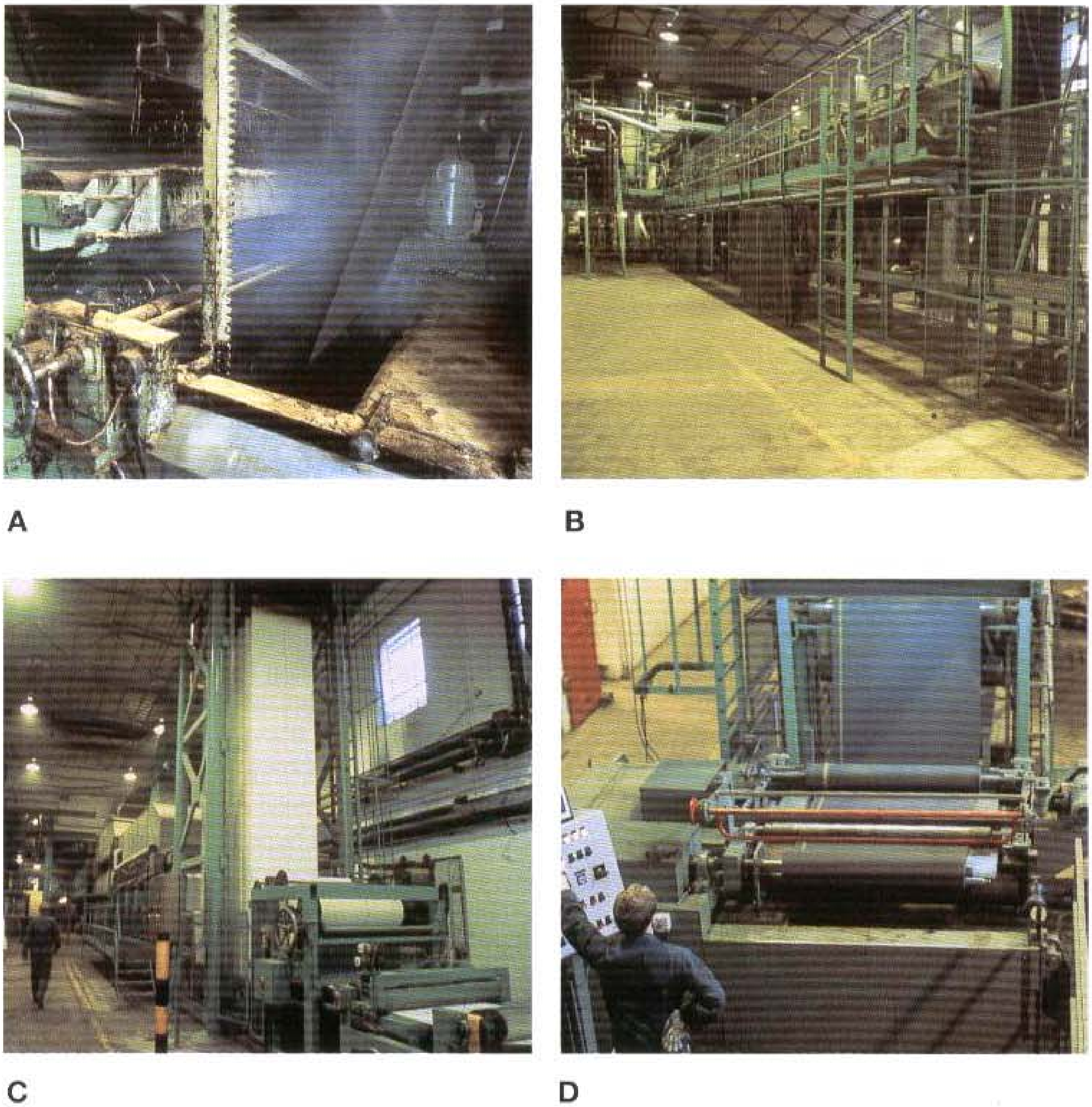
The purpose of the saturant bitumen is to thoroughly wet the carrier to prevent it from acting hygroscopically and "wicking" water. With very heavy polyester carriers it also serves as a primer and ensures a good bond to the coating grade bitumen as well as excluding air bubbles which can result in imperfections in the finished felt. In the UK, 200 pen bitumen is typically used. For very open carriers such as hessian and for glass fleece which is easily impregnated a saturant is not needed.

8.1.3.7.3 Coating materials

The coating bitumen requires a high flow reistance to avoid permanent deformation under hot climatic conditions and a penetration which is high enough to prevent cracking when the felt is unwound, ie greater than 20 dmm is considered suitable. The penetration should, however, not be too high (maximum 70 dmm) to avoid problems of puncturing. Typical grades used in Europe are shown in table 8.13. In addition to these grades, many felt manufacturers use non-standard grades by blending their own binders. Mexphalte R115/15 is frequently used for this purpose. Coating is usually carried out at around 180°C, depending on the grade, and to a finished coating layer thickness of 1 - 6 mm depending on the type of felt.

In the UK most felts are manufactured using bitumens containing filler. This has the effect of increasing viscosity, coating density and softening point (see section 7.22, figures 7.3, 7.4 and 7.5) and decreasing penetration. Fillers, which are usually added at concentrations of 20 - 45 per cent, are typically silica, limestone, slate dust and talc. Filled bitumens require a temperature of around 190°C for coating.

High performance felts increasingly use polymer modified bitumen for coating (with and without filler). Due to their higher viscosities these materials need to be applied at a higher temperature than normal oxidised grades of bitumen and are typically used at 190°C.



Photograph 8.4 — Roofing felt production line:

A: coating tank; B: coolers; C: looper; D: rolling, cutting and packing (reproduced courtesy of Callenders Ltd, Basildon, UK)

Country	Coating grades		
Germany	R100/45	R95/35	
France	R100/40	R90/40	
Netherlands	R110/30	R95/35	R85/25
UK	R105/35	R115/15	R95/25
Denmark	R110/30		
Switzerland	R95/35		
	Adhesive grades		
Germany		R85/25	
France	R110/30	R100/40	
Netherlands	R110/30	R85/25	
UK	R95/25	R105/35	R115/15

Table 8.13 — Typical bitumen grades used in roofing applications in Europe

8.1.3.7.4 Thermoplastic rubber modified bitumen roofing

Blown bitumens have been used for the production of roofing felts for many years and continue to provide satisfactory performance in a wide variety of circumstances(8). Nevertheless, advances in building techniques have necessitated the development of very high performance roofing felt systems incorporating carriers and coatings with a high degree of elasticity and improved durability.

The steady development of felt roofing has been driven by the economics of the building industry and of energy conservation. In building construction, roofs have become much lighter with longer spans between supports inevitably resulting in much more movement in the roof structure. These substrate movements may be directly transferred to the roofing felt layers which must be sufficiently flexible, elastic and resistant to permanent deformation at all service temperatures to accommodate the movement without losing their waterproofing performance. The introduction of high levels of thermal insulation in roofs has resulted in the waterproofing materials (ie felts) experiencing much higher and much lower temperatures (thermal shock) and consequently much higher strains which also change at much higher frequencies. The resulting substrate movements may also be much more pronounced if synthetic insulation materials are used with a high coefficient of thermal expansion. The use of synthetic construction materials with a high coefficient of thermal expansion for the manufacture of roofing accessories such as ventilation pipes and drain pipes also contributes to the addition loads exerted onto roofing felts.

These developments in the building industry have led the drive to improve quality and performance which cannot be met by the use of conventional bitumens or manufacturing technology. Improvements to the performance of oxidised bitumen by means of conventional blowing technology appear to have reached the limits with grades such as R100/40 and R105/35. Further blowing does not yield bitumens with the required degree of flexibility to meet the new demands and modifications with plasticisers (to improve low temperature performance) and fillers (to increase softening point) have also reached their performance limits.

One further important factor which influences the choice of material for roofing is cost, particularly that of labour. Labour costs may be decreased by reducing the number of layers of felt (plies) applied to the roof.

However, to compensate for the decreased degree of security of the built up roofing system more severe requirements may be set in respect of flexibility at low temperature, resistance to permanent deformation and resistance to puncture, all aimed at reducing the risk of damage during application. Furthermore, costs can be reduced by extending the working season of the contractor's labour force. This may require the ability to apply roofing felt at lower ambient temperatures. Thus, the requirement for better flexibility at low temperature becomes important and can be met only by more elastomeric systems.

The improvement in the flexibility of a roofing felt cannot be provided solely by the use of a flexible carrier such as a polyester fleece. Under low temperature conditions adequate flexbility can be provided only by a combination of a polyester fleece and a polymer modified bitumen coating.

It is possible to satisfy the requirement for improved flexibility, elasticity and flow resistance in roofing membranes by the use of 100 per cent polymer based materials such as PVC, butyl rubber or EPDM. However, owing to constraints on cost these materials can usually be considered only as single-ply membranes. Moreover, their splicing and application techniques deviate from common roofing practice and therefore these materials tend to be limited to the types of projects where specialised labour can be afforded.

8.1.3.7.4.1 Advantages of bitumen/TR coatings over traditional systems

Bitumen/TR compositions are widely used for the manufacture of high performance roofing felt and have a number of advantages over blown bitumen systems which include:

- improved fatigue resistance: the accommodation of repeated thermal movements of the roof
- improved flexibility: especially at low temperature, enabling contractors to lay felt under colder weather conditions than with conventional bitumen
- improved strength: to allow a reduction in the number of plies of felt by replacing in whole or part the blown bitumen coated system by a bitumen/TR system
- improved resistance to permanent deformation, puncture and tear at 60 to 70°C which allows the system to be walked on during construction with a high degree of assurance that no damage will result
- improved elasticity, resulting in a greater capacity to bridge movement of cracks and joints.

Thermoplastic rubber modification of the bitumen satisfies all the above requirements in as much as these materials have the necessary high and low temperature properties (ie cold bending -25 to -35°C and flow 80 to 100°C) as required by the coatings. They also provide elasticity and fatigue resistance to the roofing felt, thus prolonging service life.

Practical attribute required	Sheet properties		Coating properties	
Compliance to roof structure movements	Crack bridging ability at service temperature (-20 to 80°C)	> 2mm	Elongation at break Permanent set	> 500% < 10%
Low temperature properties for application	DIN cold bend	< -20°C	Fraass temperature	< -35°C
High temperature properties in service	DIN flow resistance, no flow at 80°C		Stiffness modulus at 10^5 secs Softening point, R & B	> 20N/m^2 > 100°C
Workability/handling	Resilience Adhesion	good good	Penetration at 25°C Viscosity at coating temp	< 80dmm < 4000cP
Long term performance	Durability in service — not less than 10 years Fatigue life in service —not less than 10 years			

Table 8.14 — Minimum roofing felt performance requirements

8.1.3.7.4.2 Selection of bitumen/TR modified roofing compounds

Compositions of thermoplastic rubber with compatible or penetration grades of bitumen are commonly used as coatings for roofing felt. The performance of these coatings has been intensively studied and much data is available(8,9,10,11,12,13,14,15,16,17). Long experience in the roofing industry has provided a basic definition for the performance of a roofing felt, see table 8.14.

The selection of a bitumen/TR compound for premium quality roofing membranes usually involves three steps(12). The first is governed by what may be called "product performance characterisation" criteria, on the basis of which products are generally put into broad performance categories. For roofing materials these criteria include:

- penetration	- walk-on ability during application
- softening point	- flow resistance at high temperature
- flow temperature	- flow resistance at high temperature
- cold bending	- cold weather flexibility
- permanent set	- susceptibility to wrinkling over joints
- elongation at break	- ability to bridge cracks.

The second step is based on in-house handling criteria such as:

- viscosity	- pumping, coating, impregnation
- storage stability	- compatibility, homogeneity, handling.

The third step is governed by long term performance criteria such as:

- durability	- resistance to ageing and weathering
- fatigue life	- ability to resist repeated elongations.

Area	T_{flow} (min.)* °C	T_{cb} (min.)** °C	T_{flow} - T_{cb} (ΔT)*** °C
Arctic	80	-40	120
Northern/central Europe	90	-30	120
Central/southern Europe	100	-20	120

*T_{flow} (min) = minimum flow temperature
**T_{cb} (min) = minimum cold bending temperature
***ΔT = service temperature range

Table 8.15 — Service temperature range for different European climatic regions based on DIN requirements

The product performance characterisation and handling criteria are related to the type and concentration of the polymer and to the grade of bitumen, whereas the long term performance criteria are more closely related to the bitumen composition.

The product performance criteria obviously vary for different climatic conditions. Table 8.15 gives the average requirements under DIN 52123 for resistance to flow and cold bending fracture for arctic, northern/central European and central/southern European climatic conditions.

The difference, ΔT, between the minimum flow temperature and the minimum cold bending temperature remains a constant 120°C and is often termed the "service temperature range". In order to obtain a service temperature range of 120°C, an addition of twelve to fourteen per cent of TR is generally required for a penetration grade of bitumen. In figure 8.4 it appears that the 120°C service temperature range can be achieved with eleven to thirteen per cent of TR. However, this figure is based on average data and may not be sufficient for some types of bitumen. The ΔT is practically independent of the grade of bitumen used, as can be deduced from figure 8.5.

The effect of different grades of TR, each with a styrene content of 30 per cent, on the service temperature ranges of blends of twelve per cent TR in a low asphaltene bitumen are shown in figure 8.6. By judicious choice of the TR grade a suitable formulation can be achieved to withstand most climatic conditions. The polymers themselves can be formulated to suit particular manufacturing conditions. In figure 8.6, the polymers TR 1184 and KX 500 have similar blend properties but the molecular structure of the KX 500 polymer has been adjusted to give a lower viscosity at 180°C.

The choice of the bitumen grade for the production of a roofing membrane is based primarily on the flow and cold bending requirements of the coating. Its behaviour during application in functions such as walk-on ability and permanent set is a significant constraining factor in developing suitable formulations. Good walk-on ability is particularly important during the laying of the felt. The penetration of the bitumen/TR blend is considered to be a good indicator of its walk-on ability. For many premium bitumen/TR blends a penetration at 25°C of </= 60 dmm is adequate for the unfilled compound which means the base bitumen penetration should be below 200 dmm, as can be seen from figure 8.7. In addition the finished felt should be sufficiently resilient to resist the effects of compression when walked on.

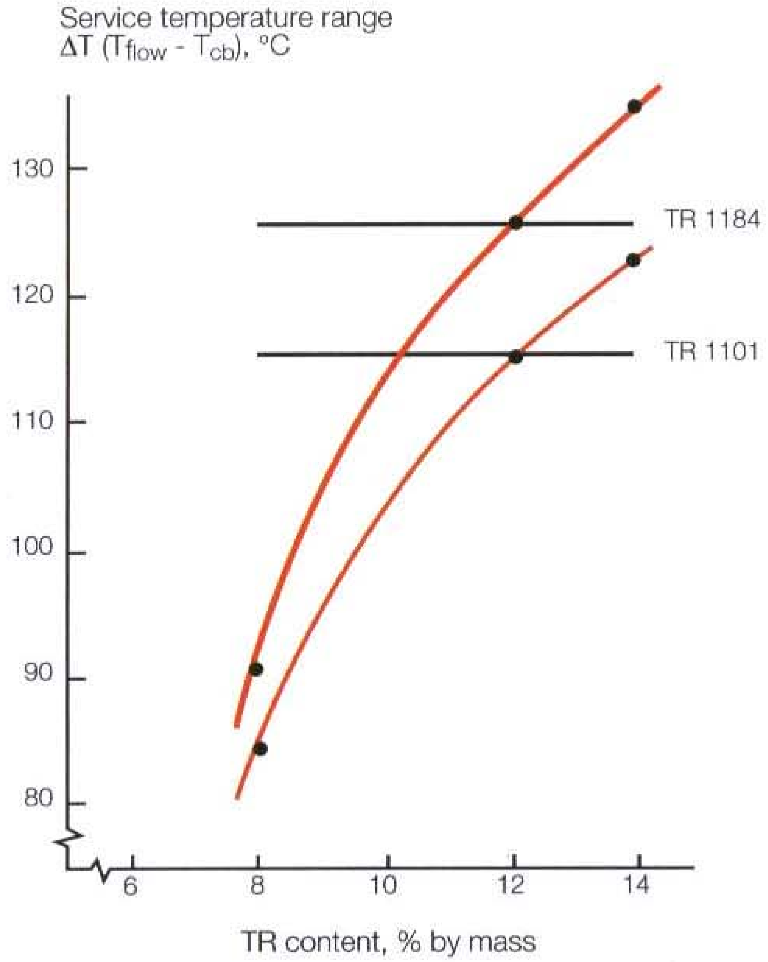


Figure 8.4 — **Effect of TR concentration in 200 pen bitumen on the service temperature range (average values).**

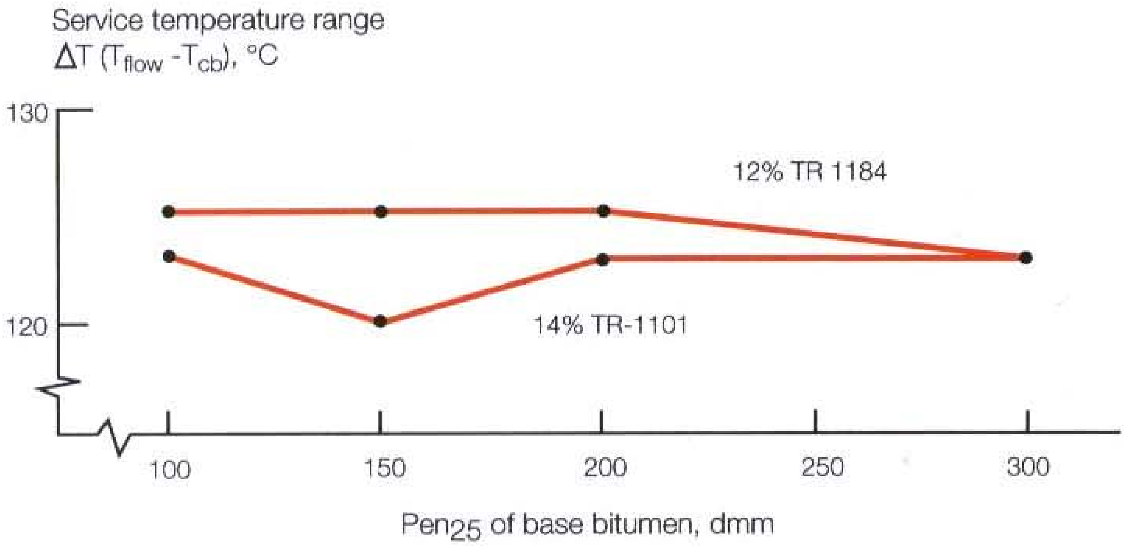


Figure 8.5 — **Effect of the penetration value of the base bitumen on the service temperature range (average values).**

Property		No filler	10% by volume limestone filler (Wigro)
Penetration at 25°C.	dmm	77	60
Softening point (R & B)	°C	100	102
Viscosity at 180°C	mPa.s	1200	1800
Flow temperature,pass	°C	80	80
DIN Cold bend, pass	°C	-25	-25
DIN Elongation at break	%	2300	2000
Permanent set	%	8	15

Table 8.16 — Effect of filler on formulation properties

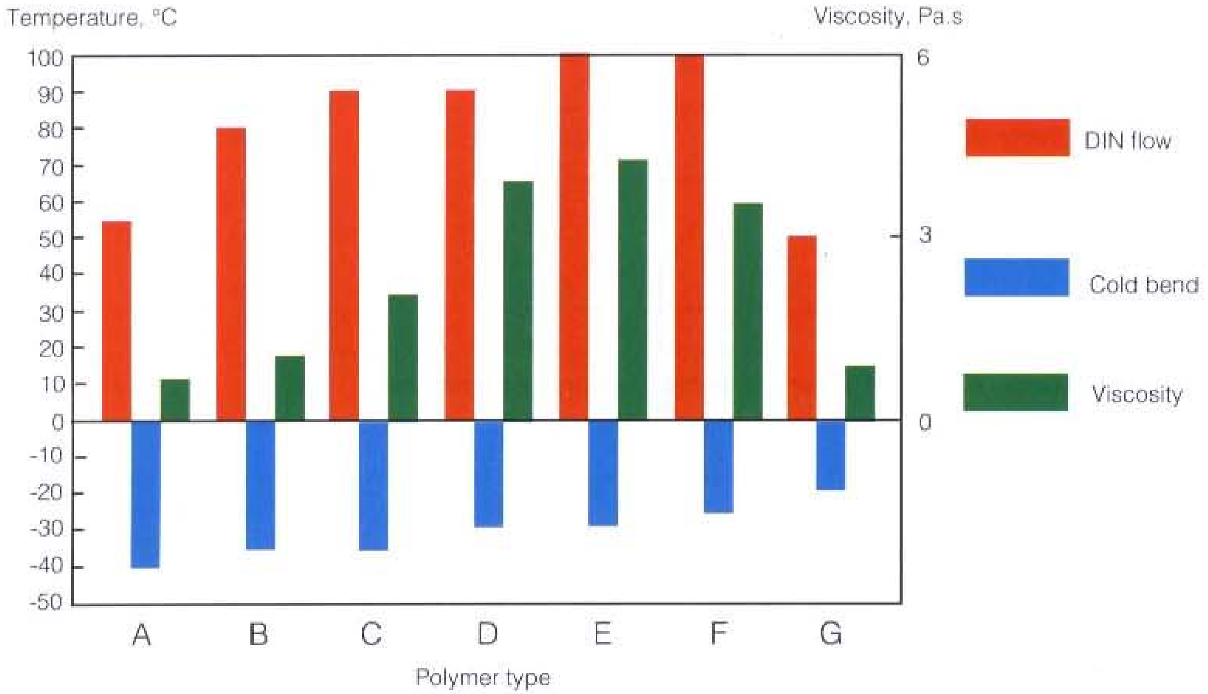
The permanent set property is indicative of the elastic characteristics of the product and is a measure of the susceptibility of the roofing felt to produce wrinkles over joints after a large number of expansion and contraction cycles. It is measured after 24 hours of relaxation following elongation; in the cases cited here, after 1500 per cent elongation at 25°C. Figure 8.8 shows that the permanent set increases dramatically when the penetration of the base bitumen is below 70 dmm. It should also be noted that the permanent set of the bitumen/TR compound is affected significantly by the addition of filler. The amount of filler added is commonly restricted to 10 to 15 per cent by volume (typically 20 to 35 per cent by mass) as the properties are then only marginally affected, see table 8.16. Above this level the flexibility or the elasticity of the materials is rapidly reduced with increasing filler content, see figure 8.9. The magnitude of the effect on the bituminous system is very much dependent upon the type of filler used.

The chemical reactivity of fillers has a significant effect on the durability of the roofing felt. Ageing tests at elevated temperatures have demonstrated that neutral fillers such as chalk and ground limestone have a small but significant influence on the permanent set value. Slate dust (a natural silicate with an active surface and good acid resistance) promotes ageing of the felt and produces a much higher permanent set value. Fly ash is not recommended for use with bitumen/TR systems as this filler may contain active metal complexes which accelerate the ageing process and break down of the polymer. Table 8.17 summarises the effect of accelerated ageing on the tensile properties and permanent set of bitumen/TR compounds containing various fillers.

Filler	Softening point, °C	Pen @25°C dmm	Maximum stress MPa			Ultimate elongation %		Permanent set %			Flow temp pass, °C	
Months at 70°C	—	—	0	1	3	0	3	0	1	3	0	3
No filler			2.2	2.0	0.7	1800	1800	6	20	40		
30% Chalk	52.5	106	1.8	1.7	0.6	1750	1350	15	45	—	85	80
30% Limestone	50.5	109	2.0	1.5	0.6	1600	1100	25	45	—	90	90
30% Slate dust	47	109	1.9	1.3	*	1600	850	32	70	—	85	80
30% Fly ash	49	105	1.7	0.8	*	1600	650	15	50	—	85	80

14% Cariflex TR -1101, 86% 200pen bitumen
* ductile

Table 8.17 — Ageing of filled bitumen/TR systems



	Molecular Weight	Polystyrene content %	Polymer type	Cariflex grade	Service temperature range ΔT °C
A	low	29	linear SBS	TR-1102	95
B	medium	31	linear SBS	TR-1101	115
C	medium	30	lin/radial SBS	KX-500	125
D	high	30	radial SBS	TR-1184	120
E	high	30	radial SBS	TR-1186	130
F	high	35	radial SBS	KX-204	125
G	low	15	linear SIS	TR-1107	70

Figure 8.6 — Performance properties of blends of 12% Cariflex TR in low asphaltene 200 pen bitumen as a function of polymer type

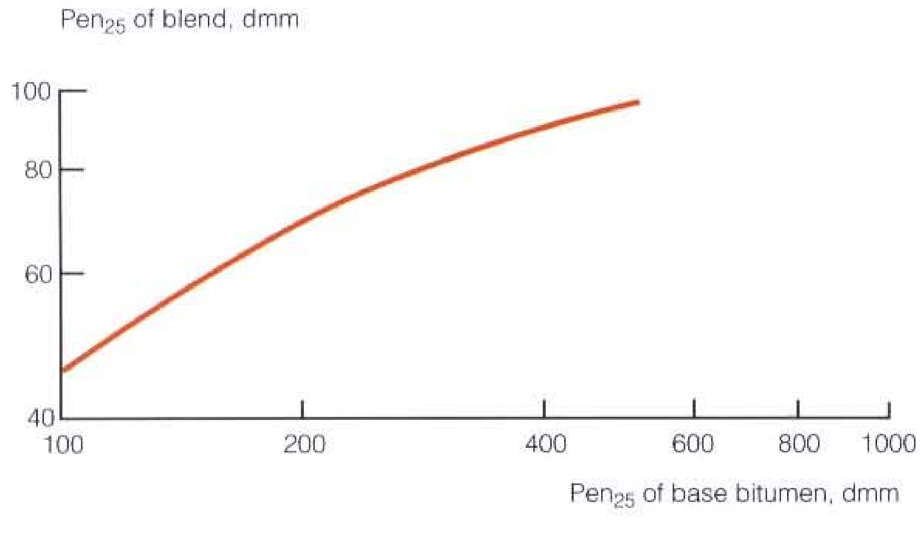


Figure 8.7 — Average penetration values for bitumen containing 12% Cariflex TR 1101 or TR 1184

Formulation			
TR content		% mass	12 to 14
Penetration at 25°C of base bitumen		dmm	70 to 300
Properties of bitumen/TR blends			
Service temperature range	ΔT = Tflow -Tcb	°C	> = 120
Elasticity	Permanent set	%	< 20
Walk-on-ability	Penetration at 25°C	dmm	< = 80

Table 8.18 — Bitumen/TR formulation constraints

The foregoing indicates that there are some basic formulation constraints which apply to all premium bitumen/TR roofing compounds and these are summarised in table 8.18.

The requirements with respect to flow and cold bending properties then determine the type and grade of TR which are the most appropriate for the service conditions under consideration. This is illustrated in figures 8.10 and 8.11 for TR-1101 and TR-1184 respectively.

The linear polymer TR-1101 in a soft bitumen might therefore be preferred for low temperature flexibility, but a combination of the branched copolymer, TR-1184, and a hard bitumen is to be recommended for high temperature flow resistance.

Typical bitumen/TR formulations suitable for the various European climatic regions are illustrated below:

- For arctic conditions: a compound based on fourteen per cent TR-1184 in 300 pen bitumen.
- For north/central Europe: a formulation based on fourteen per cent TR-1184 in 150/200 pen bitumen or twelve to fourteen per cent TR-1184 in 200/300 pen bitumen.
- For south/central Europe: a composition based on fourteen per cent TR-1184 or TR-1186 in 80/100 pen bitumen or twelve to fourteen per cent TR-1184 in 100/150 pen bitumen.

Whilst in some cases the product performance characterisation criteria will be satisfied with less TR, the amounts given above will ensure better intrinsic quality and performance, particularly with respect to fatigue resistance.

8.1.3.7.4.3 Comparison of APP and TR polymers in high performance roofing systems

Only two types of polymer have achieved significant commercial success in bituminous roofing applications. One type is the thermoplastic polyolefin group, the plastomers, the other is the thermoplastic rubber group, the elastomers. The most prominent plastomer in the roofing field is atactic polypropylene, see section 7.2.3.2.2, whilst the most commonly used of the thermoplastic rubbers are the styrenic block copolymers, see section 8.1.3.7.4.

Modifier		APP	TR (SBS)
Concentration,	% mass	10 to 30	10 to 20 (normally c. 12)
Softening point, (R & B)	°C	100 to 150	100 to 140
Viscosity at 180°C	Pa.s	0.3 to 2.5	0.9 to 4.0
Elongation at break	%	200 to 400	1500 to 2000
Breaking stress	kPa	2 to 3	10 to 15
Cold bend temperature, pass	°C	-10 to -20	-20 to -40

Table 8.19 — Typical properties of bitumen modified by APP and TR

The two groups of polymers are chemically and physically quite different and this difference is reflected in their properties when the polymers are dissolved in bitumen, see table 8.19. The bitumen/TR blends have better elasticity as is demonstrated by their superior elongation at break, elastic recovery value and high impact resistance at low temperatures.

The improved properties of polymer modified bitumens allow fewer plies of felt to be applied than are required with blown bitumen. They are more durable and consequently last longer than conventional felts and, particularly with bitumen/TR systems, they are more resistant to cracking and can be applied in either cold or hot ambient conditions.

The early TR systems used to modify bitumens comprised linear SBS polymers, making the materials flexible to temperatures as low as -40°C and giving resistance to flow at about 80°C. This made these systems ideally suitable for low temperature climates and hastened their rapid acceptance in Scandinavia. A number of years later the radial TRs were introduced which gave a wider service temperature range than the linear systems and allowed resistance to flow at up to 100°C or higher, see figure 8.6. Radial polymers such as TR-1184 or TR-1186 now predominate in the industry, and are used successfully in Spain, Greece and southern France as well as the more temperate regions. In Spain bitumen/TR systems comprise 70 per cent of the polymer modified roofing production.

APP modified bitumens have higher softening points and resistance to flow at higher temperatures than bitumen/TR systems. This is a side effect of the necessity to use high levels of APP in bitumen to achieve flexibility at low temperatures(18). However, as roof temperatures do not normally exceed 90°C, the requirement for very high softening points is not so important.

The availability of both linear and radial grades of TR makes it possible to adjust both the high and low temperature properties as desired, by the selection of different ratios of the various TRs with bitumen. By contrast there are limited opportunities for adjusting formulations in a similar manner with APP.

In parallel with the development of better felt coatings and carriers there have also been developments in application techniques. The traditional methods of fixing roofing felt are the roll and pour technique utilising a hot bitumen adhesive (mop applied), see section 8.1.3.8, or loose laying and ballasting. The latter method has been largely discontinued. Newer, widely used techniques which include torching (heat application by flame), cold adhesive bonding, self adhesive systems, mechanical fastening and hot-air guns are replacing these traditional fixing systems.

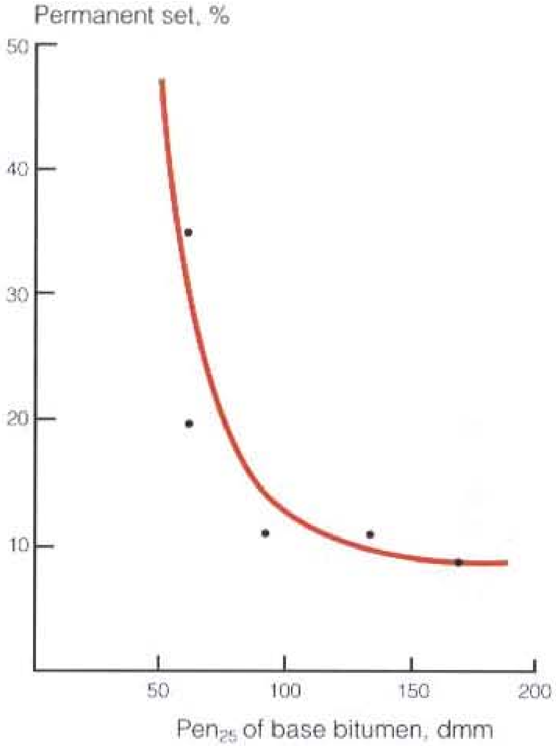


Figure 8.8 — **Relationship between permanent set of bitumen/TR blend (at 25°C after 1500% elongation) and penetration of base bitumen**

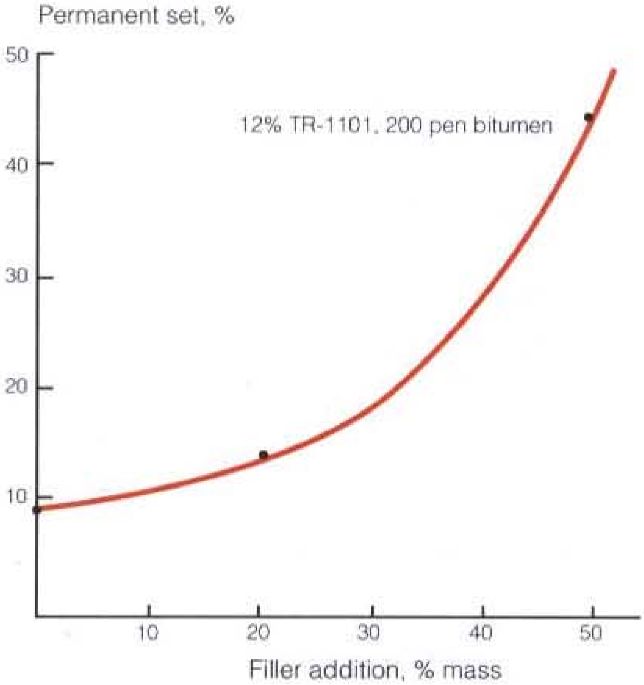


Figure 8.9 — **Effect of filler addition on permanent set (at 25°C after 1500% elongation) of bitumen/TR blend**

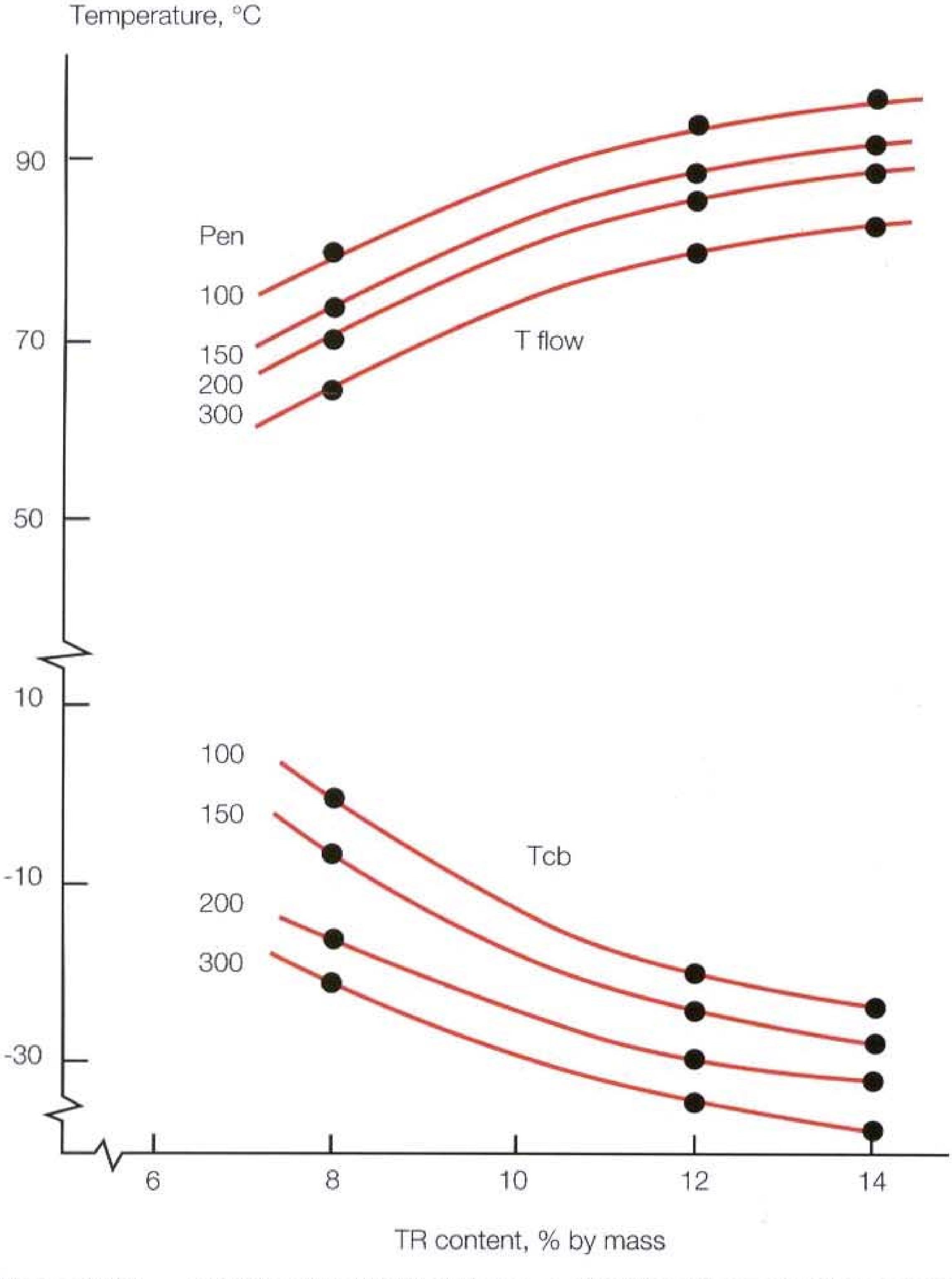


Figure 8.10 — Cariflex TR 1101 in bitumens of different penetration values — effect on flow temperature and cold bend temperature

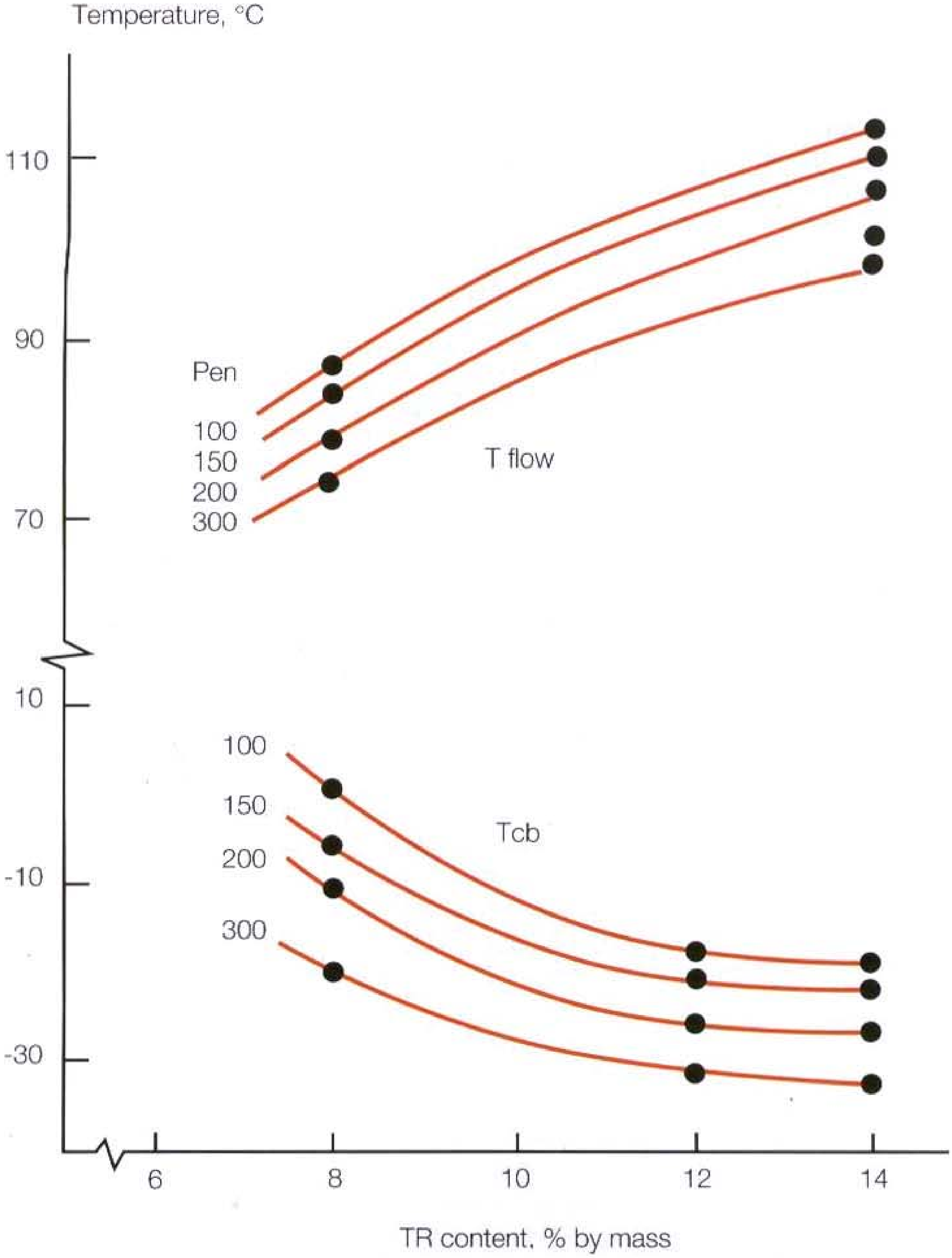


Figure 8.11 — Cariflex TR 1184 in bitumens of different penetration values — effect on flow temperature and cold bend temperature

Bitumen/TR systems have in the past been erroneously considered unsuitable for torching due to the vulnerability of the butadiene mid-block to thermal degradation by the hot torch. In practice, no problems have been encountered by the use of flame applied systems and the adhesion to roof substrates is unrivalled. Accelerated weathering tests on torched and control sections of bitumen/TR systems have shown that there is no significant difference in long term performance of the two(19).

By contrast APP modified systems cannot be laid by mopping or by the use of cold applied adhesives. In some cases where torch applied APP roofing has been applied over oxidised bitumen materials, either onto old felts or onto new materials, long term adhesion problems have been observed, due to exudation at the interface. This exudate is thought to be a mixture of low molecular weight material from the bitumen carrying some low molecular weight APP. The versatility of the bitumen/TR systems is self evident by comparison with the restricted number of methods of application for the bitumen/APP systems.

Many studies of the effects of ageing on bitumen/TR systems have taken place and have shown that, contrary to expectations, these systems have a very good resistance to ageing and have outstanding durability, see section 8.1.3.9. This has been reported(20) to be due to the counteracting reactions of bitumen oxidation and polymer chain scission which tend to maintain the creep behaviour of the materials. Vonk and co-workers at the Shell Research laboratories in Amsterdam have also demonstrated the excellent resistance of bitumen/TR systems to thermal oxidative degradation, see section 7.2.3.3.4.1(13).

Many accelerated ageing studies have taken place to quantify the behaviour of bitumens modified by TR and APP(19,21,22), some have included comparisons of TR with APP(21,22,23,24,25,26,27) whilst others have included natural exposure(23,27,28,29) and one(30) different types of APP. The criteria for assessing the effects of ageing have included changes to the softening point, penetration and cold bending temperature, extension at break, elastic recovery, creep behaviour, surface appearance, fatigue life, dimensional changes and fissuring. However, because of their simplicity and the ability to directly compare the results, the first five tests are the more commonly reported.

In summary, the relative performance of TR and APP modified systems is as follows:

- Both APP and TR modified bitumens have better ageing characteristics than blown bitumen.
- Surface protected bitumen/TR systems age more slowly than unprotected systems. This has been less significant for APP systems, although recent papers suggest that age crazing of bitumen/APP systems is more widespread than originally thought(31).
- The principal effects of bitumen/TR ageing are a slight reduction in softening point, a reduction in penetration and a rise in cold bending temperature. For bitumen/APP systems, softening point and penetration are less affected, whilst cold bending temperature also rises, as it does for TR systems. In both cases elongation at break is reduced.
- The significance of the above changes is not equal. The change in softening point for the TR systems leaves them generally well over 100°C and thus satisfactory for practical applications. The change in elongation of APP and TR systems may drop to about one third of the original starting value. For

bitumen/TR systems the starting values are about 1,500 to 2,000 per cent compared with 200 to 400 per cent for the bitumen/APP systems. The reduction is much more significant for the latter. However, both systems are considerably better than oxidised bitumen whose elongation may drop to zero. The reduction in the elongation on ageing is also reflected in the change in cold bending temperature which is essentially a strain related property.

- Although there is no generally agreed correlation between accelerated ageing and natural weathering, acceleration factors of from 44 to 50:1 have been quoted. For the bitumen/TR systems this has led to estimated service lifetimes of up to 30 years.
- Large scale practical experience in the south of France(28,29,32) has shown no significant deterioration with bitumen/TR systems for periods of up to fifteen years.
- APP systems are produced from different grades of polymer and it has been shown(30) that variations in viscosity and crystallinity can induce very different ageing properties with, in the worse case, the cold bending temperature rising to +16°C.
- Optimisation of the ageing behaviour of bitumen/TR systems is possible by the use of blends of branched and straight chain TRs(21).
- In general, bitumen/TR modified roofing felts can be applied by all normal fixing techniques; they are suitable for a wide range of climatic conditions from Scandinavia to the Middle/Far East, and their ageing performance, particularly when mineralised, is at least as good as, but often superior to, both blown bitumen and APP-modified systems.

Bitumen/APP coatings have commonly been perceived to be the most appropriate materials for high temperature environments such as southern Europe, with bitumen/TR systems being more suitable for the colder regions due to its superior low temperature flexibility. However, the very high softening points and resistance to flow of the bitumen/APP systems tend to be higher than practical circumstances require and those achievable by bitumen/TR coatings are generally good enough. This is supported by the fact that more than 70 per cent of the Spanish market for roofing felt utilises bitumen/TR systems. In 1992, in western Europe where more than 600 million square metres of roofing felt were produced, about 34 per cent of manufacturers used TR, some 32 per cent incorporated APP and the balance used oxidised bitumen, see figure 8.12. In the USA (30 million square metres) APP and TR hold an equal 20 per cent share of the roofing market, whilst in Japan (50 million square metres), TR is the most used polymer.

8.1.3.7.5 Felt surfacing materials

Roofing felt is generally surfaced with mica, talc or, more usually, sand to prevent rolls sticking during storage or with coarse mineral granules which, as well as preventing sticking during storage, are applied to provide:

- resistance to weathering by absorbing UV radiation,
- fire resistance by decreasing the surface availability of oxygen,
- decorative finish,
- reduction in surface temperature of the bitumen coating during service to reduce the rate of ageing.

8.1.3.7.5.1 Mineral granules

Most of the granules used in the UK are made from crushed slate which is used in its natural colours of pale grey, blue-grey and green-grey. However, elsewhere granules are made from coloured crushed slate and coloured crushed rock and are available in a wide range of bright colours.

The development of good quality granules is worth mentioning here to demonstrate the required properties. In an attempt to improve on the somewhat dull colours available from natural slate and, possibly, with a view to reducing costs a light river-gravel has been used. The buff granules turned out to be porous and led to failures caused by severe blistering. The first attempts to colour natural slate granules used paints based on natural resins and drying oils. These materials had poor weather resistance and after only a few years the granules weathered to the colour of the base rock. Crushed brick and porcelain have been used and clay graded to granule size and vitrified has also been tried as mineral surfacings. Pigments were usually incorporated with the clay to give red, brown and buff colours. The crushed brick and clay granules tended to be porous and caused blistering and staining. The light coloured granules produced from crushed porcelain had these bad properties as well as that of being translucent. They became detached from the felt due to weathering of the bitumen under the granule. Early ceramic granules based on quartz also suffered in this way but were later improved when they were made fully opaque. Today materials most commonly used for surfacings are slate, quartz and slag which are generally coloured.

8.1.3.7.5.2 Other surfacing materials

As well as mineral granules, metal-faced roofing felt is increasingly used on prestige buildings. Aluminium foil can be incorporated into the felt during manufacture to produce a highly reflective or matt finish. The foil can be textured in a variety of patterns and coloured to give silver, copper or lead finishes. Metal-faced felt is more expensive to produce and to apply as great care is needed to avoid marking the facing during manufacture, transport to site and application.

8.1.3.8 Methods of application

It is not the intention here to cover the practicalities of application or design but to cover only the general methods of fixing. For more information the reader is referred to industry bodies and manufacturers many of whom produce publications and advice on application techniques and design principles.

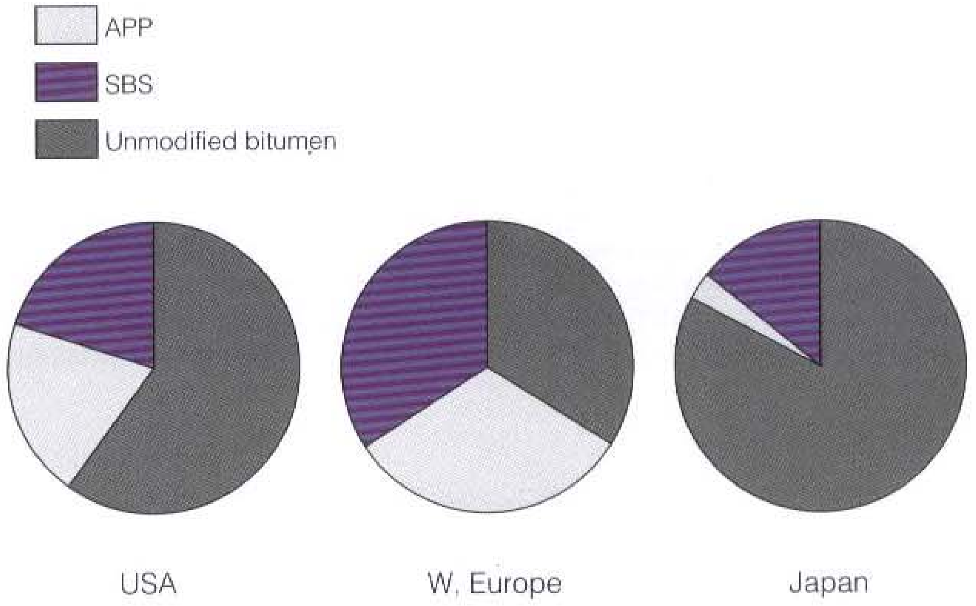


Figure 8.12 — SBS, APP and unmodified bitumen roofing membranes manufactured in western Europe, USA and Japan in 1992

8.1.3.8.1 Nailing

The first layer of felt on any roof must be firmly anchored to the substrate. For wooden structures nails are normally used. These are usually galvanised with large flat heads to provide maximum resistance to pull-through. For simple buildings such as garden sheds, where only a single layer of felt is used, dome-headed nails are applied. The edge of the dome cuts partially into the felt and provides a seal to prevent ingress of water where the felt has been punctured.

8.1.3.8.2 Hot adhesive

The traditional method of fixing subsequent layers of roofing felt is to use hot oxidised bitumen as an adhesive in a technique known as 'pour and roll'. Hot oxidised bitumen is poured onto the roof deck immediately in front of a roll of felt as it is unwound into its final position. The process requires skill and co-ordination between pourer and roller as the rate of cooling precludes any adjustment if it is not right the first time.

To ensure maximum service life from a built-up felt system it is essential to use an adhesive which has the same characteristics as the binder in the felt. For conventional bitumen felt R85/25 or a similar grade is normally used. For bitumen/TR felts, which vary considerably between manufacturers, either conventional oxidised bitumen or a bitumen/TR adhesive can be used which is best obtained from the same manufacturer as the felt. For new roof construction, roofing insulation board can be used which has the first felt layer bonded at the factory.

One of the disadvantages of the pour and roll technique is the lack of control over what is probably the most critical part of a built up system. Adhesive is usually heated in a bitumen kettle and transferred to a bucket with a spout for pouring. The kettle requires slow heating to melt the bitumen adhesive and is usually lit at the start of the day. As the job progresses and binder is applied to the roof, the kettle is topped up with solid binder broken from a keg or with small preformed shrink-wrapped blocks. Despite the efforts of the industry to develop codes of practice it is frequently the case that no temperature control mechanism is fitted to the kettle and hence the bitumen is overheated leading to excessive hardening. With prolonged and severe overheating the bitumen may crack to form light ends which can produce softening. Kettle fires due to bitumen auto-ignition are not uncommon. In spite of all this, the roofing industry is not beset with problems caused by failures of the bitumen adhesive which is, possibly, a testament to the ability of bitumen to withstand mistreatment.

8.1.3.8.3 Thermally bonded (torch-on)

Torch-on roofing felts are specially manufactured with a thicker layer of bitumen on the base of the felt, which is covered with a thin plastic film to prevent pick up of dust and detritus which could possibly reduce adhesion. The felt is fixed to the roof by the application of heat from a propane torch or hot-air gun whilst the felt is being rolled into position. The thin protective layer of plastic film melts during this process.

The propane torch (often multi-headed) is played onto the base of the felt as it is unwound. The adhesive layer of the felt melts and forms a small pool on the deck and the felt is rolled forward at such a rate as to keep the molten pool at a minimum. Skill is required in moving the felt forward at the appropriate rate. The adhesive for torch-on felts is effectively contained within the felt and means that the felt is necessarily a heavyweight grade. This causes problems in both manufacture and application where molten binder tends to flow off quickly. One way round this is to use polymer binders such as bitumen/TR which have a higher viscosity. Typically, around twelve per cent TR is used in torch-on felts although up to twenty per cent is used by some manufacturers.

The advantages of this method are that it is quicker than the pour-and-roll technique and, since the adhesive is heated only for a short period, it is less likely to degrade. Also, because it is an integral part of the felt it is not possible to use the 'wrong' adhesive. Disadvantages are risk of burn-through if the felt is heated too strongly, and increased fire risk during application. In Scandinavian countries the use of torch-on techniques employing naked flames is banned due to the high risk of fire during construction.

8.1.3.8.4 Cold adhesive

Two principal types of cold adhesive exist for bonding roofing felt to the substrate. One is the self adhesive type of roofing felt in which the adhesive is incorporated into the base of the felt, and the other is the cold applied adhesive system, such as Shell Tixophalte (see chapter 9), which utilises a very strong thixotropic bitumen/TR adhesive.

For a cold adhesive to work properly it requires a consistency which enables it to be easily applied yet will hold the felt firmly without flow immediately after application. At the same time it must possess enough flow to 'wet' the surface of the felt and the roof substrate to ensure a good watertight bond.

Emulsion systems are unsuitable because they would trap water within the BUR system and cause blistering. Likewise, solvent systems are unsuitable because the solvent tends to soften the felt and, because it is prevented from evaporating, the adhesive stays soft for a long period of time. The most suitable cold adhesive systems are bitumen/TR compositions which are naturally very tacky. The adhesive can be incorporated into the felt and protected by a waxed paper backing. On site the paper is removed and the felt rolled gently to ensure a good bond.

Systems such as this have been on the market for some years but the amount used at present is relatively small. The reasons for this low utilisation include variable performance, increased cost, industry conservatism and difficulty of application with conventional bitumen grades. Nevertheless, with increasing environmental awareness the industry is bound to move further towards cold adhesives in the future.

8.1.3.8.5 Partial bonding

Apart from the first layer of roofing felt on a roof which may be nailed to the substrate, all the other layers must be bonded using bitumen. The traditional method has been the pour-and-roll technique which produces full bonding of the felt to the substrate. More recently partial bonding where spots or stripes of bonding bitumen are used to stick down the roofing felt has become increasingly popular. The partial bonding technique for fixing roofing felt is used to prevent the entrapment of moisture between the plies of roofing felt in a built up roof, allowing the moisture to be vented at the edges of the roof. Full bonding, in which the whole roof area is covered in adhesive, whilst giving excellent adhesion, can result in the formation of blisters, leading to subsequent weakness in the integrity of the roof, if moisture is inadvertently trapped under the felt.

It is essential when using this method to ensure that edges are satisfactorily bonded. Partial bonding can also be used with torch-on felts where the adhesive is attached to the felt in stripes during manufacture.

8.1.3.9 Ageing properties of roofing materials

The in-service performance of a roofing felt is, perhaps, one of the most difficult attributes of the material to simulate in the laboratory. The combined effects of UV radiation, atmospheric oxidation and the cyclical influence of temperature and weather serve to produce chemical changes in the roof coating which affect the ability of the materials to satisfactorily protect the integrity of a building. When investigating the suitability of new materials for use in roofing applications, their long term effectiveness is of paramount importance.

The durability of roofing materials may be influenced by a wide variety of environmental factors(14), see table 8.20.

8.1.3.9.1 Conventional roofing felt

For conventional roofing felts containing oxidised bitumen the influence of environmental factors that will cause the bitumen to age harden, and the long term performance of the materials, are well understood. Normally, the penetration of the coating falls and the softening point rises whilst the materials become more brittle and susceptible to cracking.

Environmental factors	Potential effects
Heat	Loss of extensivity Embrittlement Crazing
UV radiation	Loss of extensivity Embrittlement Crazing Change of appearance
Water	Erosion Hydrolysis Swelling Frost damage
Oxygen, (ozone), carbon dioxide hydrogen sulphide, sulphur dioxide, sodium chloride.	Chemical changes
Bacteria	Rotting
Plant life	Root penetration

Table 8.20 — Factors which affect the durability of felt roofing

Typically, an oxidised bitumen with a softening point of 110°C and a penetration of 30 dmm will harden to 150°C softening point and 15 dmm penetration over a period of about 10 years(15), see table 8.21. Van de Schaaf has suggested that this was equivalent to an artificial ageing period of 80°C for about six weeks and is in line with the Shell Research assumption that six months ageing at 60°C is equivalent to about eight years in practice, see table 8.22. The French CSTB testing regime of 70°C for six months equates to more than ten years of actual service life. The data in table 8.22 derived after ageing for six months at 60°C is typical of the type of ageing to be expected with oxidised bitumens.

The progress of this oxidation/ageing process is well understood in practice for conventional bituminous materials and a typical roofing felt with a "rag" carrier will give a service life of five to seven years if laid with great attention to detail, primarily due to failure of the carrier itself. Felts utilising a glass fleece carrier will fail after a service life of seven to twelve years due to failure of the coating through age hardening leading to cracking. More highly elastic carriers such as polyester can survive possibly for twelve to fifteen years mainly due to the increased

		Accelerated ageing		Natural ageing	
Ageing conditions		Fresh	6 weeks at 80°C	Fresh	10 years on a roof
Softening point, (R & B)	°C	116	165	110	150
Penetration at 25°C	dmm	27	11	30	15
Elongation,	%	90	—	—	—
Permanent set,	%	35	—	—	—
DIN Cold bending, pass	°C	+7.5	+35	—	—

Table 8.21 — Ageing of blown bitumen(9)

Bitumen	Property								
	Softening point, °C			Penetration @ 25°C, dmm			DIN Cold bending, pass, °C		
	Fresh	Aged	ΔT	Fresh	Aged	ΔT	Fresh	Aged	ΔT
R100/45	110	151	+40	42	20	-22	-12	2	+14
R100/25	105.5	129.5	+24	23	12	-11	0	12	+12
R85/25	86.5	108.5	+22	24	11	-13	4	20	+16
R110/30	105	159	+54	26	10	-16	-2	18	+20
R95/25	90.5	101	+10.5	30	20	-10	-2	0	+2
R100/40	95.5	100	+14.5	38	27	-11	-4	0	+4
R90/30	89	99.5	+10.5	28	23	-5	0	2	+2

Table 8.22 — Ageing behaviour of oxidised bitumens (ageing for 6 months at 60°C)

binder thickness on the carrier. A thicker binder film will take longer to age and to achieve a critical penetration value leading to fracture of the bitumen. In all cases, large extensions due to substrate movement cannot be accommodated and will lead to premature failure of the bitumen and subsequent water ingress. The combination of elastomeric coating and flexible polyester carrier enables the roofing felt to withstand very high strain levels in service without fracture of the bitumen or rupture of the carrier. These very high performance membranes are believed to have a service life of up to 30 years and guarantees up to 20 years are now commonly being given by manufacturers.

8.1.3.9.2 Reliability of accelerated ageing tests

Both the in-service and accelerated ageing characteristics of the bitumen/TR class of binders are less well understood because these materials have been in-service for a relatively short period of time. One of the main difficulties in validating the suitability of a candidate system for a new or existing application is in finding or establishing laboratory tests capable of predicting the long term durability of these systems under service conditions. For roofing membranes one method is to expose them to accelerated ageing under controlled laboratory conditions; however, accelerated ageing tests are not yet sufficiently reliable to give a definitive measure of product durability and service life.

Ageing conditions	Ageing factors*	
	1 month at 60°C	1 month at 80°C
Stress-strain properties, 23°C		
Strain at break (coating)	17	112
Stress at break (coating)	14	56
Strain at break(complete)	16	112
Zero crack test, -20°C		
Extension at break (carrier)	8	120
Stress at break (carrier)	10	60
Stress at 5 mm extension	15	120

* months outdoor ageing to achieve same change as after 1 month accelerated ageing

Table 8.23 — Ageing factors for bitumen/TR coated roofing felts (glass fibre carrier)

Ageing conditions	DIN flow, pass °C	DIN Cold bend, pass °C
Initial	85	-35
5 years outdoors	80	-35
3 months at 60°C	75	-30
2 weeks at 80°C	70	-30

Table 8.24 — Ageing of felts under different conditions

Table 8.23 illustrates the confusion that can occur when interpreting the results of ageing experiments. The data presented shows the rate of change of different properties (ageing factors) at two different ageing temperatures, 60°C and 80°C. In the zero crack test, the 'extension at break (carrier)' changes the least quickly at 60°C, but is the fastest at 80°C. In table 8.24 while there is little change in DIN flow resistance after five years on a roof, there is too rapid a change in properties after two weeks at 80°C, which is said to be equivalent to three months at 70°C, which in turn is supposed to be equivalent to five years in-service performance on a roof. It has also been shown(23,33) that polymer degradation which happens very rapidly in the accelerated laboratory tests does not apparently happen even after ten years in-service performance on a roof.

One final cautionary word on the validity of accelerated ageing tests is illustrated in table 8.25. A series of well accepted commercially available roofing felts was subjected to accelerated ageing for 6 months at 70°C following which they were tested to determine their cold bend and DIN flow properties. The felts contained approximately the same amounts of thermoplastic rubber (twelve to fourteen per cent) but resulted in dramatic differences in performance particularly in respect of the reduction in apparent service temperature range which varied from 15°C (felt 2) to 45°C (felt 8). In view of the wide variety of bitumens used in the felt production, the use of both thick and thin coatings, glass and polyester carriers and the incorporation of different fillers in the compounds, no direct relationships should be

Sample No.	DIN Cold bend, pass °C		DIN flow, pass °C		ΔT*, °C	Appearance flow
	before	after	before	after		
1	-10	+5	100	80	-35	slight
2	-30	-30	110	95	-15	slight
3	-25	-10	95	90	-20	slight
4	-20	-15	105	85	-25	slight
5	-15	-15	100	80	-20	slight
6	-30	-25	110	90	-25	moderate
7	-25	-15	110	95	-25	none
8	-15	+10	105	85	-45	moderate
9	-20	-10	120	95	-35	none
10	-20	**	85	**	—	excessive

* reduction in apparent service temperature range

** too much flow to permit testing after ageing

Table 8.25 — Effect on commercial roofing felts of ageing for 6 months at 70°C

sought from this data. That the ageing conditions for this ageing test are quite severe is acknowledged within the industry, but nevertheless there is also the possibility that formulation techniques and practices may vary. It is noteworthy that the best result was obtained on a linear polymer of medium molecular weight, in contrast to what might have been expected, and underlines the necessity for total design of a roofing felt encompassing the carrier, the coating (all ingredients) and the membrane thickness.

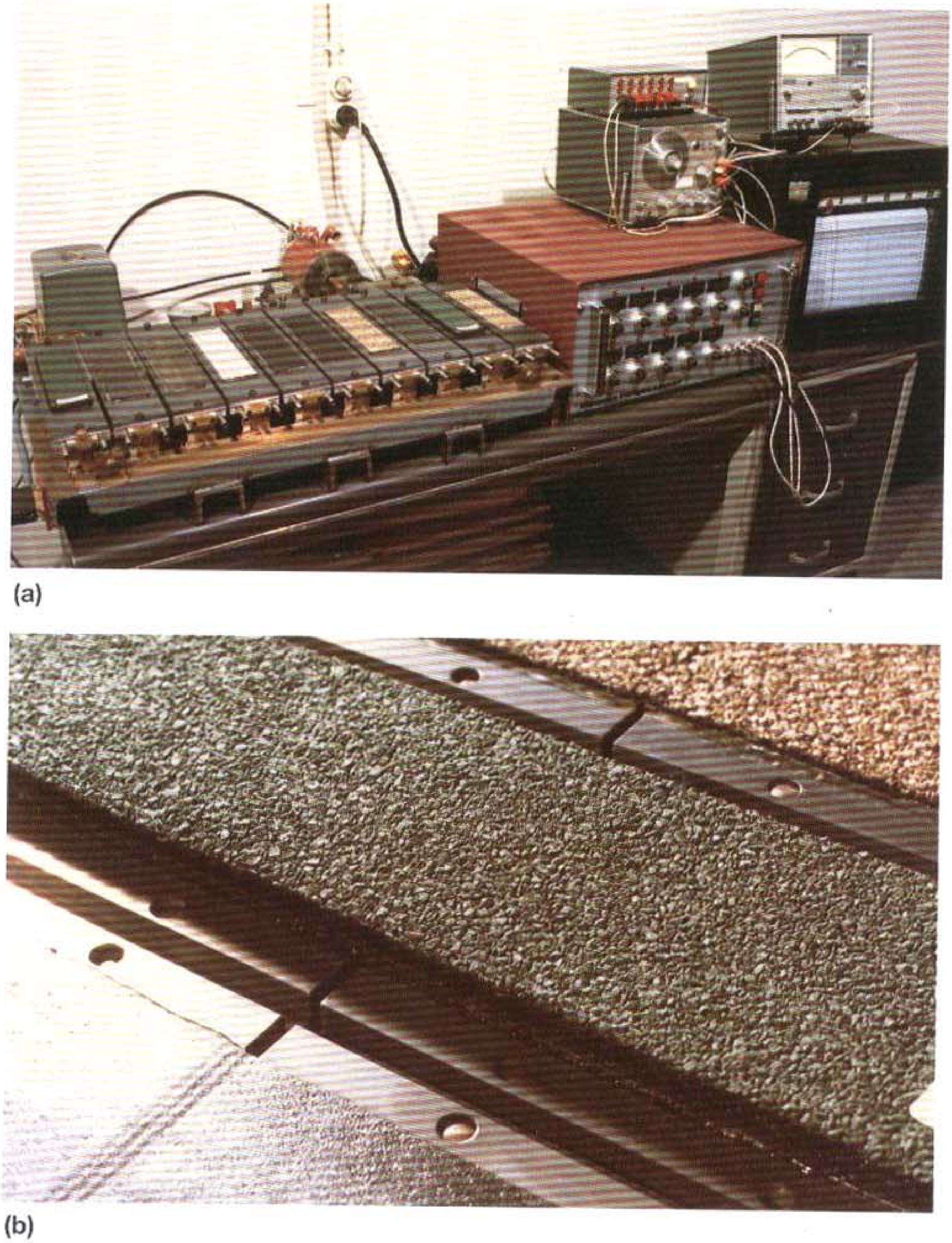
Any discussion of accelerated ageing performance should be conducted with an awareness of the weaknesses of the methods used for ageing the materials. The relationship between laboratory ageing and real performance is one of continuous investigation and much research and development continues to be conducted to build up good correlations.

8.1.3.9.3 Accelerated ageing of bitumen/TR roofing materials

The exposure of thin layers of bitumen/TR roofing materials to air, UV and high service temperatures has raised concerns regarding its ageing performance and its susceptibility to oxidative degradation. However, accelerated ageing tests and field trials over a 20 year period have demonstrated the excellent durability of these materials(34).

As described above, laboratory ageing of roofing felt coatings is commonly conducted by simple heat treatment in an oven, typically at 60 to 80°C. After heat ageing, roofing materials may be evaluated by a number of standardised tests, such as the zero crack test, the fatigue resistance test and the cold bending test described below(9).

- *Zero crack test.* This test was developed by Shell Research to measure the crack bridging ability of a sheet membrane material. The roofing felt sheet, 200 mm x 50 mm, is fixed to a pair of steel plates using an epoxy resin adhesive. The two coated plates are conditioned in an environmental chamber at the test temperature. The sample plates are inserted into a tensile testing machine and the gap between the plates is increased at the rate of 0.1 mm/min. The extension at break of the coating is measured at failure, see figure 8.13(a).
- *Fatigue resistance test.* This test was devised by Shell Research to simulate the type of movement which occurs in roof structures and can be conducted on new or aged specimens. Samples prepared in the same manner as for the zero crack test are mounted on a machine capable of oscillating the steel plates between a gap width of 1 mm and 2 mm at a predetermined rate. The number of cycles to failure is measured in this test. The equipment used is similar to that illustrated in figure 8.13(a).
- *Cold bending test (according to DIN 52123).* A strip of the membrane is bent over a mandrel of 30 mm diameter within five seconds at the test temperature as illustrated in figure 8.13(b). When being bent, the upper surface of the membrane is stretched and no deformation is assumed in the lower membrane surface in contact with the mandrel, because bitumen is taken as an incompressible material. Furthermore a constant elongation rate over a period of three seconds up to completion of the bending is assumed. The appearance of a crack in the strip of membrane is taken as the failure criterion in this test.



Photograph 8.5 — Shell Research roofing felt fatigue testing: (a) general view of apparatus; (b) close-up of fatigue test (note wrinkling and cracking in lower and upper samples compared to Cariphalte FR sample in the centre)

Typical properties	Roofing felt type		
	1	2	3
Cold bend test at -25°C (30mm, 5 s)			
Initial properties	pass	pass	fails at 0°C
12 months at 60°C	pass	fail	—
28 months outdoors	pass	nd	—
Zero crack test at -25 °C (Extension at break), mm			
Initial properties	>5	2.8	—
6 months at 60°C	4 -5	2.3	—
28 months at 60°C	4 -5	nd	—
Fatigue life at 23 °C (2 cycles/h), number of cycles to failure			
Initial properties	>10,000	6,500	1
6 months at 60°C	>10,000	2,100	—
12 months at 60*C	>10,000	1,600	—
28 months outdoors	>10,000	nd	—

Type 1	Highly modified elastomeric system using special compatible bitumen
Type 2	Medium performance elastomeric system using penetration grade bitumen
Type 3	Typical conventional oxidised bitumen system (R100/45 or R95/35)

Table 8.26 — Ageing performance of roofing felts of different qualities

The cold bend test, zero crack test and fatigue life test are useful performance indicators for screening candidate materials. Experience of using these types of tests suggests that ageing specimens for six months at 60°C approximates to eight years of service life on a roof in a European environment. More recently in Western Europe six months ageing at 70°C in an air ventilated oven has been correlated with 25 to 30 years service on a roof[34].

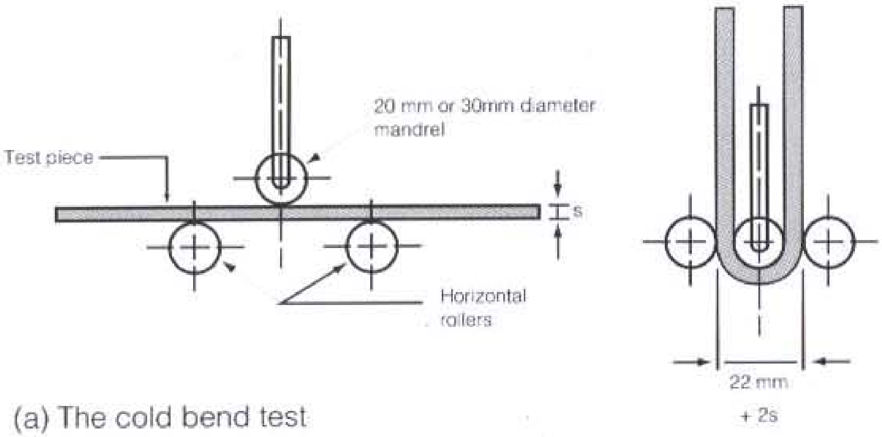
Table 8.26 typifies the ageing performance of three qualities of roofing membranes, Types 1, 2 and 3. The roofing felts were typically 2 mm thick, based on a compound containing 30 per cent of filler and supported on a 50 g/m^2 glass fleece.

The performance of the Type 3 membrane is typical of an R95/35 or an R100/45 oxidised bitumen on a glass carrier. The performance of the Type 2 membrane typifies those materials containing a bitumen/TR coating formulated using conventional penetration grade bitumen. The Type 1 material is typical of a membrane made using a highly compatible bitumen modified with TR. The data clearly shows the vastly superior ageing properties of the bitumen/TR systems when compared to normal oxidised bitumens.

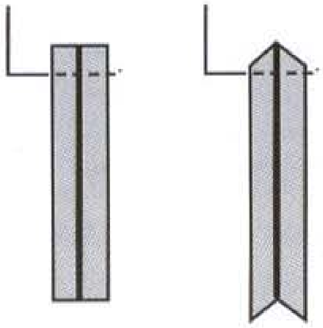
Roofing felt based on 30 per cent APP has performed similarly to blown bitumen in these ageing tests and is representative of the Type 3 material.

8.1.3.10 Criteria for the selection of a roofing felt

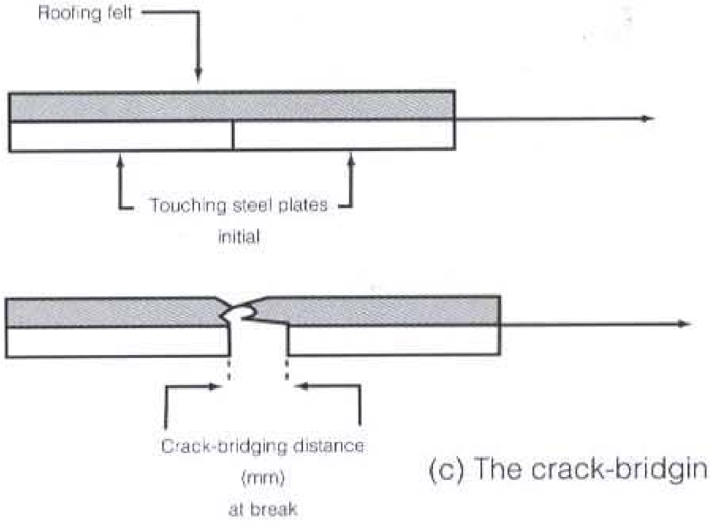
Stiffness modulus, elasticity, flow, fracture and fatigue resistance are all factors which have an influence on the selection of the appropriate type of BUR system for a particular type of roof[8]. Experience has shown that the stiffness modulus is a suitable criterion for linking the practical requirements of roofing applications with the properties of bituminous materials as determined by routine tests. For example, critical stiffness modulus levels have been associated with the critical temperatures found in the DIN 52123[35] cold bend and flow tests.



(a) The cold bend test



(b) The DIN flow resistance test



(c) The crack-bridging and

Figure 8.13 — **Crack bridging, fatigue, cold bend and flow resistance apparatus. Schematic diagrams**

The use of the concepts described below provides a sound mechanical basis for the selection of an appropriate grade and type of roofing felt.

8.1.3.10.1 Stiffness modulus and elasticity

An optimal design of a bituminous roofing system requires an understanding of the relationships between the rheological properties of the bituminous product and its essential performance requirements such as elongation at break and resistance to fracture, flow and fatigue. Jongepier(36) has shown, using a mathematical model based on dynamic and creep experiments on a variety of bitumens, that a valid and useful key mechanical-rheological property for describing these primary requirements is the stiffness modulus.

The stiffness modulus, S, is defined as the ratio of tensile stress, σ, to strain, ε, depending on temperature, T, and loading time, t:

$$S(T,t) = \sigma/\varepsilon$$

Taking a desired performance requirement such as a particular resistance-to-flow temperature, or a minimum fracture temperature at the appropriate time of loading, in combination with the penetration index of the bitumen, the required stiffness modulus can be derived using Van der Poel's nomograph(37).

For bitumens with a high PI value, however, the nomograph is of limited use. For bitumen/polymer systems it cannot be used at all. In such cases the stiffness modulus can conveniently be measured using the sliding plate rheometer(38) or a rotating plate rheometer.

Figure 8.14 shows the stiffness modulus/loading time characteristics for typical oxidised and penetration grades of bitumen compared with two bitumen/TR systems. At short loading time the bitumen/TR system has a similar stiffness to a soft, 80/100 penetration grade bitumen, making it less susceptible to cracking at low temperature, whilst at high loading time it has a stiffness equivalent to that of a highly blown, R110/30 oxidised grade bitumen, making it less susceptible to flow at higher temperatures. Figure 8.14 also shows that the bitumen/TR systems are much less susceptible to the influence of loading time than conventional bitumens resulting in an "elastic plateau".

The stiffness modulus, however, does not fully describe the elastic properties of the bitumen under conditions of high mechanical stress or strain. Significant information of that type is obtained by measuring the permanent set after recovery from strain, see section 8.1.3.10.3.

8.1.3.10.2 Flow of a bituminous layer under its own weight

A bituminous layer (1) flows under its own weight, w_1. The layer carries another layer of material (2) with weight, w_2, as illustrated in figure 8.15. The amount of flow, y, is calculated from

$$y = \frac{3\,h \sin\alpha}{S} \left(\frac{W_1}{2} + W_2\right) \quad \text{.... Equation 1}$$

where: y = shear displacement

h = thickness of the bituminous layer

α = angle of inclination

S = stiffness modulus.

The weights w_1 and w_2 are taken per unit area; for a 1 mm layer w = 1 kg/m^2 = 10 N/m^2, representative of pure bitumen. Utilising the above equation, the critical stiffness values for the on-set of flow in a roofing system under various conditions, as discussed below, can be calculated.

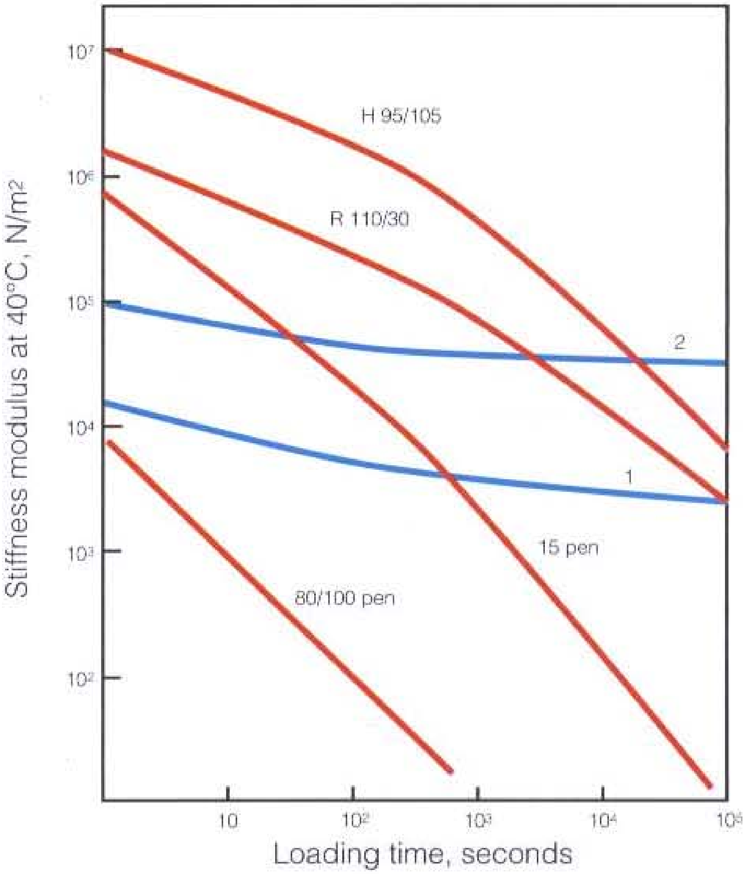
- DIN flow test (DIN 52123). A 3 mm test slab is suspended vertically for a period of 2 hours at temperature T. The slab is made up of two 1.5 mm bitumen layers, one on either side of the fixed carrier. The flow is observed visually and its onset is characterised by the amount, y, being equal to the thickness, h. Onset of flow in the DIN flow test is then equivalent to S = 22 N/m^2 (see table 8.27). For a more severe criterion of the onset of flow, eg y = 1/2h, the critical stiffness S = 45 N/m^2.
- Single ply on inclined roof. For a 3 mm single ply (weight 30 N/m^2) fixed to the substrate with a 1 mm mopping layer the onset of flow is characterised by S = 52 N/m^2 (table 8.27, case a). The weight of a layer of aggregate chippings (15 N/m^2) is included. If the membrane is substantially stiffer than the mopping grade bitumen, the deformation may be assumed to take place in the mopping layer only. With an equal amount of flow the critical stiffness is 21 N/m^2 (table 8.27, case b).
- BUR system on inclined roof. Considering a three-ply system, normal practice requires that the bottom membrane is nailed to the substrate. The remaining part consists of a middle mopping and membrane layer and a top mopping/membrane layer loaded with aggregate chippings as specified in the first example. For simplification, it is assumed that the mopping and coating bitumens are of the same grade and that the total construction has the same temperature throughout. The critical stiffness for onset of flow in this case is 85 N/m^2.

For a more complete discussion of the DIN flow test and cold bend test the reader is recommended to see Bats(39).

From the above calculations, the conditions of the flow test according to DIN 52123, carried out on a three millimetre membrane strip, indicate a calculated critical stiffness modulus level of 20-50 N/m^2 for the onset of flow, and actual test data, as presented in table 8.28, clearly confirm the calculation.

Furthermore, it has been observed that no flow is to be expected if the stiffness modulus has a value of 100 N/m^2 or higher. Since the DIN flow test is widely accepted for its practical significance, these stiffness modulus levels can be used in estimating the risk of flow.

The conditions of the DIN flow test are representative of a single ply membrane on an inclined roof, or of the top layer of a more complex BUR system, since this layer includes the weight of a layer of chippings. Hence, if the lower layers of such a BUR system have a negligible contribution to the total amount of flow, for instance because they have a lower temperature, the DIN flow test remains representative of the whole system. If conditions are such that flow



1 = 100 pen bitumen containing 6% TR 1101
2 = 100 pen bitumen containing 10% TR 1101

Figure 8.14 — Stiffness modulus/loading time susceptibility at 40°C of conventional bitumen/TR blends

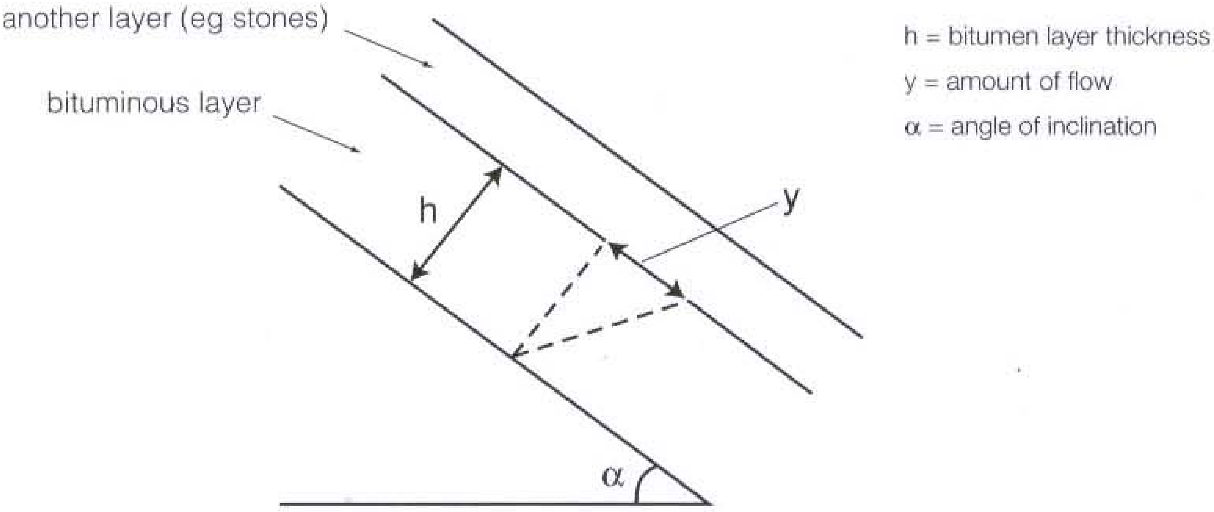


Figure 8.15 — Flow on an inclined roof

Variable	Unit	DIN flow test	Single ply				BUR system
			(a)	(b)	(c)	(d)	
α	degrees	90	30	30	30	30	30
h	mm	1.5	3.5	1	3.5	3.5	7
W_1	N/m^2	15	40	10	40	40	80
W_2	N/m^2	—	15	45	—	15	15
y	mm	1.5	3.5	3.5	3.5	1.5	7
S	N/m^2	22	52	21	30	120	83

Table 8.27 — Specification variables in equation 1 for several cases

Property	R85/25	R95/35	R110/30	R100/40	Bit/SBS blends	
					TR1101	TR1184
No flow acc. to DIN 52123 (T_1), °C	60	75	85	80	85*	95*
Stiffness at T1 and 2 h loading, N/m^2	100	90	110	90	100	100
Onset of flow DIN 52123 (T_2), °C	65-70	80-85	90-95	85-90	95*	105*
Stiffness at T_2 and 2 h loading, N/m^2	30	30	20	20	30	30

* Highly dependent on the TR type, the TR content and bitumen used.

Table 8.28 — Flow properties of roofing binders

is to be expected throughout the whole system, a higher critical stiffness level is required. However, the stiffening effect of filler in the bitumen, membrane carriers, etc, reduces this level in practice.

Addition of filler to the bitumen and aggregate chippings on top of the membrane increases the weight of the system and consequently increases the amount of flow. However, it is known that the addition of 25 per cent by mass of filler increases the stiffness modulus of the filled system by a factor of approximately 1.8 with respect to pure bitumen(40). Since the density is a factor of 1.2 higher, the net stiffening effect of the filler is 1.8/1.2=1.5. In terms of the DIN flow test this can be interpreted as an improvement of about 5°C in critical flow temperature.

The mineral surfacings generally applied to the top layer of a BUR system to protect it from the effects of UV ageing have been found to reduce the temperature of the membrane by at least 10°C, which is equivalent to an increase in stiffness modulus of a factor of four. In table 8.27, cases c and d, it is demonstrated that for an inclined roof (30 degrees) the use of a mineral layer reduces the flow because the increase in stiffness outweighs the effect of the increased weight due to the mineral.

The consequence of the above is that if a black panel (bare felt) temperature of say 100°C on top of a roof is to be considered, a bituminous compound with a DIN flow resistance of 85°C will suffice, because the filler gives a 5°C improvement of the flow resistance and the top temperature is reduced by at least 10°C owing to the top ply being covered with 1.5 kg/m^2 mineral aggregate.

8.1.3.10.3 Theory of temperature-induced fracture in bituminous roof covering

The phenomenon of temperature-induced fracture has been observed in bituminous pavements of roads in Canada. It has been related to the fracture properties of the bitumen binder in the asphaltic concrete mix(41). The critical fracture temperature T_{crit} was found from a calculation of the build-up of stress as a consequence of thermal contraction. Fracture takes place if the thermal stress σ_{th} in the bitumen reaches a critical value $\sigma_{th,crit} = \frac{1}{3}p$, where p is the critical hydrostatic tension characteristic of the cohesive strength of the bitumen(41,42). Hills' concept of thermally induced fracture is validated for the case of roofing membranes by the experimental "glass plate test". In this test a one millimetre layer of bitumen is adhered to a glass plate and cooled to fracture at a cooling rate of 10°C/h. The fracture temperature in this test was found to be practically equal to the aforementioned critical temperature.

The mechanical constraint that determines the relation between the critical thermal stress $\sigma_{th,crit}$ and the hydrostatic tension, p, is very similar to the situation of a roofing membrane adhered to the substrate. It is thus concluded that the method is relevant to calculate the critical fracture temperature of oxidised-grade bitumens in relation to their use in roofing membranes. It can be inferred from the Fraass data that the critical thermal stress $\sigma_{th,crit}$ varies from a value of 500 kN/m^2 for zero-PI bitumens (this value was adopted by Hills) to a value of 140 kN/m^2 for bitumens with PI = +6. The fracture temperatures and the associated stiffness modulus due to thermal contraction are detailed in table 8.29.

When considering critical fracture it is necessary to distinguish between the conditions of loading time and strain prevailing during application (laying) of the roofing felt and those prevailing in service.

The time during which the roofing felts are loaded during application (eg unrolling, folding over edges) are of the order of 0.1 to several seconds. The strain levels may be as high as ten to twenty per cent, see section 8.1.3.10.4. Two types of test are in use to rank candidate roofing products in this respect and to establish minimum application temperatures, viz. the Fraass Test (DIN 1995-U6; IP 80) and the cold bending test (DIN 52123). Test conditions and results are given in table 8.29 for a number of roofing bitumens. The stiffness modulus levels at break have been obtained from actual test results and Van der Poel's nomograph(37). It may be concluded from the above that for practical calculations a critical stiffness level for fracture may be set at, say, 5×10^7 N/m^2. Although the actual values may differ by a factor of two, the effect on the fracture temperature is estimated not to exceed 5°C.

Once applied to the roof, the material is subjected to strain levels that may vary considerably (1 to 500 per cent), depending upon the design of the roof structure, the number of plies, use of insulation, temperature drop, the occurrence of mud or dirt pools, etc. Generally, these strain levels develop at long loading times (hours), unlike those prevailing during application.

Hills'(41) work on thermally induced cracking of paving grade bitumens, summarised above, has been extended to roofing bitumens. The resulting fracture temperatures and stiffness moduli listed in table 8.29 demonstrate that a range of stiffness moduli at fracture is found which again approaches 5×10^7 N/m^2. This supports the use of such a critical stiffness level in the calculation of critical strain levels or fracture temperatures for practical conditions. It should be noted that even at temperatures slightly higher than those found in table 8.29 for thermal contraction, there is a real chance of fracture if the roofing is additionally subject to a different type of loading, eg wind loading.

As indicated earlier, the strain levels in service may vary widely. In table 8.29, fracture temperatures are also incorporated for a number of roofing products at various strain levels. The data give a survey of the low temperature fracture properties of a wide range of bituminous roofing materials and thus facilitate a choice of the appropriate material for application in practice. It is clear that the best performance is that of the bitumen/thermoplastic rubber blends, although the less expensive blown bitumens still cover a wide range of strain levels at low temperatures.

8.1.3.10.4 Deformation of roofing felts under application conditions

When being unrolled, the roofing felt is stretched and elongation occurs:

$$\text{Elongation} = \frac{(R_2 - R_1)}{R_1}$$

where R_1 and R_2 are the inner and outer radius of the felt on the roll.

If the smallest diameter of a roll is assumed to be 15 cm, then the elongation values found are as follows:

Thickness of felt,	mm	3	4	5	6
Elongation of inside bitumen,	%	4	5	7	8

The loading time associated with unrolling is estimated to be of the order of 0.1 to several seconds.

In the cold bending test (according to DIN 52123) a strip of the membrane is bent over a mandrel of 30 mm diameter within five seconds. When being bent, the upper surface of the membrane is stretched and no deformation is assumed in the lower membrane surface in contact with the mandrel, because bitumen is taken as in incompressible material. Furthermore a constant elongation rate over a period of three seconds up to completion of the bending is assumed. The following is obtained:

Elongation rate, λ (t) $= d/R(t) = d/(R_mT) \times t$

Elongation rate, λ $= d/(R_mT)\ \ s^{-1}$

Elongation at completion of bending, λ (t = 3s) $=d/R_m$

where:

d = thickness of membrane (mm)

R_m = radius of mandrel = 15 mm

T = time at completion of bending = 3s

For a 3 mm membrane, $\lambda = 20\%$.

An important requirement of a roofing system is its ability to accommodate:

high strain levels, and,

repeated strain (fatigue resistance).

These properties depend on the cohesive strength of the bituminous compound *and* on its capability to recoil elastically. Indicative of the latter is the amount of permanent set as observed after relaxation of stress. It is particularly in these properties that blown bitumens and bitumen/TR systems differ, see tables 8.30, 8.31 and figure 8.16.

The fatigue resistance of a few BUR systems has been tested under conditions similar to those of the zero crack test(9,43) in which the test geometry reflects the situation of a crack or joint in the roof substrate. The capability of the BUR system to accommodate the large strains involved near the gap depends on the visco-elastic properties of the bituminous compound and on the strength of the carrier material in the membrane(44,45). Clearly, the bitumen/TR systems are superior with regard to crack bridging capacity.

An overview of the most relevant data for felt manufacturing, application and service is presented in table 8.31 using which, candidate roofing materials can be chosen in relation to their in-service performance requirements.

Obviously, a choice of the less expensive R-grade bitumens is appropriate in cases where no large strains are to be expected. With combinations of high strain levels, frequent strain repetition and very low temperatures, the bitumen/TR polymer blends offer the most appropriate solution. Also, the combined use of roofing felts based on R-grade and bitumen/TR in a BUR system may be considered as an economic intermediate.

8.1.3.11 New developments

8.1.3.11.1 Venting layers

It is widely recognised that some of the problems which occur on felt roofing systems are induced during the application stages and/or because of poor design. One such problem, blistering, is believed to be caused by water vapour trapped within the felt layers during application. On a sunny day when the roof temperature can reach 80°C the water vapour expands rapidly causing the felt layers to part and so weakening the waterproofing layer. In an attempt to overcome this particular problem, venting layers have been increasingly incorporated between the felt layers. These work by providing a continuous network of permeable pathways for water vapour to migrate within the waterproof membrane. One edge of the venting layer is left open to the atmosphere to provide an escape route for the vapour.

The venting layer is perforated so that the layers above and below it can be bonded to each other. It can be made of something fairly sophisticated eg glass or other inert fibre, or something very simple, eg a non-bonded sand finished layer of felt. Both materials will do the same job satisfactorily.

Within the industry there are mixed views regarding the whole concept of venting layers. Their usage has increased rapidly even though there is no data to show their efficacy or otherwise. In Scotland, which is subject to very high wind uplifts, they are not used because they reduce the bond strength of the BUR system. It should be noted here that with TR modified felts the incidence of blistering and debonding is very much reduced because of the improved adhesion and bond strength.

8.1.3.11.2 Carrierless felts

One of the most recent developments in roofing felts is the introduction of membranes which contain no fibre carrier. The felt consists solely of a thick layer of bitumen polymer binder

Roofing material	Application				Service						
	Fraass λ = 1.5% t = 11 s		Cold bending*** λ = 20% t = 3 s		Thermal contraction**** t = 1 h		Fracture temperature, °C t = 2 h				
	T	S	T	S	T	S	λ, %				
	°C	10^7 N/m^2	°C	10^7 N/m^2	°C	10^7 N/m^2	5	10	20	100	500
R75/30	-16	10	0	3	-41	20	-32	-25	-21	-10	-4
R85/25	-20	10	0	4	-38	10	-29	-23	-16	-5	+3
R85/40	-23	7	-10	3	-46	9	-38	-31	-26	-12	-4
R95/35	-22	5	-7	1.5	-44	7	-36	-29	-23	-9	+2
R100/40	-26	5	-10	2	-49	6	-43	-31	-24	-9	+5
R110/30	-18	5	0	1.8	-42	5	-34	-24	-16	+1	+14
R100/45	-29	4	-13	1.5	-53	4	-46	-35	-27	-10	+4
Bit./TR 1101	<-40	—	-35	70	<-50	—	<-40	<-40	<-40	<-40	-20
Bit./TR 1184	<-40	—	-28	30	<-50	—	<-40	<-40	<-40	<-40	-20
Bit./APP**	~ -20	—	-5	—	—	—	—	—	~ -20	~ -10	—

Table 8.29 — Fracture temperature* and stiffness modulus at indicated conditions of elongation λ and time of loading t

* Typical average values
** Atactic polypropylene
*** 3 mm membrane
**** cooling rate 10°C/hour

	1-ply systems				2-ply systems		
1st membrane	Bitumen	Bitumen	TR/Bitumen	TR/Bitumen	Bitumen	Bitumen	TR/Bitumen
2nd membrane	—	—	—	—	Bitumen	TR/Bitumen	TR/Bitumen
Carrier	glass	polyester	glass	polyester	glass	glass	glass
Adhesive	epoxy	epoxy	epoxy	epoxy	R-grade	R-grade	R-grade
No. of cycles to failure a)	1	300	1500-3000 b) >10 000 c)	1500-3000 b) >10 000 c)	500	>10^4 c)	>10^4 c)
do. after ageing 1 year at 60°C d)	—	—	>10-200 b) 5000 c)	—	—	—	—

Table 8.30 — Fatigue resistance of BUR systems

a) Movement between 1 and 2 mm gap width, starting with 0 mm gap width
b) Observed with incompatible bitumen/TR systems
c) Observed with fully compatible bitumen/TR blends
d) 1 year at 60°C is equivalent to ten years outdoors

with a TR content of around twenty per cent and the usual finishes. These felts provide excellent resistance to rupture and because of their inherent elastic recovery possess a self-healing ability if punctured.

One drawback to this material is that it cannot be made on a conventional felt machine but must be extruded. As well as involving a high capital cost, the complex extrusion machines are not without their problems. The bitumen/polymer binder is extruded at a much lower temperature than similar materials used on a felt coating machine and, coupled with the much higher polymer content, can give rise to problems of 'memory effect' in the finished felt resulting in wavy edges and making the felt difficult to lay. As well as this, the very high polymer content tends to reduce the stickiness of the felt and can give reduced bond strength.

8.1.3.11.3 Polymer systems

A great number of polymers have been evaluated in bitumen for use in roofing applications with varying degrees of success. However, only two polymer systems, atactic polypropylene (APP) and styrene-butadiene-styrene (SBS), are used to any great extent each accounting for around 30 per cent of the total European market. These two materials are treated more fully in sections 7.2.3 and 8.1.3.7. In addition to these bitumen/polymer systems there are several non-bitumen membranes which are also used in roofing. Examples are:

PVC - Polyvinyl chloride
EPDM - Ethylene propylene diene monomer
CPE - Chlorinated polyethylene
CSPE - Chlorosulphonated polyethylene
PIB - Polyisobutylene
ECB - Ethylene copolymerbutylene
Butyl rubber - Isobutylene Isoprene

These membranes are all laid as large sheets (in some cases several hundred square metres) and are frequently supplied in a single roof-sized sheet. They are fixed down by screwing or partial bonding with the laps sealed on site, or they may be simply weighted down with ballast. The sheets are supplied approximately 1 mm thick and are used in a single layer. Some of the materials are available in bright colours whilst others are black. Their greatest weakness is that they comprise one single layer of protection against the ingress of water.

8.1.4 Liquid roof membranes

A waterproof roofing layer can be applied cold in liquid form either as an emulsion or as a cutback. A layer of bitumen on its own would not be sufficiently strong to ensure long term waterproofing and therefore liquid-applied layers are used either for repairs to existing membranes, as a top-up coating to extend the life of an existing sound roof or, with some physical reinforcing, to allow application of a thick coating.

Emulsions are normally based on soft penetration grade bitumens and are thickened to allow application by trowel or sputter gun. They are applied over an open fibre mat of polyester, glass or chopped glass, see photograph 8.6. They are suitable for application onto flat or low-slope roofs.

Felt manufacture		Application	Service			
Grade	Viscosity. @ 180°C	Min. handling temperature λ=5 - 10% t=3s	DIN Flow pass temperature	Fracture temp λ=20%, t=2 h	Elongation at break (a) $\lambda=1/3$, S^{-1} @ 20°C	Permanent set
	mm^2/s	°C	°C	°C	%	%
R75/30	490	-2	50	-21	—	—
R85/25	480	+1	60	-16	50	>40
R85/40	450	-10	60	-26	200	>150
R95/35	740	-7	75	-23	140	>100
R100/40	1400	-7	80	-24	90	>50
R110/30	2000	0	85	-16	30	>20
R100/45	1400	-12	80	-27	100	>50
Bit/TR linear	1500-3000 b)	<-40	85	<-40	1500-2200 b)	<9 c)
Bit/TR radial	3000-4500 b)	<-40	95	<-40	1500-2200 b)	<12 c)
Bit/APP	above 100 000 b)	~ -15	125	~ -20	400	>300

a) Determined on compound dumbbells ASTM D 1708-70 according to method ASTM D 2523-66T/D 412.

b) Depending on the polymer content and bitumen type.

c) Value applies to 1500% elongation and 24 h relaxation

Table 8.31 — Overview of primary properties and requirements

Photograph 8.6 — Spray application of the Monoform fibre/emulsion roofing system

Cutbacks may be based on hard penetration or even oxidised grades. Nearly all, if not all, cutback coatings contain rubber polymers, either natural or synthetic, to give the final coating elasticity and improved adhesive properties. In addition, wetting agents, thickeners and fibres may also be included to give consistencies suitable for brush, squeegee or gun application.

8.1.5 Problems associated with felt roofing

Contrary to what might be expected, water lying on a flat roof will not damage the felt but will protect it from the sun, by cooling the surface and reflecting UV light, and from air oxidation. The main problems encountered with felt roofing include:

- poor design
- poor workmanship during application
- mechanical damage caused by:
    - foot traffic
    - pigeons or squirrels
    - falling branches from trees
    - plant roots
    - thermal movement
- blistering
- staining
- bleeding
- delamination
- slippage.

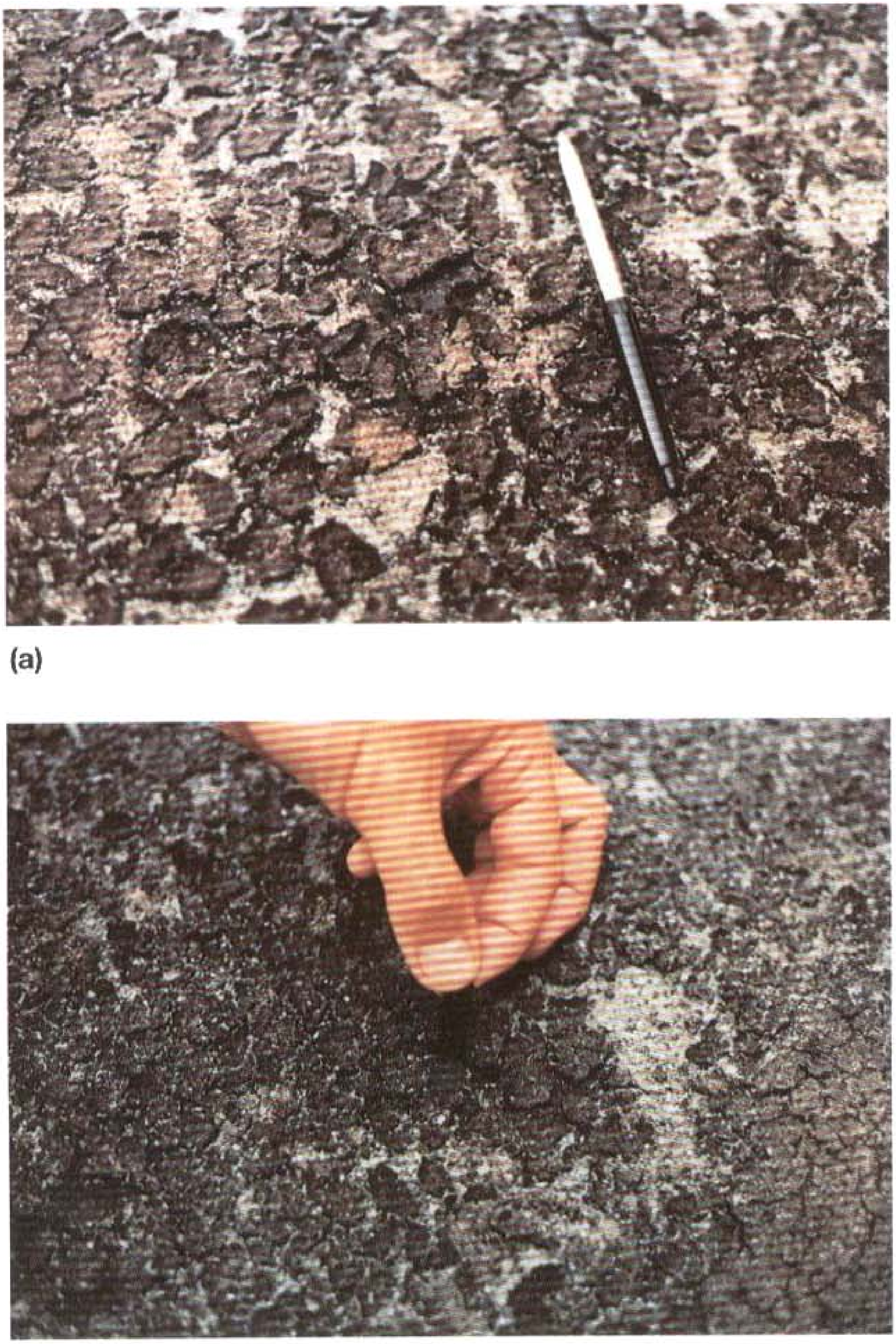
Of these the first three categories are self explanatory and are not discussed here.

8.1.5.1 Blistering

Blistering occurs when water is trapped within a BUR system. Water can enter a BUR system during application, from the substrate below or from the top during service. On a sunny day the water is converted to vapour and undergoes a huge expansion in volume causing a blister. The blister gets worse with the cycle of sunny days and cool nights which tends to draw more water into the felt system. Although not necessarily producing a leak in itself the blister shows that water is trapped within the BUR system. Before the blister can be repaired the point of water ingress must be located. The incidence of blistering is reduced with the use of TR modified felts because of their improved adhesion and bond strength.

8.1.5.2 Staining

Staining occurs when an oily component from the bitumen stains the mineral finish causing a slight darkening. It is particularly noticeable if the felt is new or if it occurs in an uneven manner. After a short time natural weathering darkens the felt and any staining becomes unnoticeable. Where staining is very severe it is indicative of a bitumen which is not



(a)

(b)

Photograph 8.7 — Close-up view of a roof damaged by mud curling homogeneous, that is, its component parts are not in balance with each other. Such bitumens may give rise to other problems such as delamination. Most bitumens, however, produce only a small amount of staining and give no problems in service.

8.1.5.3 Bleeding

Bleeding is the name given to the phenomenon where binder bleeds through pinholes in the felt and stains the mineral finish. It is caused by an excess of saturant bitumen remaining in the felt after manufacture. The soft bitumen leaks through a small hole possibly caused by a mineral particle puncturing the coating layer.

8.1.5.4 Delamination

Delamination can occur within a roofing felt if the coating grade possesses a high Oliensis compatibility value. Here a reaction between the saturant grade and the coating grade causes oil to exude at the interface and leads to disbonding. A similar problem can occur if the adhesive and coating grades are not of the same type. Problems such as this are almost non-existent today.

8.1.5.5 Slippage

Slippage occurs when the felt applied to a sloping roof moves under the force of gravity. It is usually caused by using the incorrect adhesive (or more rarely the incorrect felt) for the conditions of slope and temperature encountered. It is a problem of specification, or lack of it, rather than the materials used.

8.1.5.6 Mud curling(46)

A phenomenon called "mud curling" is well known for conventional bituminous felts, polymer modified felts and other bituminous structures. The phenomenon takes the form of alligator pattern cracking of the upper coating of the roofing felt with isolated islands of the coating contorted to expose the uppermost layers of the carrier. The damage does not usually extend below the carrier and the waterproofing performance of the roofing system is not impaired, although the appearance of the surface may cause concern.

Many environmental factors contribute to the occurrence of mud curling; however, the predominant factors include:

- the formation of a coherent layer of extraneous matter on the upper felt surface.
- ponding on flat roofs.
- cycles of sun and rain.

Examples of extraneous matter include mud, dust, sand, salt, pollen, leaf debris, saw dust, dairy product residues, flour, algae and bird droppings. Mud curling is rarely reported on roofing based on blown bitumen because such conventional systems are usually protected with a thick (four to six centimetre) layer of gravel or chippings. This layer protects the felt surface against mud curling or hides its presence. By contrast, bitumen/polymer systems are often laid with a single layer of surface chippings applied in the factory.

The fact that very few occurrences of cracks have been reported on bitumen/TR which has a stiffness almost the same as that for an R100/45 bitumen (approximately 2 x 10^4 N/m^2) may indicate that strain at break (about 100 per cent for an R100/45 compared to about 2000 per cent for a bitumen/TR compound) is a more important parameter than stiffness alone.

On the basis of laboratory investigations a mechanism has been suggested for the propagation of mud curling, see figure 8.17. The term "mud" has been used to illustrate the nature of the problem and could be substituted by any other coherent extraneous material. In the progress of the mud curling effect a number of steps have been identified:

- A wet mud layer is initially formed on top of the layer of felt on the flat roof, especially where water is able to stand, see figure 8.17.:2.
- On drying, the deposit forms a coherent film which contracts and subsequently cracks. The mud curling effect is then the result of shear stresses imposed on the roofing felt by shrinkage of small islands of the cracked deposit layer which retracts pulling chippings away from the felt surface. After the mud has been washed away by rain fall, areas of exposed coating begin to appear, see figure 8.17: 3 to 5.
- Continuous oxidation, weathering, exposure to UV radiation and heat/cold cycling will generate small cracks which will be propagated in time into larger alligator cracks.
- If a further layer of mud forms and shrinks on drying, grooves are created in the areas of bare coating which are distributed in the same pattern as alligator cracks, see figure 8.17: 5 to 7.
- Due to the continued heating and cooling cycles, many of the islands bonded by the alligator cracks contract, disbond from the carrier and finally curl up to produce a "mushroom" effect, see figure 8.17: 8.

This mechanism has been observed and studied in the laboratory using time lapse photography.

A number of different types of roofing felt (conventional oxidised, bitumen/TR and bitumen/APP) were subjected to examination in a mud curling test cycle. These tests showed that conventional oxidised bitumen was more susceptible, creating deeper cracks and more pronounced curling. Bitumens with a lower PI were more resistant to the effect than those of higher PI, whilst those blown bitumens with the same softening point gave better performance with increasing stiffness. Filled coating compounds tended to produce a better result than unfilled materials of the same composition, but the effect was relatively small. Comparisons of polymer modified materials showed that those of higher polymer content were the most resistant to damage. The ranking of bitumen/TR and bitumen/APP was difficult because the APP tended to produce a rougher surface texture of the overall coating with many broad shallow grooves, whilst the bitumen/TR tended to produce a relatively smooth surface with some deeper cracks.

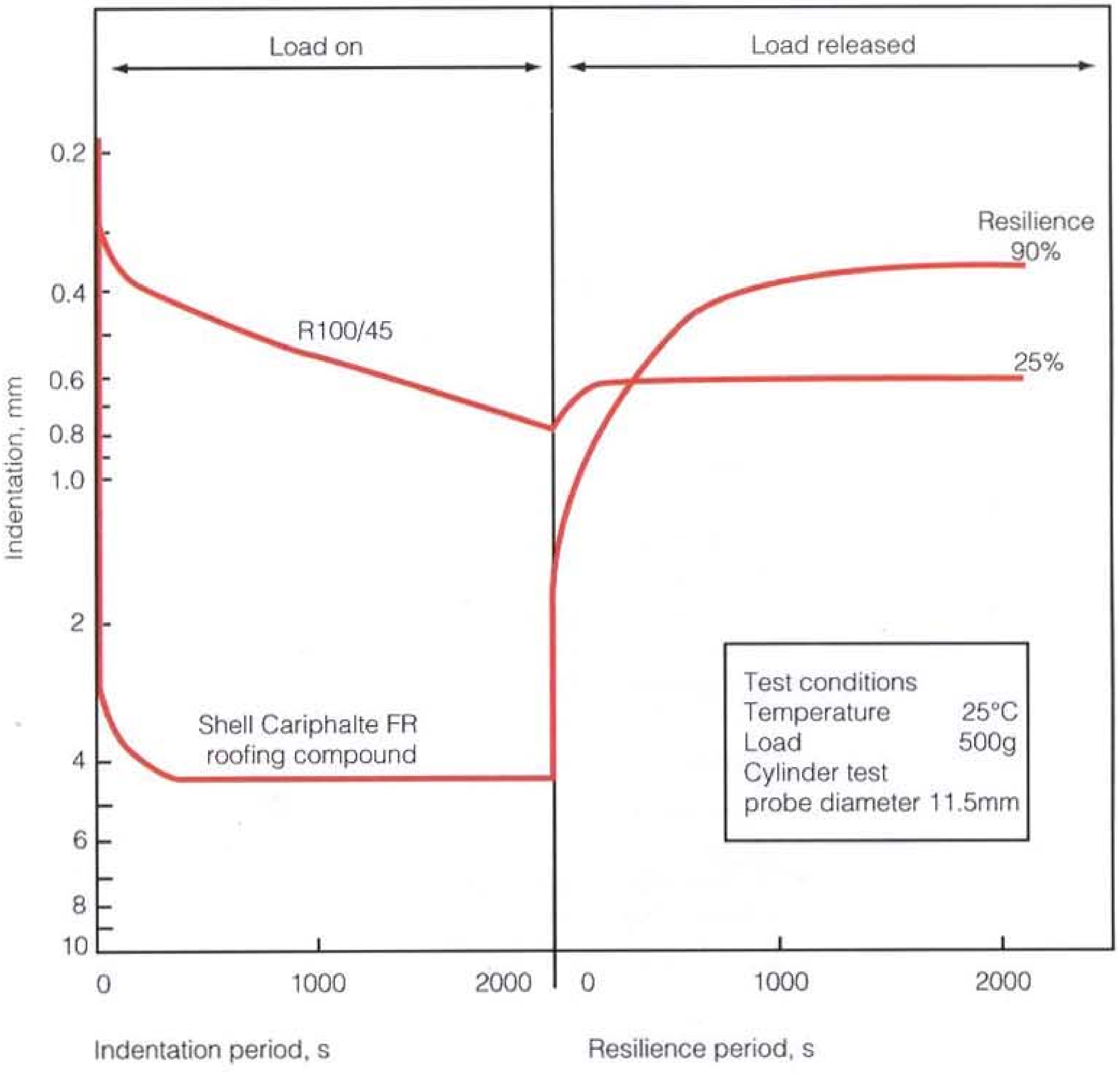


Figure 8.16 — Indentation set and elastic recovery of bitumens

The occurrence of mud curling can be avoided by taking some simple precautions:

- Ponding. Airborne materials can be swept into ponded areas on roofs. As the water evaporates the extraneous matter is deposited and accumulates to form a coherent layer on the upper roofing sheet. To avoid this situation care should be taken to eliminate localised depressions and ponded areas from the roof.
- Chippings. The cap sheet should be protected using gravel or chippings in order to reduce the shear forces on the bituminous layers generated by the drying mud. Good adhesion of the ballast should also be ensured during their application.
- Thickness of upper felt coating. The thickness of the bituminous coating on some roofing felts may be less than 0.5 mm between the carrier and the layer of chippings. This layer may be too thin to bond adequately to a sufficiently thick chipping layer. This could lead to chipping disbondment with subsequent exposure of the smooth upper coating or even the carrier.
- Use of filler. The use of filler in the coating will improve the resistance of a felt to mud curling, however, this advantage is relatively small.
- PI of blown bitumens. Lower PI bitumens should be used where lower temperature susceptibility and/or flow properties of these grades are adequate to meet performance requirements.
- Coating compound. A high content of TR in a bituminous coating will substantially reduce the risk of mud curling due to the greater ability of the coating to absorb strain in the coating layer.

8.2 Damp-proof courses

Damp-proof courses are used to prevent the movement of water through the walls or floors of buildings and other structures. Horizontal courses prevent water rising vertically through the wall; vertical damp-proof courses or tanking prevent the horizontal movement of water through underground walls. There are three types of damp-proof courses:

- liquid applied bitumen layers;
- membranes;
- mastic asphalt.

A bitumen layer can be applied to walls or to floors as a non load-bearing layer about three millimetres thick between two layers of cement concrete. The bitumen can be applied either as an emulsion or as a solvent-based solution. Mexphaltes 50 and 70 pen are used for this purpose.

For load-bearing walls a waterproof felt, similar to a roofing felt must be used. These felts are made in exactly the same way as roofing felts but are usually heavier at around 3 - 4 kg/m^2 finished weight. In all cases the bitumens used are the same as for roofing felts, eg 200 pen as a saturant and blown grades for coating. Damp-proof felts may also contain a layer of

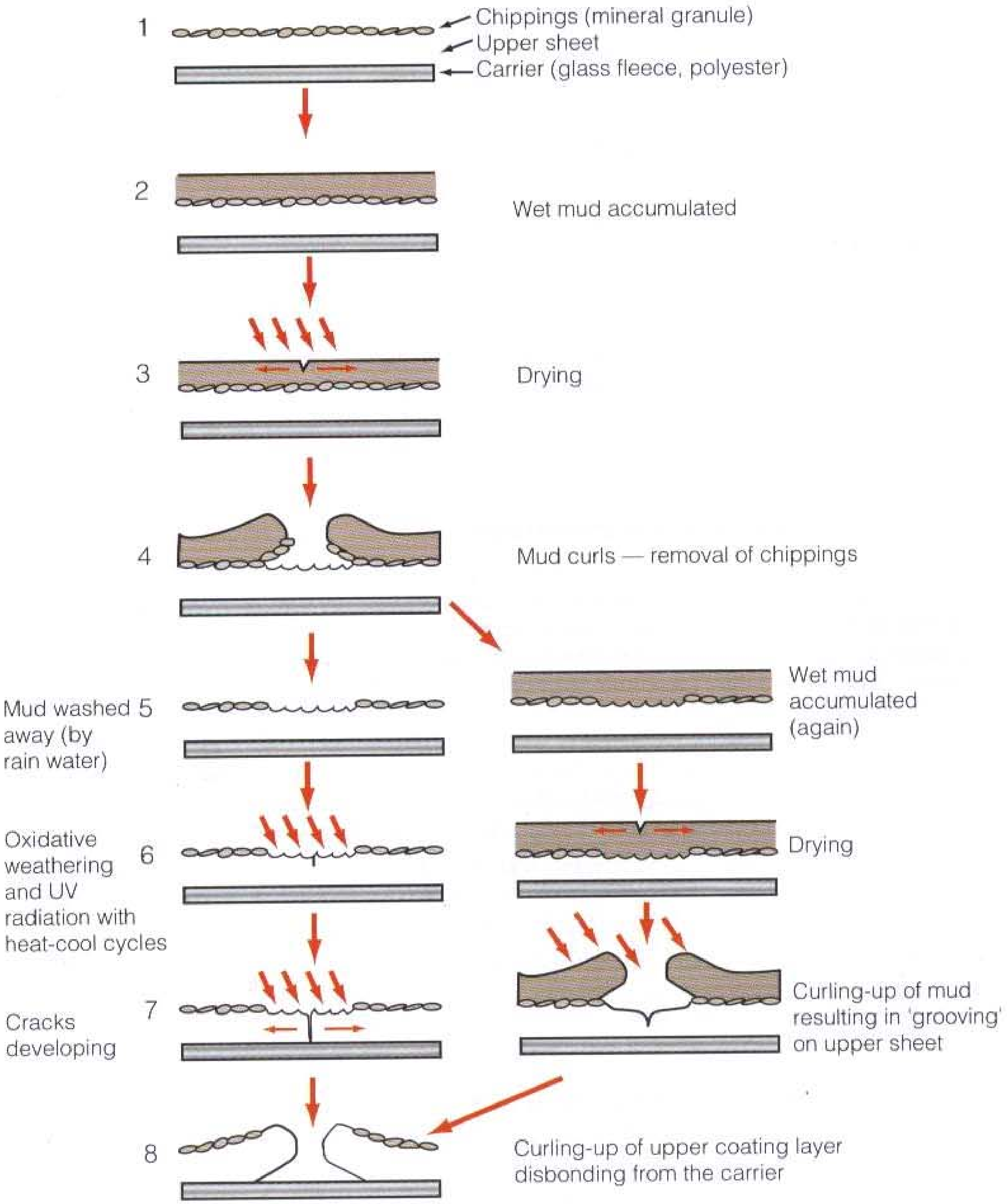


Figure 8.17 — Mechanism to explain mud curling on bituminous roofing

lead, copper or aluminium foil for greater security.

Felts can also be applied to vertical walls using the same materials and methods as on roofs. Increasingly, cold-applied self adhesive membranes are being used. These materials are based on bitumen/thermoplastic rubber, see section 9.3.

8.3 Waterproof paper and board

Bitumen is widely used for the waterproofing of paper and boards for packaging and building (cardboard, chipboard, hardboard etc). The choice of bitumen depends on the process used and is usually a matter of compromise:

- soft bitumens given good penetration of the paper or board at low treatment temperatures and the finished product is flexible, but its surface may be tacky;
- hard bitumens require higher coating temperatures and give a more rigid product but a less tacky surface which is capable of being used at high temperatures.

8.3.1 Impregnation of paper and boards

The paper or board is immersed in a bath of hot bitumen at a temperature such that the viscosity is less than 200 cSt (0.2 Pa.s) Lower viscosities can be used to give lower residence times and higher throughput. Boards may be treated under pressure in an autoclave. Paper is also impregnated by application of bitumen to one or both sides by means of rollers and then passing over hot rollers. The paper or board is of such a porosity that it will absorb bitumen easily. Its water content must be lower than about six per cent to avoid foaming. Papers are produced at weights varying from 80 - 400 g/m^2 with a bitumen content at around 40 - 50 per cent. Mexphalte 200 or Mexphalte 100 containing up to 10 per cent paraffin wax is normally used. Where non-tackiness is essential, or a high degree or rigidity is required, H grades (usually H80/90) with ten per cent wax can be used.

Impregnation temperatures vary between 130 and 180°C depending on the grade used and the strength of the paper or board. Boards are sometimes impregnated cold by dipping in a bitumen solution. Mexphaltes R80/25 or H80/90 in trichloroethylene are used.

If coating without impregnation is required the same hot-coating techniques are used but with harder bitumen such as Mexphalte H100/120, H80/90 or R115/15 to which five to ten per cent of paraffin wax is added.

8.3.2 Laminated paper and boards

These products consist of two or more layers with a film of bitumen as adhesive between them. The bitumen is applied by means of rollers to one or both surfaces which are then pressed together. A fibre or other reinforcing material (aluminium or copper foil) may be included in the sandwich. Both smooth and crepe laminated papers are produced at weights from 100 to 400 g/m^2 with a bitumen content of about 25 per cent. Mexphaltes R75/30 and R85/25 are commonly used or R115/15 for hot climates.

Bitumen may be incorporated as an emulsion into the slurry of fibres and water during the manufacture of the paper and board. The finished paper or board is passed between heated rollers until the bitumen spreads throughout the fibres. Special emulsions of hard bitumens such as Mexphaltes 15 pen or H80/90 are used.

8.4 Adhesives

8.4.1 Requirement of the binder

Bitumen is an excellent adhesive. On moderate warming it becomes sufficiently fluid to be easily applied, it tends to stick to most dry surfaces, and at ambient temperatures it is sufficiently stiff to provide a firm location for the article concerned. The choice of grade usually depends on the avoidance of brittleness at the service temperature. This is usually achieved if the penetration is greater than 15 - 20 dmm. Subject to this limit and assuming there are no difficulties with high application temperatures, low penetration grades should be chosen in order to minimise flow or slip under shear stress. In cases where the adhesive will be subject to significant shear stress, the softening point should be 50°C above the service temperature. These two requirements can usually be met by choosing blown grades such as Mexphalte R85/25 or R115/15.

8.4.2 Priming

The bitumen is applied hot or, in cases where this is unsatisfactory because of, for instance, too rapid cooling, in solution form. In hot applications the use of primer is advised to ensure good adhesion. The primer should be based on the same bitumen that is being applied and could be, for example, a 50 per cent solution in an aromatic solvent.

8.4.3 Wetting agents

Wetting agents can be added to bitumen to increase the stickiness of the adhesive. Wetting agents are highly polar, surface active compounds which have the effect of decreasing the angle of contact between bitumen and substrate. They increase the wetting ability of the bitumen and some will even enable the bitumen to displace water.

8.4.4 Flow

All bitumens flow under long loading times. If the stress is known the flow can be estimated by calculating the stiffness of the bitumen under the loading conditions of time and temperature (see section 5.9). If the application is such that the adhesive will be subjected to substantial stress for a long period of time, then it must be reinforced by mechanical means, such as pegging or nailing. Flow resistance can be increased by the incorporation of five to ten per cent by mass of fibrous filler in cases where flow caused by shear stress is expected to be a problem.

8.4.5 Applications

8.4.5.1 Floor tiles (including parquet floors)

A typical adhesive would be based on Mexphalte R85/25 or R75/30 which can be applied hot to give a coating of about 0.5 mm thick. Alternatively the bitumen can be mixed with 25 per cent of an aromatic solvent and applied cold but care is needed to avoid staining problems. A fibrous filler is often added to modify the flow properties of the bitumen.

8.4.5.2 Plastics

In general, standard bitumen and solutions are not recommended as adhesives for plastics or polymers.

8.4.5.3 Roofing felts

Roofing felt adhesives are invariably selected from the blown grades (see section 8.1.3.8.2). Mexphalte R95/25 is most widely used but Mexphalte R105/35, R95/25 and R115/15 are also used for cold, medium and hot climates respectively. Mexphalte R115/15 is also used in moderate climates for steeply sloping roofs. Other grades used in Europe for this application are 90/40, 100/ 40 and 100/30.

8.4.5.4 Emulsions

In general emulsions are not normally used as adhesives because of the difficulty in losing the water after breaking. If the water is prevented from leaving the bitumen, the binder will not develop its full strength.

8.4.5.5 Polymer/bitumen adhesives

Many modern bitumen adhesives combine the good adhesive properties of bitumen with the elasticity of TR polymers. Cold applied adhesives can be used to fix roofing felt. Shell 'Tixophalte' is a cold-applied thixotropic adhesive which can be applied from a cartridge. It has excellent wetting properties and can be applied in wet conditions. It contains TR but because of its thixotropic nature does not produce strings, drip, flow or sag. It is used as an adhesive, sealant and as a general leak repair medium, see chapter 9.

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Chapter 9 - Bitumens used in the construction industry

9.1 Waterproofing for concrete bridge decks

9.1.1 General

Concrete bridge decks must be protected from the ingress of water, particularly during winter when it is likely to contain salt applied to de-ice roads. Regular use of sodium and calcium chlorides leads to deterioration of the concrete which can become porous and give rise to corrosion of the steel reinforcement. To be suitable, a waterproofing material needs to be:

- easy to apply
- able to withstand site traffic
- able to perform for a long time (greater than twenty years) as it is not normally renewed with the road surfacing
- unaffected by the high temperature of asphalt during laying
- able to withstand fracture if the deck slab develops cracks caused by shrinkage, thermal movement or traffic
- strongly adherent to the substrate and resistant to shear in service
- economic.

There are three classes of material which are commonly used for this purpose, namely mastic asphalt, prefabricated sheets, and resin systems, although this latter class is not discussed here.

9.1.2 Mastic asphalt

Mastic is usually applied by hand in two layers, each of about ten millimetres thickness. A second layer is always applied so that any blow holes, cracks or joints in the first layer are covered. Blow holes occur when water trapped in the pores or micro-cracks within the concrete vaporises and forces its way through the mastic while it is still warm. Blowing in the first layer is quite common and holes appear as small bulges three to six centimetres in diameter with often a small hole two to three millimetres in diameter in the centre. To prevent the formation of blow holes it is normal to blind the concrete with either sand or filler before the mastic is applied or, more usually, to apply a single layer of sheathing felt. The mastic applied directly on top immediately melts the coating bitumen but leaves in place the fibre reinforcement network which provides pathways for vapour to follow. Glass fibre mat can be used in place of the sheathing felt.

9.1.3 Prefabricated sheets

9.1.3.1 Flexible sheets

Sheets of roofing felt are used without a mineral finish. The sheets are adhered to the concrete with hot bitumen using either the pour-and-roll technique or using torch-on felts.

Because of the need to withstand site traffic, heavy weight felts incorporating polymer binders (both SBS and APP) are increasingly used.

As well as hot-applied sheets, cold-applied self-adhesive membranes are also used. These are usually of the bitumen/SBS type and are laid onto a primed surface. A protective second layer of rigid board would normally be applied to prevent damage by traffic.

9.1.3.2 Rigid sheets

Rigid sheets ten to fifteen millimetres thick, two metres long and one metre wide (approximately) are also laid using the roll-and-pour technique with hot bitumen adhesive. The sheets are similar to a very heavy roofing felt and are butt jointed. A second coating consisting of roofing felt is then applied to seal the joints, again using the roll-and-pour technique. Rigid sheets may be used as the waterproofing layer or may be applied as a protective over a thinner waterproofing layer underneath.

Photograph 9.1 — Torch-on roofing felt being applied to waterproof a concrete bridge deck. (Photograph courtesy of Cambridge Asphalt Co Ltd)

9.1.4 Choice of materials

The choice of available systems is huge and selection will depend upon a host of conflicting requirements including the engineer's personal preference. A strong reason for selecting mastic asphalt is that it is jointless(1). It has also been concluded from an independent study(2) that a large number of membrane failures are caused by poor workmanship, damage by site vehicles and application under poor weather conditions.

9.2 Bearing piles

In the 1960s the increasing use of reclaimed land and filled sites for building and construction resulted in a much wider use of piled foundations, but introduced a hitherto little recognised phenomenon - negative skin friction, see figure 9.1.

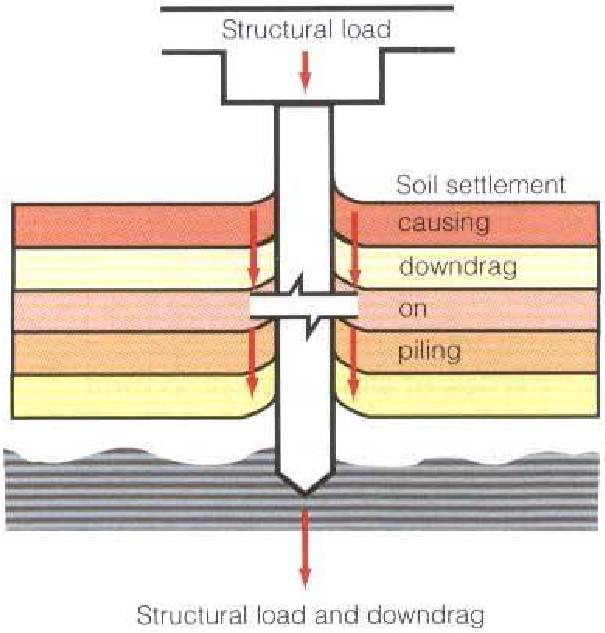


Figure 9.1 — Effect of soil settlement on a bearing pile

Settlement of fill, or similar soil movement due to superimposed loadings, was found to be capable of increasing the effective loading on piles by as much as 100 per cent or more of their design capacity. A bitumen compound was developed which, when applied at a suitable thickness, would shear within itself under the slow soil movements associated with ground settlement. In shearing, the compound transmits only a negligible proportion of the "downdrag" to the pile or other supporting surface.

Although this is the primary requirement, a number of other criteria have to be met to produce a practical and technically suitable material for general site use. In summary the material must:

- be applicable on site with a minimum of equipment;
- resist flow at ambient temperatures for long enough to install the piling without significant sagging of the coating;
- resist detachment when piles are hammered;
- resist possible upward flow due to horizontal soil pressures;
- resist significant penetration of coarse angular soil particles after driving;
- not reduce the effective soil support needed to prevent buckling of a pile.

Shell has developed Bitumen Compound SL[3,4,5,6,7,8,9] which conforms sufficiently closely to the range of requirements above to be acceptable from both the practical and technical points of view, see table 9.1.

Bitumen Compound SL is a solventless, hot-melt bituminous compound which is produced in two grades, Standard and Tropical, to cover most of the conditions likely to be encountered in service, except those of extreme heat and extreme cold. It is applied hot to

Bitumen Compound SL	Standard	Tropical
Colour	Black	Black
Method of application	By heating and pouring	By heating and pouring
Maximum heating temperature (°C)	180	190
Typical application temperature (°C)	150	160
Product density kg/m^3	1000	1000
Coverage	1 kg/m^2 per mm thickness (and pro-rata)	1 kg/m^2 per mm thickness (and pro-rata)
Flash point in container, (COC), (°C)	250 min	250 min
Storage life	Indefinite	Indefinite

Table 9.1 — Typical properties of slip layer compound

the surface of piles which can be driven as soon as the compound has cooled to ambient temperature. It is a visco-elastic solid and consequently it behaves like a hard rubber under the short loading times of piling hammer blows. This property enables it to be driven through a variety of soils without significant damage to, or stripping of the coating, so that the full thickness remains intact throughout installation of the pile.

Once in position, and when subjected to the much slower loadings resulting from consolidating or moving soil, the slip layer assumes fluid properties and shears within itself. It is this viscous shearing action which eliminates load transmission through the coating, caused by relative movement between its two surfaces.

The use of a slip layer compound in no way reduces the friction occurring between soil and pile during driving. It functions purely by shearing within itself after the pile has been installed. Although primarily intended for pre-cast or other driven piling, Bitumen Compound SL is equally suitable for in-situ piling where application is feasible.

Following the success of field trials, the first large-scale commercial contract using bitumen slip layers was awarded to the Dutch firm, NV Nederlandse Bouw-Maatschappij NBM at the beginning of 1971 for driving 2000 foundation piles for Shell Nederland Chemie plants at Moerdijk. Each pile was treated with a nine metre long bitumen slip layer, and up to 75 piles were treated per day. The first contract was completed in June and a further contract for another 3000 piles treated with bitumen slip layer was then placed with NBM.

9.2.1 The effectiveness of a slip layer

Downdrag loadings on uncoated surfaces due to soil movement are difficult if not impossible to predict with accuracy, and these can in practice considerably exceed the anticipated value. By using a slip layer, the effect of any excess loadings is largely eliminated as the coating transmits only a small percentage of any extra load. In this way, its use constitutes a valuable "insurance policy" against the potentially serious effects of loadings beyond the design limits of the piling.

Practical post-installation evidence of the effectiveness of Bitumen Compound SL is contained in a report(10) on the instrumented performance of coated piles supporting a road bridge abutment at Newhaven, Sussex. In addition, graphs of the percentage negative skin friction reduction actually measured on-site in Japan are given in figures 9.2 and 9.3(11).

Section 9.2.3.1 illustrates the calculation of loading transmitted through a slip layer. As a guide, however, the reduction of downdrag load due to negative skin friction, or other soil movement, when using an appropriate thickness would exceed 90 per cent.

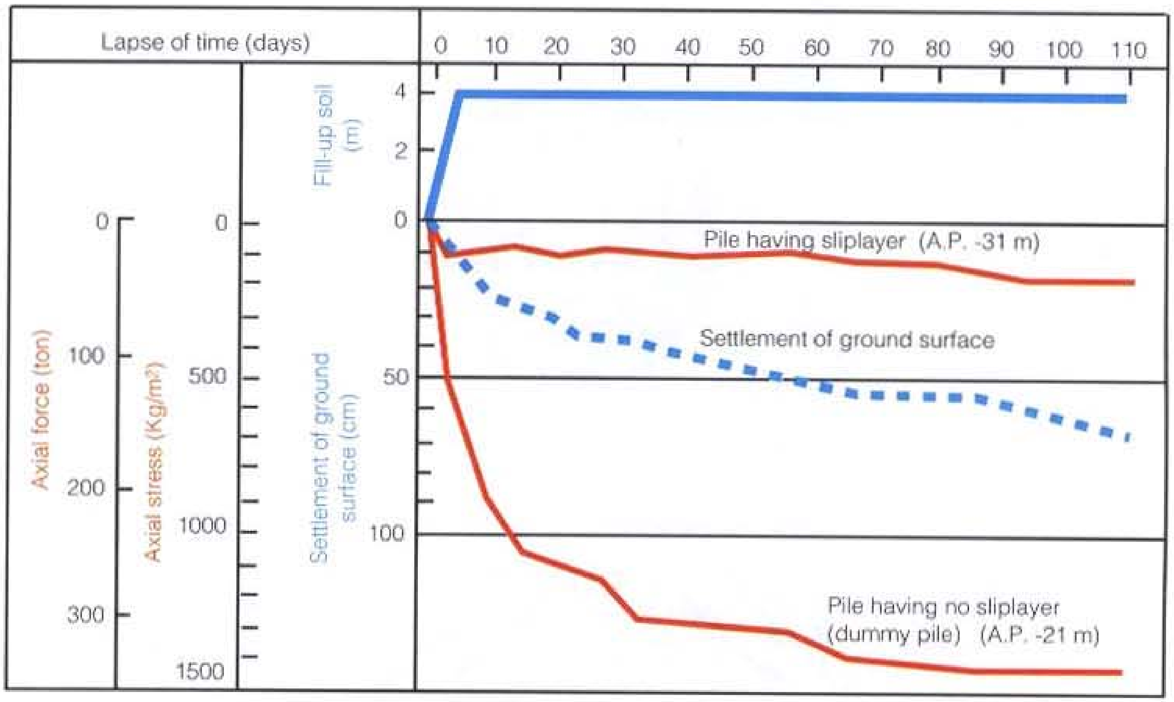


Figure 9.2 — Change with time of axial force on pile (11)

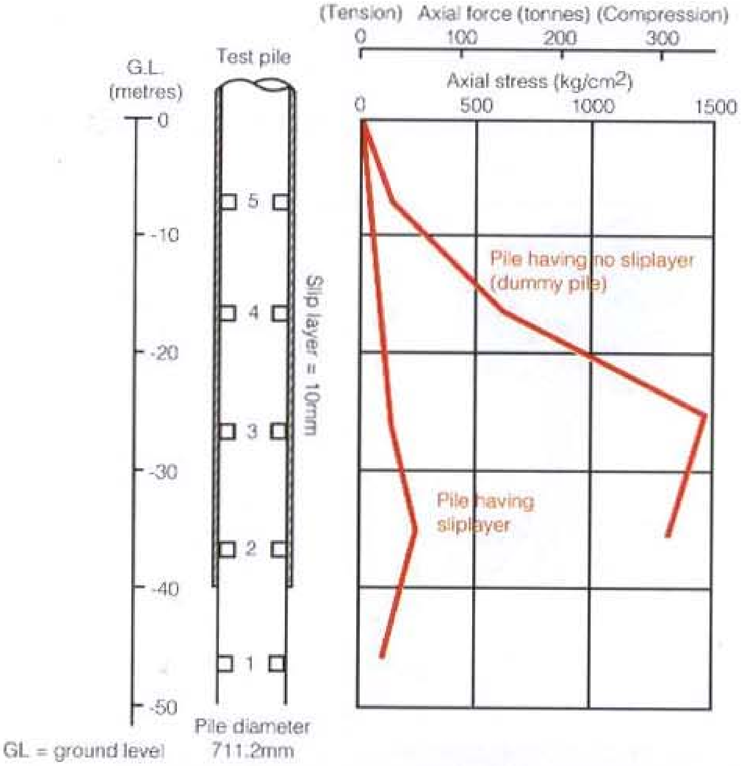
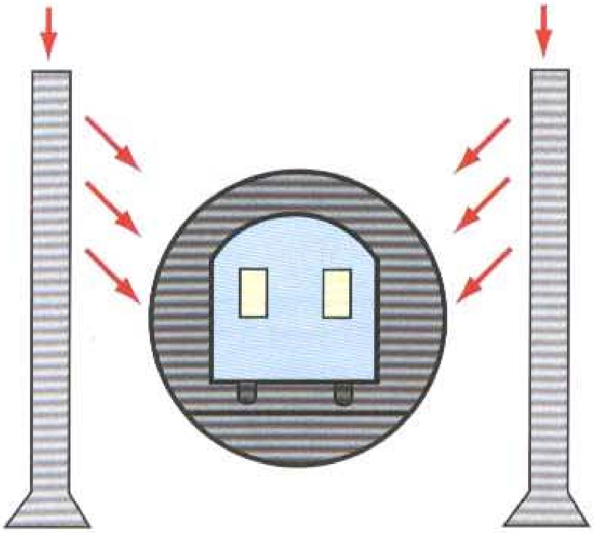


Figure 9.3 — Distribution of axial force on pile(11)

Figure 9.4 — Load transfer from pile shaft to tunnel



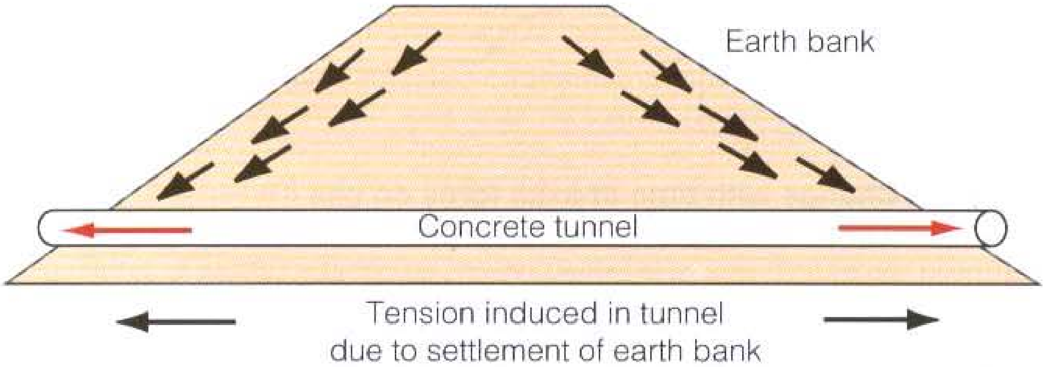
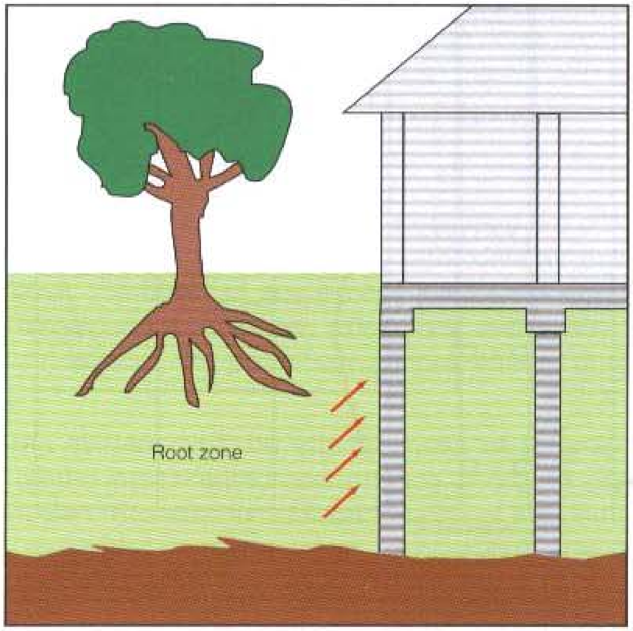


Figure 9.5 — Frictional loading on buried surfaces, eg earth bank

Figure 9.6 — Upthrust and down-drag on piling caused by seasonal shrinking and swelling of clay near tree root zone



9.2.2 Uses

Typical conditions where the use of a bitumen slip layer can prove highly effective include:

- piling subject to negative skin friction and superimposed soil loadings;
- prevention of structural load transfer from piling to adjacent sensitive underground structures (eg rail tunnels), see figure 9.4;
- prevention of frictional loading on buried surfaces eg basements, tunnels, old foundations and sheet piling, see figure 9.5;
- "clay-heave" situations in piled building foundations, see figure 9.6;

and many more where relative movement between solid and buried surfaces can cause unacceptable additional loading.

9.2.3 Load transmission through Bitumen Compound SL

Where a pile or other structure is to be coated with a bitumen slip layer compound, the frictional drag, caused by moving soil, transmitted through the coating, is a function of:

- temperature of coating (ie soil temperature);
- expected rate of settlement or movement of soil;
- thickness of coating;
- flow characteristics of the coating under load.

The temperature, rate of settlement and coating thickness are generally easy to obtain, or to assume. The flow characteristic under load is more complex and involves detailed knowledge of the behaviour of the slip layer compound under different conditions. However, in order to avoid complicated calculations for every individual situation, a range of constants (K), which take into account the flow characteristics of the coating, have been calculated. These, when incorporated into the appropriate formula, enable an approximation of the downdrag, or other type of loading transmitted through a coating of Bitumen Compound SL, to be obtained.

In devising the formula, it has been assumed that there is a 100 per cent bond between the soil and the coating, and between the coating and the surface to which it is applied. This is the worst situation and anything less than 100 per cent bond at both faces will result in a reduced load transmission from the moving soil through the coating to the structure.

9.2.3.1 Calculation of stress transmitted through a coating of Bitumen Compound SL

$$\text{Stress} = K \times \frac{g}{c}\ \text{N/m}^2 \text{ of surface area}$$

where: K = constant, see tables 9.2 and 9.3

g = anticipated rate of ground settlement or movement (mm/year)

c = coating thickness (mm).

To obtain the total load transmitted, the resultant figure is multiplied by the surface area over which the soil movement is expected.

Average soil temperature °C	5	6	8	10	12	14	16	18	20
K value	16.8	13.4	8.4	5.0	3.0	1.7	0.95	0.5	0.33

Table 9.2 — Bitumen Compound SL (standard grade) values for constant, K

Average soil temperature °C	12	14	16	18	20	22	24	26	28
K value	436	234	140	86	56	40	25	17	10

Table 9.3 — Bitumen Compound SL (tropical grade) values for constant, K

It should be noted that although the settlement (or movement) is expressed in terms of mm/year, this may not be the amount of settlement occurring over twelve months. If, for example, most of the settlement were expected in the first six months, amounting to say 100 mm, this would be entered in the formula as 200 mm/year ie the maximum rate of settlement, expressed in terms of mm/year.

9.2.3.2 Values for constant, K

The values for the constant, K, are related to the temperature of the coating, ie the anticipated soil temperature. Soil temperatures in the UK are generally of the order of 10°C. However, tables 9.2 and 9.3 provide K values for a range of soil temperatures, applicable to the Standard and Tropical grades of Bitumen Compound SL respectively.

9.2.3.3 Example calculation

This section gives a simple method for the estimation of the downdrag due to ground settlement. Some authorities and consultants may favour the use of other methods for computing this information.

For maximum security (resistance to mechanical damage, resistance to long-term penetration by soil particles, application errors, etc), ten millimetres can be considered to be the appropriate coating thickness. However, depending upon the degree of ground settlement, soil constituents, anticipated duration of settlement and other factors, this can be reduced, but should never be less than three millimetres. Generally a thickness of six millimetres is regarded as a suitable optimum.

Using the Standard grade of Bitumen Compound SL on end-bearing piles in a region where a rate of ground settlement of 250 mm/year is anticipated:

- From table 9.2, K for 10°C = 5.0
- Coating thickness is assumed to be 6 mm
- The downdrag stress transmitted through the coating is therefore:

$$\frac{5.0 \times 250}{6} = 208 \text{ N/m}^2$$

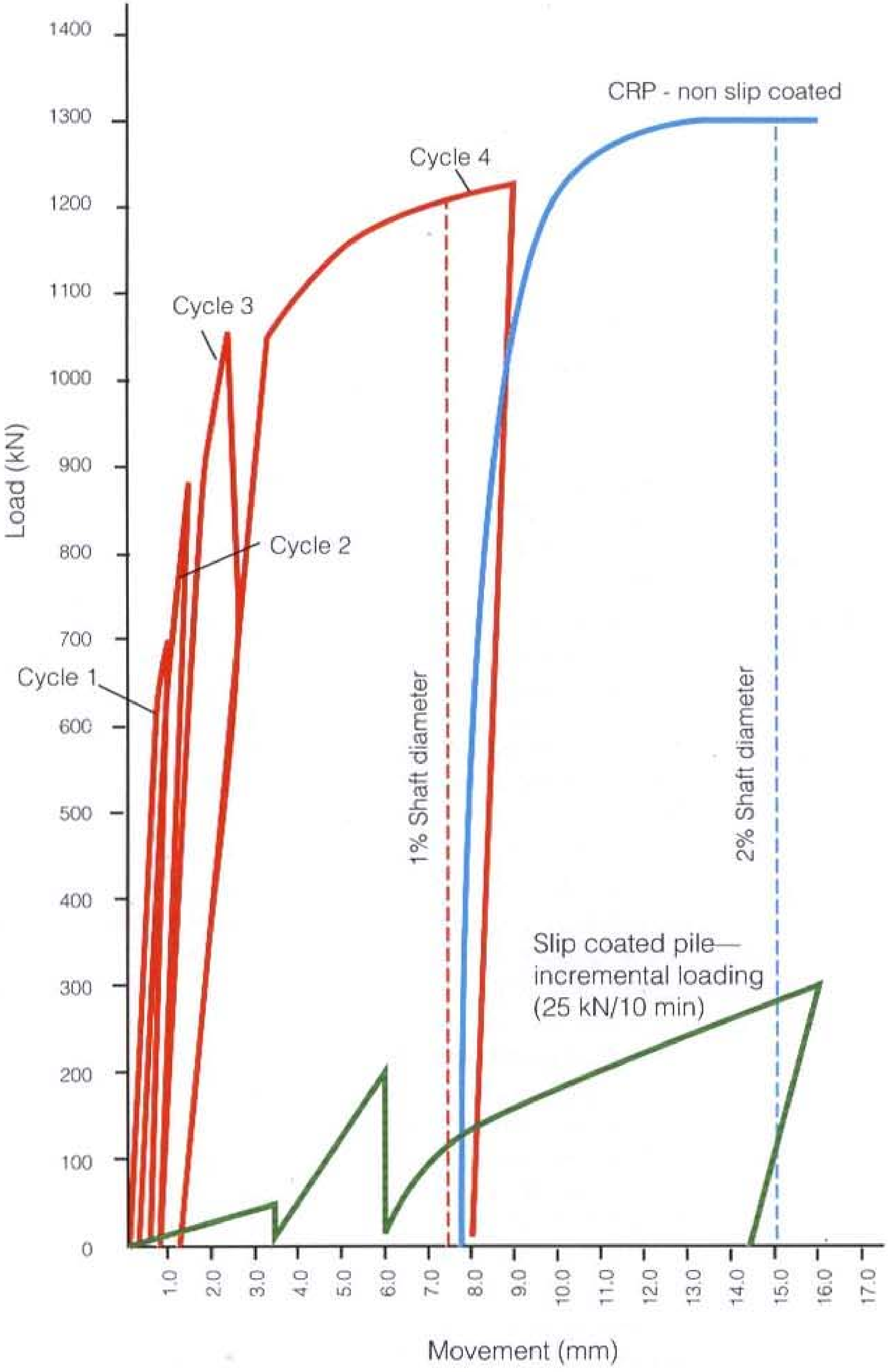


Figure 9.7 — Effectiveness of Bitumen Compound SL. Results of loading tests on coated and uncoated piles (Reproduced by kind permission of Ove Arup & Partners)

If the surface area of the pile subject to soil movement were say, 25 m^2, the total downdrag load on the coated pile would be 25 x 208 = 5.2 kN.

It is suggested that a safety factor of two is used to allow for temperature and other variations; therefore, in the above example a total downdrag of say 10 kN would represent a safe working load. This, in practical terms, would be considered negligible. The downdrag load on uncoated piles is difficult to predict accurately, but in general the reduction in downdrag loading by using an appropriate thickness of Bitumen Compound SL would exceed 90 per cent, see figures 9.2, 9.3 and 9.7.

9.2.3.4 Test-loading of coated piles

Where piles which have been coated with a bitumen slip layer compound are to be test-loaded, the following points should be borne in mind:

- This should always be done in comparison with an identical uncoated pile installed to the same depth and in the same location as the coated one. The two piles should, however, be far enough apart for there to be no loading influence between them.
- The coated pile should be in the ground for a long enough time to allow the temperature of the coating to stabilise with the ground temperature, before loading. This is especially important where test piles are constructed in situ, the coating having been pre-applied to a permanent casing. Heat created by hydration of the cement during setting can raise the temperature of the coating well above that of the soil. If test-loading is carried out before the coating temperature has reverted to the soil temperature, the results are likely to be of little value unless the actual coating temperature can be measured.
- The formula for calculating the anticipated rate of pile settlement under loading should be regarded as a guide to performance rather than an accurate prediction. This is because:

    of necessity loading is carried out over a relatively short time and the relationship between load transmitted and the time during which it is transmitted, is not necessarily straight-line;

    relatively small variations in coating temperature can have a significant effect on load transmitted (see tables 9.2 and 9.3); although when performing in service any total load variation from this cause is likely still to be negligible; it can be wrongly interpreted when measuring actual values recorded during short-term loading tests; these cannot of course correspond to the conditions to which the piling will be subjected in service;

    it is virtually impossible to ensure a precise and uniform coating thickness; as the load transmitted through the coating is directly proportional to its thickness, any variation in uniformity and/or thickness is likely to reflect in the test results.

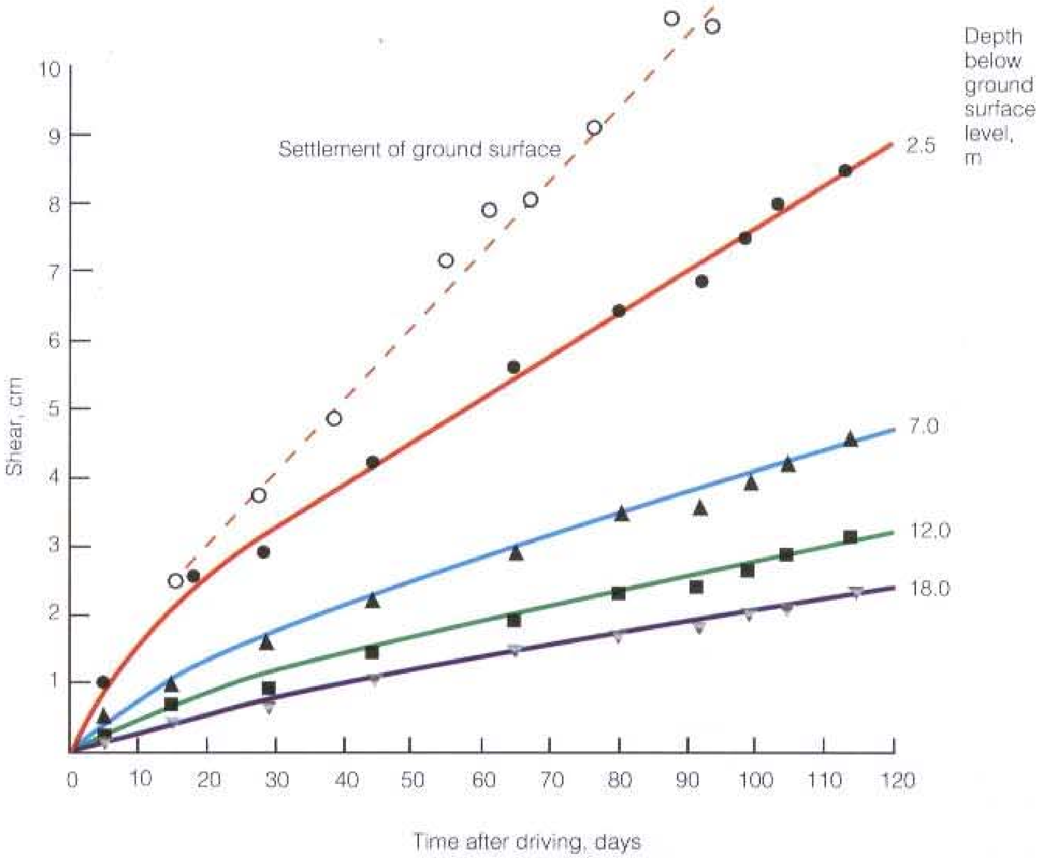


Figure 9.8 — **Shear in a bitumen slip layer at 8 mm from the pile surface and at different depths as a function of time**

9.2.3.5 Measurements on coated concrete piles at Moerdijk

A trial with bitumen slip layer compound on bearing piles was conducted at the Shell Nederland Chemie plant near Moerdijk in Holland to check whether the negative friction that would be expected could be reduced sufficiently to make the method economically attractive.

The shear in the bitumen layers was measured at regular intervals over a period of about four months after driving. Figure 9.8 shows, for one of the test piles, the shear in the bitumen layer at about 8 mm from the concrete surface and at different depths below the surface of the soil, as a function of time. In figure 9.8 the settlement of the surface is also represented. From the measurements it appears that, after a short time, the shear of the bitumen layer proceeds almost linearly with time, ie in the circumstances (long loading time) the bitumen practically behaves as a viscous liquid.

The relationship between the shear in the bitumen layer and the distance to the pile surface is only by approximation a linear one. In the trial, the shear rate at the surface of the ten millimetre thick slip layer was found to be a factor of about 1.3 greater than the rate at eight millimetre distance from the pile surface. Using the same factor, the shear stress was calculated at different depths along the slip layer of the pile. Calculating the total shear force (negative friction) by integrating the shear stress over the total layer surface, a value of about 3×10^4 N, ie about three tonnes, was found.

9.2.4 Suitable piling systems

Bitumen Compound SL can be used with most piling systems either as they are, or with appropriate modifications. As a hot-melt compound which solidifies by cooling, it has to be pre-applied before piling is installed. This can be carried out on such piles as:

- pre-cast concrete (including "shell") piles,
- H-section steel piles,
- circular steel casings,
- steel sheet piling,

and is usually applied on site.

It cannot be used on continuous flight auger or similar in-situ piling unless some form of precoated liner can be installed in the shaft prior to concreting. Such a liner need only be substantial enough to support the coating until concreting has been completed.

Slip layer compound has been successfully applied to in-situ vertical surfaces such as concrete walls and columns and on brick walls and piers (eg to isolate them from externally superimposed loadings). A practical technique has been established for this, which consists of "casting" panels of slip layer compound onto Kraft paper, then applying the panels while still warm to a primed surface.

In most cases, slip layer compound is required to be installed through relatively soft, compressible soils, which are the ones most likely to create negative skin friction. In some cases however, the coated piling has to be installed through denser layers of sand/gravel due to the characteristics of the strata concerned.

Firmly adhered slip layer compound provides a tough abrasion-resistant coating under hammer-blow loading times, and when driven through sand of medium density should suffer little damage except at the leading edges. The denser the sand or the harder the ground, the greater is the possibility of damage to the coating and where doubt exists, it is safer to drive test piles and/or consider alternative methods of installing the piles. The latter might for example consist of pre-boring using a CFA rig and injecting Bentonite slurry instead of grout to maintain the bore. The coated piles are then installed through the slurry.

Whatever the conditions, however, where coated piles have to be driven, the most important requirement is that the slip layer compound is firmly bonded to the pile surface. It is always wise to test the adhesion before driving the pile.

9.2.5 Application of slip layer compound

9.2.5.1 Area to be coated

Normally, only that part of the pile upon which negative friction is anticipated needs to be coated. Those parts of a pile which rely primarily upon positive friction for their bearing capacity should be left untreated. A distance of about ten times the pile diameter (or width) from the bottom should be left untreated to avoid adverse effects on the pile bearing capacity. This is not so important if piles are driven to set on rock, ie are purely end-bearing.

9.2.5.2 Condition of surface to be coated

Concrete should have cured sufficiently to achieve its required strength and concrete piling should also be allowed to cure out of the moulds as long as possible prior to coating, to permit maximum dissipation of internal moisture. Excess moisture, if trapped, could adversely affect adhesion of the hot-applied compound. The pile surfaces should be clean, dry and free from laitance prior to priming.

Steel surfaces should be clean, dry and free from any poorly adhered coating, loose rust or mill scale.

It is important that any surface (including primed surfaces) to which slip layer compound is applied should be dry, as the presence of free moisture could impair adhesion. This includes frosted surfaces which may appear dry but become wet as the hot bituminous compound instantaneously melts the ice particles.

9.2.5.3 Priming

Bitumen Compound SL will bond tenaciously to most completely clean dry surfaces without a primer. In practice, however, such a clinical condition is rarely achieved, so concrete and steel surfaces should always be primed first - with one exception:

> Steel surfaces which are grit-blasted down to bare, clean steel, and all remaining dust/powder removed, can be coated with slip layer compound without the prior application of a primer provided this is done immediately and before the cleaned surface has started to oxidise or collect dirt.

To prime steel or concrete surfaces, apply primer by brush or spray at about 0.2 litres/m^2 and allow to dry completely before over-coating. The primer normally dries in several hours but it is probably safer to allow it to dry overnight before applying the slip layer compound.

9.2.5.4 Application techniques

Slip layer compound should first be melted by heating gently to about 150°C. In order to avoid localised overheating a double-skinned bitumen boiler should be used. Application techniques will vary depending upon factors such as:

- shape and type of pile,
- pile length,
- number of piles to be treated,
- whether to be treated on site or elsewhere.

9.2.5.5 Minor damage

Minor damage to the coating (eg from slings or small scrapes), or localised surface irregularity has no significant effect on overall reduction of downdrag. If, however, the bitumen is completely removed over small areas, it is advisable to fill these in to ensure continuity of coating.

9.3 Protective membranes

Protective membranes are used to protect structures from damage by water, salts in ground water or from ingress of water. They are used extensively on concrete structures where corrosion of reinforcing steel is prevented and are used both vertically and horizontally. Originally roofing materials were used, both felts and mastic asphalt, but these have now been joined by high-performance bitumen/polymer membranes. These membranes are normally self-adhesive and applied cold. They are supplied with a plastic film on the surface for ease of handling and have a peel-off backing to reveal a self-adhesive face. Being only one to two millimetres thick, they easily follow the contours of the structure. To ensure maximum adhesion the structure must be clean and dry and is normally primed with a highly penetrative bituminous primer. For vertical faces of in-ground structures where such membranes have been applied it is essential to add an appropriate protection board to prevent squeezing of the soft bitumen material when ground compaction is effected next to the buried vertical surfaces.

Most membranes of this type use similar formulations to premium roofing felt, eg a soft bitumen such as 200 pen containing about ten per cent of an SBS polymer and specially formulated to have strong self-adhesive properties. The membranes are often carrierless, that is, they are not based on a woven mat for their dimensional stability.

Typical applications for this type of product would include:

- concrete bridge decks,
- lining water towers and reservoirs (iron and concrete),
- earthworks against concrete bridges,
- cellars, underground car parks etc.

9.4 Bituminous sealants and adhesives

It is in the nature of buildings and constructions that wood, brick, concrete, metal, asphalt and other surfaces contain cracks, discontinuities and joints which require to be filled to preserve the integrity of the structure and to protect it from the ingress of water. Not only are there discontinuities in construction work, but the sizes of the discontinuities tend to change as a result of the natural drying and shrinkage of building materials and the expansion and contraction of the structure due to diurnal temperature changes and seasonal temperature variations. Temperature variations in particular may induce complex behaviour in a structure as different materials expand and contract at different rates(12,13), see table 9.4.

Exacerbating the interaction between materials in a structure is the phenomenon known as thermal shock. This is produced when ambient temperature either rises or falls considerably over a very short time interval, perhaps through cooling by rainfall or due to sudden shade on an otherwise hot and sunny day. The consequences of thermal shock for a building structure are usually rapid and repeated dimensional changes at joints.

The most commonly encountered form of movement in a building is associated with shrinkage due to loss of moisture from hygroscopic materials such as timber and concrete. This, too, is a cyclic process related to atmospheric relative humidity and some examples of movement in materials caused by the influence of moisture are given in table 9.5.

Materials	Linear coefficient of expansion 10^{-6} per degree C
Brickwork (horizontal)	5.9
Brickwork (vertical)	8.3
Glass	8.5
Granite	9.0
Concrete	16.2
Steel	16.2
Copper	16.6
Aluminium	25.2

Table 9.4 — Coefficients of expansion of various building materials

Material		Movement, per cent	
Concrete	- drying shrinkage	0.05	
	- wetting expansion (moisture movement)	0.03	
Brickwork (12)	- allow for movement equal to half the thermal expansion		
Timber(13)		Tangential	Radial
	- Douglas fir	15	1.2
	- Iroko	0.78	0.5
	- Mahogany	1.9	1.5
	- English oak	2.5	1.7
	- Parana pine	2.5	1.7
	- Western red cedar	1.9	0.8

Table 9.5 — Movement of building materials under the influence of moisture

In order to minimise the effects of dimensional changes in a building or structure, expansion joints are designed into them. Having deliberately created a discontinuity, a sealant must be used to fill the joint. The sealant must be weatherproof under all conditions, must be durable without cracking or disintegrating and should absorb movement without transmitting disruptive forces from one element of the structure to the next.

9.4.1 Properties of a sealant

The modern sealant industry began in France during the eighteenth century with the invention of linseed oil putty(14) - the word putty dervies from the French 'potée' which in rough translation means 'a pot full' - and putty is still extensively used in glazing. Modifications to linseed oil by heat treatment and blending have extended the application of linseed oil to the series of sealing compounds known as oil based mastics. Improvements to sealant performance have kept pace with changes in the building industry as materials have progressed through natural rubbers to synthetic rubbers, providing materials which can seal joints which are under continual strain, non-setting movement accommodation sealants, compression joint sealants and gaskets.

The basic service characteristics required from a sealant include:

- deformability,
- flexibility,
- resistance to flow,
- thermal stability,
- durability,
- adhesivity.

The requirements for a sealant are extremely complex as it must be mobile and readily deformable in order both to facilitate its application and to take up movements in the building structure when in service. However, it must also be flexible and be capable of absorbing cyclic movements without permanent distortion. Once in the joint, the sealant should exhibit thixotropy and not flow under its own weight, even over a long time scale. Its properties must be maintained over a wide thermal spectrum to prevent excessive changes in viscosity or ageing. The sealant must be resistant to the effects of water, UV radiation and weather without hardening or stiffening in service whilst maintaining strong adhesion to the substrate.

These characteristics may be provided by a combination of a liquid binder and a fibrous or powdered filler. Bitumen has been widely used as the binding medium for joint sealants in compositions which may also contain polymers to enhance flexibility, elasticity and cold temperature properties.

Bitumen based sealants provide adequate adhesive strength to withstand the normal stresses and strains encountered in a building joint. The adhesive strength of sealants, while difficult to define adequately, is generally sufficiently high and is usually greater than the cohesive strength of the bulk of the material. It is the balance between adhesive and cohesive strength which is important in order to maintain the seal. The stresses and strains caused by joint movements are readily neutralised by the distortion of the sealant. Bitumen sealants often show very good adhesion and in time become tough and difficult to remove. However, at low temperatures they can become very hard and brittle. It is at low temperatures that joints may open and the sealant be exposed to tensile strains. In this instance, the force required to stretch the hardened bitumen sealant may be greater than its adhesive strength, resulting in the inevitable failure of the bond. Nevertheless, bitumen sealants, overall, provide a sound compromise and are worthy of consideration especially where colour is unimportant and joint movement is likely to be small(14). The more recent developments in bitumen based sealants which incorporate polymers and thixotropic bitumens extend the service temperature range, adhesivity and flexibility of these materials quite considerably.

9.4.2 Bituminous sealing and adhesive compounds for buildings and construction

By far the commonest sealing materials found in building and construction work are the bituminous roofing materials such as roofing felt, underslating felts, damp proof courses and tanking membranes which are covered in chapter eight, and the liquid roofing systems such as Flintkote which are covered in chapter six. This section will concentrate on that group of bituminous materials used as adhesives and joint sealants.

9.4.2.1 Joint sealants for roads

Bituminous joint sealants are commonly used for sealing expansion joints and shrinkage cracks associated with concrete carriageways. Concrete pavements are subject to stresses caused by thermal expansion and contraction and to the effects of moisture content. If these stresses are not accommodated, then uncontrolled cracking of the concrete can occur, especially where long continuous lengths of carriageway have been constructed. The normal method employed to alleviate this type of problem is to install expansion joints at regular intervals along the carriageway so that expansion and contraction of the concrete can occur without damage. In order to preserve the integrity of the pavement this joint must be filled and this is commonly achieved using a bituminous joint sealant, see figure 9.9. This type of expansion/contraction joint is commonly installed across the carriageway but may be required to be installed along the carriageway, particularly where the carriageway slab width exceeds four to five metres.

Another problem associated with concrete carriageways is that of shrinkage cracking due to the setting process which induces stresses in the concrete slab. These stresses may be relieved by random cracking of the concrete slab. In order to prevent random cracking of the slab, contraction joints may be provided in the slab to relieve these stresses, see figure 9.10. The contraction joint is made by placing a layer of building paper against one surface of the slab before casting the next section to it. This prevents adhesion of the abutting concrete faces. The joint so formed may not necessarily be filled and the concrete faces are abutting. Reinforcement is not continued through the joint and where dowel bars are present, they must be coated with release agent on one side of the joint to accommodate movement of the joint. Slots of about 20 mm width and 25 mm depth are provided at the top of this joint which is normally filled with a bituminous sealant.

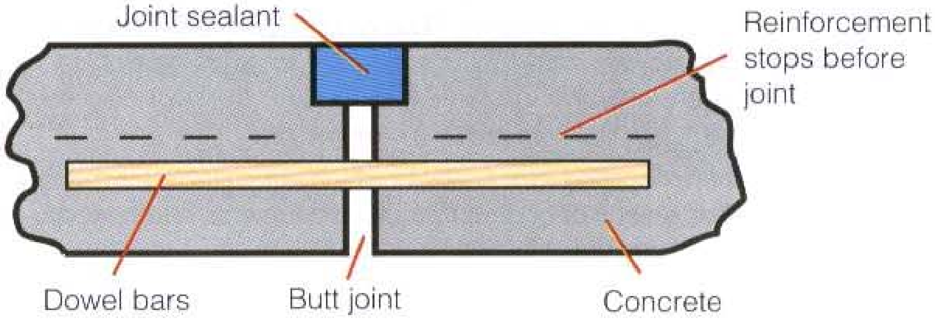


Figure 9.9 — Expansion/contraction joint

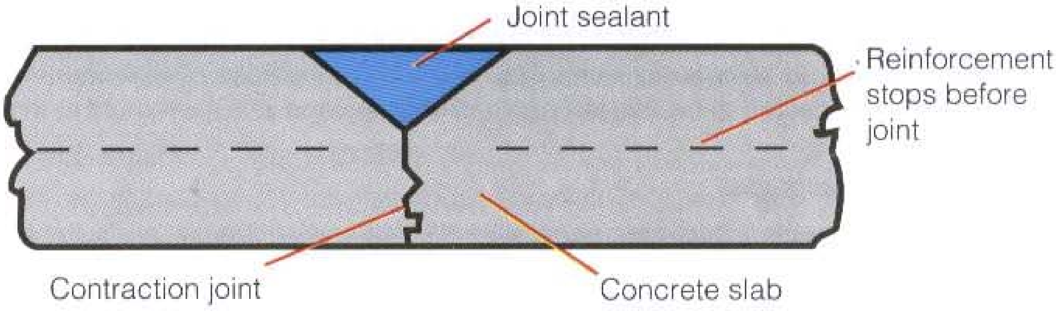


Figure 9.10 — Contraction joint

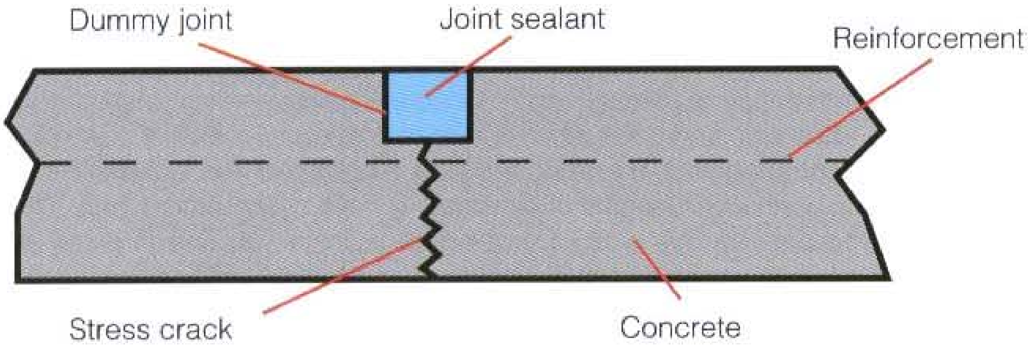


Figure 9.11 — Dummy joint

One further method of stress relieving concrete carriageways is to use "dummy joints" which form planes of weakness in the concrete slab. The dummy joints comprise grooves cut into the concrete pavement at regular intervals to a depth of about one third of the slab thickness. When sufficient stress has been developed in the concrete slab, cracking occurs where the slab is thinnest, ie at the dummy joint. The grooves are filled with a suitable bituminous joint sealant. For particularly deep grooves, the top 25 mm may be sealed using a joint sealant, with the remainder packed with a suitable joint filler to reduce costs, see figure 9.11.

The purpose of the joint sealant in these examples is to maintain the impermeability of the concrete structure and to prevent passage of water through the slab into the subgrade with its consequent damage to the pavement foundations. The danger of frost heave due to water freezing in the joint and under the slab is also a potential problem in cold climates. The sealant also prevents the joints from filling with detritus, particularly small stones which could prevent the joint from functioning properly. The riding quality of the concrete pavement may also be impaired if the riding surface is uneven due to gaps caused by expansion joints. Modern joint sealants are effective in creating not only a seal but also a bridge across the joint to reduce the shock of the wheel passing over the joint.

There are a number of hot applied joint sealants which are suitable for this type of application: they include penetration grades of bitumen, oxidised bitumens, and specially formulated, high performance, bitumen/rubber compounds.

9.4.2.2 Suitability of bitumens for use as joint sealants

9.4.2.2.1 Penetration grades

Penetration grades of bitumen are rarely used for joint sealing on their own due to their low PI and susceptibility to temperature changes. Penetration grades of bitumen are used only where there is expected to be little temperature variation and little movement at the joint.

9.4.2.2.2 Oxidised grades

Some grades of oxidised bitumen, particularly R85/40 and equivalent, are suitable for sealing saw cuts and joints where there is expected to be the minimum amount of movement in the joint. Their wide service temperature range and good adhesion make them particularly suitable for this type of application.

9.4.2.2.3 Bitumen/rubber compounds

Hot poured bitumen/rubber joint sealants vary from heterogeneous mixtures, such as bitumen with ground scrap tyre rubber, to more finely dispersed mixtures of bitumen with linear uncrosslinked rubbers. Under short loading times these materials may show a rubber elastic response, but at long loading times and particularly at high ambient temperatures they merely behave as a high PI (high viscosity) bitumen. Consequently, these types of material may fail due to their excessive plastic deformation and through penetration by solid matter. They are rarely suitable for use in high extension, dilatation joints.

The enhanced performance of bitumen/thermoplastic rubber compounds (see chapter seven), however, make this type and class of material very suitable for many joint sealing and adhesive applications. The enhanced elasticity of the bitumen enables the sealant to follow both rapid and slow joint movements, even at temperatures down to -20°C, without problems. Conversely, high temperature performance is also enhanced with no creep or sag of the sealant at high ambient service temperatures. The improved adhesion and superior ageing properties make them suitable for use under the most exacting of circumstances.

9.4.3 Proprietary joint sealing materials

9.4.3.1 Cariphalte JS

Cariphalte JS is a high-extension, hot poured bitumen/TR sealant for horizontal joints in pavements and buildings. It comprises a homogeneous mixture of a thermoplastic rubber polymer, chemical additives, bitumen and filler, a compound with the following distinct advantages:

- almost 100 per cent rubber elasticity and high extension at service temperatures ranging from -20°C to +60°C;
- very high resistance to flow, even at service temperatures as high as 60°C;
- excellent pourability without segregation of the incorporated rubber at temperatures well below the maximum permissible heating temperature of the bitumen/TR composition.

When used in combination with the concrete primer, Cariphalte CP, excellent adhesion is achieved even under wet conditions, in the presence of salts, and when subjected to high extensions over prolonged periods of time. Cariphalte JS is resistant to dilute mineral acids and alkalis, but, in common with many bitumen/rubber compounds, will soften and swell in contact with hydrocarbon solvents, mineral or vegetable oils, fats and petroleum fuels.

The sealant/primer combination of Cariphalte JS and Cariphalte CP is able to meet a number of standard joint sealant specifications, including:

- Belgium	Type Bestek No 150
- Germany	DIN 1996
- Netherlands	KVBB/RWS 1967
- Switzerland	SNV 671625a
- UK	BS 2499-A1 (1973)
- USA	ASTM D 1190

Standard test method			Specification	Typical result
Cone penetration, 25°C	dmm	(BS 2499)	<100	50-70
Softening point, R & B	°C	(SNV 671625a)	85 min	105-115
Flow, 5 hours/60°C/75° slope	mm	(US-SS-S 1401 B)	3 max	0-1
Ball drop test at -20 °C/50g,	m	(DIN 1996)	4 min	pass
Extension test between concrete blocks at -20°C, 2 cycles	%	(BS 2499)	75 min	pass

Table 9.6 — Typical test data for Cariphalte JS joint sealant

Standard test method			Result
Specific gravity, 25°C/25°C	(ASTM D 71)		1,43 +/- 0.05
Ball penetration, 25°C	(USS-SS-S 1401 B)	dmm	4-8
Resilience @ 25°C			
after 20 s	(USS-SS-S 1401 B, modified)	%	60 min
after 80 s	(USS-SS-S 1401 B)	%	70 min
after unloading	(USS-SS-S 1401 B, modified)	%	100
Extension test between concrete blocks in constant strain tester, 50% extension at 25°C	1) 2 weeks, dry		pass
	2) 2 weeks, in tap water		pass
	3) 2 weeks, in 10% NaCl soln.		pass
	4) continued extension after tests 1, 2 and 3	%	100 min

Table 9.7a — Typical properties of Cariphalte JS joint sealant

Some typical performance data required by the specifications for the Cariphalte JS sealant/primer system are given in table 9.6 and some other properties are shown in table 9.7.

Cariphalte JS joint sealant has been used successfully since 1972 for sealing joints in mastic and cement concrete floors of car parks and joints in cement concrete pavements. Experience has shown that the combination of special compatible bitumen and thermoplastic rubber produces an extremely durable and strongly adhesive sealant. Despite signs of weathering often seen at the surface of a joint, sometimes resulting in an alligator skin pattern, no cracking penetrates to any depth into the sealant mass. Additionally, the sealant is sufficiently tough to resist penetration of the joint by stones or other solid substances.

Viscosity at 25°C,	cSt (0.001 Pa.s)	50-100
Flash point	°C	-4
Colour		light brown, transparent

Table 9.7b — Properties of Cariphalte CP concrete primer

In common with all sealants and adhesives, the performance of the material is dictated by the quality of the workmanship in application. Thorough preparation of the joints is essential, whether in asphalt or cement concrete. Joints should be cleaned using high pressure water where possible. When the joint is dry, any remaining dust or debris should be removed with an air jet. Adhesion of the joint sealant is aided by a coating of primer, which can be applied by spray gun or brush. When the primer is dry, sealant is applied at 150 to 180°C.

Tests	Units	Specification		Typical joint sealant	Cariphalte JS	Jointfill**
Specific gravity at 25°C		not specified		1.0-1.3	1.43	1.0
Softening point (R & B)	°C	>85	*6*	70-100	100	87
Cone penetration (ASTM D217) 150g, 5s, 25°C	dmm	<100 <90	*3* *7*	30-70	50	99
Needle penetration (ASTM D5) 100g, 5s, 25°C	dmm	<100 >75% after 7 days @ 70°C	*6* *6*	most pass	48 96%	115
Needle penetration (ASTM D5) 100g, 5s, -20°C	dmm	>2	*6*	—	3	—
Ball penetration 75g, 5s, 25°C	dmm	5-15	*7*	2 - 25	4	15
Resilience (ball penetration tool) 25°C, 80s	%	none	—	—	65	63
Resilience (ball penetration tool) 25°C, 20s	dmm	>60	*7*	2 - 15	45	44
Ball drop test 130g, 0°C, 2m		4 out of 5 samples pass	*1*	most pass	pass	—
Ball drop test 50g, -20°C,	m	>4	*5,6*	most pass	pass	fail
Punch test at 35°C stylus 10mm dia	mm	<10	*2*	most pass	0.9	1.8
Flow slab, 75° angle, 5 h, 60°C	mm	<10 <3	*6* *7*	3 - 5	0.1	3.5
Flow, slot, 5 hours, 45°C	% mass	<20 <15 <5	*2* *4* *3*	0 - 7.5	0	0
Flow, cylinder, 30° angle, 5 h, 60°C	mm	<20	*1*	2 - 35	0	1.5
Form stability (Nüssel) 24 h, 45°C	ratio D/h	<7.5	*5*	2 - 5	1.4	1.75
Sedimentation during heating, 2 h, 180°C	% mass	<15	*2*	—	9.6	—
Safe heating period 6 hours at pouring temperature		should still comply	*3,4*	most comply	pass	pass
Loss on heating, 5 hours 163°C	% mass	<1	*6*	most comply	0.2	—
Pourability temperature	°C	—	—	—	175	—
Safe heating temperature 30 min ΔR & B max, 10°C	°C	min 30°C above pourability temp	*6*	200-220	>230	—

* Cariphalte JS complies with the requirements of standards 1, 2, 3, 4, 5, 6, and most of standard 7 except resilience and bond test at -20°C after water immersion

** Jointfill complies with the requirements of standards 2 and 4

(1)	Netherlands specification	KVBB/RWS (1972)
(2)	Belgium specification	Type Bestek No 108
(3)	UK specification	BS 2499 (1973) type A1 high extension
(4)	UK specification	BS 2499 (1973) type A2 high extension
(5)	German specification	DIN 1996
(6)	Swiss specification	SNV 71625
(7)	US specification	SS-S-1401 B (proposed)

Table 9.8 — Typical properties of Shell proprietary joint sealants

Tests	Specification		Typical joint sealant	Cariphalte JS	Jointfill
0°C, 2 cycles, 75% (0.4%/min)	no disbonding/cracking max force 11 kg/cm²	4	most products comply	pass	pass
-20°C, 2 cycles, 75% (0.4%/min)	no disbonding/cracking max force 11 kg/cm²	3	a few products comply	pass borderline	fail
-15°C, 3 cycles, 50% (0.28%/min)	no disbonding/cracking	1	a few products comply	pass	fail
0°C, 1 cycle, (0.6%/min)	no disbonding/cracking at minimum 100%	2	most products comply	pass	pass
-10°C, 1 mm/h, (0.11%/min)	no disbonding/cracking at minimum ext 5mm (33%)	5	most products comply	pass > 10mm	fail
-20°C, 1 mm/h, (0.11%/min) before and after storage in water for 14 days	no disbonding/cracking at minimum ext 4mm (26%) Max force <10kg/cm²	6	few products comply	pass > 6mm max force 10.3kg/cm² (borderline)	fail
-29°C, 0.05 mm/min, 3 cycles before and after storage in water for 4 days	no disbonding/cracking	7	most products fail	fails after storage in water	fail

(1) Netherlands specification KVBB/RWS (1972)
(2) Belgium specification Type Bestek No 108
(3) UK specification BS 2499 (1973) type A1 high extension
(4) UK specification BS 2499 (1973) type A2 low extension
(5) German specification DIN 1996
(6) Swiss specification SNV 71625
(7) US specification SS-S-1401 B (proposed)

Table 9.9 — Bond test results of Shell proprietary joint sealants

9.4.3.2 Jointfill

Jointfill is a hot poured sealant for horizontal joints in pavements and buildings which offers good extension over a wide range of service temperature, high resistance to flow and excellent pourability at temperatures below the maximum permissible heating temperature of the material without segregation of the rubber. Jointfill is similar in composition to Cariphalte JS but contains less polymer and, consequently, has a lower technical specification, see tables 9.8 and 9.9.

Jointfill offers a practical balance between adhesion and cohesion enabling the joint sealant to bond firmly to the substrate, to absorb movements in the joint caused by expansion and contraction of the concrete or asphalt and to provide protection against the infiltration of water into joints.

9.4.3.3 Tixophalte

Tixophalte is a cold applied, bituminous adhesive and sealant, containing a polymer and a thixotropic agent, which was developed by Shell in the Netherlands. It has the ability to bond instantaneously to almost any substrate, even under cold, damp conditions. In addition, it has excellent anti-flow properties at high temperature combined with good workability arising from its thixotropic character. As a consequence this material has become rapidly accepted by roofing contractors who require an adhesive and sealant which will bond instantaneously to all building surfaces even under the most adverse of weather conditions. The principal characteristics of Tixophalte include:

- instant permanent adhesion to most building surfaces, even under water,
- cold applied direct from the container,
- no flow, drip or thread formation,
- no requirement for a primer,
- remains flexible throughout its service life,
- does not attack expanded polystyrene or polyurethane foam insulation,
- minimum waste.

Since 1980, Tixophalte has found increasing uses in the building and construction industry where it has found its largest market in emergency roof repairs, bonding of roofing felts and single ply membranes, as an adhesive for insulation boards and for detailed finishing work. In all these applications Tixophalte can be applied even under standing water and is used in the following broad areas of application:

- Roofing
  - general repairs
  - felt adhesive
  - single ply membrane adhesive
  - insulation board adhesive
  - roof coating
  - finishing and detail work
- Building
  - general sealant for metalwork, concrete and brickwork
- Hydraulic applications
  - sealant for canal linings around the water mark
- Others
  - sealing tank bases
  - sealing pylon bases
  - do-it-yourself (DIY) general purpose sealant/adhesive/coating.

9.4.3.3.1 Handling

In common with other types of joint sealant and adhesive materials, preparation prior to use of the material is vitally important to ensure a satisfactory level of performance:

- to obtain good adhesion, the substrate must be clean and any loose material should be brushed away; no substances should be present which might interfere with the adhesive properties of Tixophalte such as oil or grease contamination;
- Tixophalte will normally stick strongly under wet conditions but before proceeding with work in wet conditions, a small test patch should be undertaken to ensure that the material will stick under the prevailing conditions;
- in unusual cases, a primer can be used to assist adhesion.

Properties after evaporation of solvent		
Cone penetration at 25°C	dmm	40
Drop point	°C	200
Flow (1.5 mm, 14 days, 90°C)		none
Peel stength (DIN 30670)		
5 cm width, 1.5 mm coating thickness on steel		
10 mm per minute	N/5 cm	20
20 mm per minute	N/5 cm	30
30 mm per minute	N/5 cm	50

Table 9.10 — Typical properties of Tixophalte

Curing time	Peeling strength (N/5 cm)		
	Peeling rate (mm/min)		
	10	20	50
1 day	6	6	3
2 days	4	5	10
5 days	10	12	20
solvent free	23	33	50

Table 9.11 — Tixophalte peel strength

Insulation materials:		Adhesive strength			
		N/m^2		N/m for 4 cm strip	
Pulling rate (mm/min)		0.1	50	0.1	50
Perlite after	1 day	23,000*	67,000*	920*	2,630*
Glass wool after	1 day	15,000*	23,000*	600*	920*
Polyurethane foam after:	1 day	15,000	45,000	600	1,800
	4 days	33,000	100,000	1,320	4,000
Polystyrene after:	1 day	13,000	67,000	520	2,680
	4 days	17,000	75,000	680	3,000

* rupture in insulation panel

Table 9.12 — Tixophalte adhesive strength to insulation panels

As an adhesive for insulation boards and roofing felt Tixophalte is normally applied in four centimetre wide strips at an average application rate of 400 g/m^2. When bonding low strength insulation panels or to bond panels close to the roof edge or corners, it is recommended that the adhesion surface area is increased by increasing the number of strips applied to the roof. Subsequent curing of the Tixophalte will proceed when it is exposed to air, allowing the solvent content to evaporate, see table 9.12.

9.4.3.3.2 Typical properties of Tixophalte

The wide use of Tixophalte for fixing roofing felt is the result of its excellent properties as indicated by the results of the peel test, see tables 9.10 and 9.11. Sound adhesion of roofing felt to the substrate is necessary to prevent wind lift forces from ripping the felt from the roof. The peel test is one means of quantifying the degree of adhesion developed by the adhesive between the roofing felt and the substrate. In the peel strength test, 5 cm wide strips of a standard roofing felt are bonded to steel using a 1 mm thick layer of Tixophalte. The felt is peeled from the steel perpendicularly to the steel surface at various peeling rates and after different periods of cure. Tixophalte develops a strong resistance to peel stresses, indicating strong adhesion, very rapidly after application, see table 9.11.

Of great interest to engineers is the degree of adhesion achievable when a bond is first made. The initial adhesive strength can be seen in table 9.13 where tests were made after a cure time of only three hours. Ultimate adhesive strength is measured at various pulling rates by bonding four-centimetre strips of roofing felt to concrete using a one-millimetre thick layer of solventless Tixophalte, see table 9.14.

9.4.3.3.3 Some practical applications of Tixophalte

9.4.3.3.3.1 Waterproofing cement concrete hydraulic constructions(15)

Leaks in cement concrete structures commonly result from micro-cracks in the material which are impossible to fill individually. In these cases it is necessary to treat the entire concrete area in order to restore the impermeability of the structure. The use of Tixophalte to form an in-situ waterproof membrane has been successfully carried out in France on a concrete coal settling basin measuring 27 metres in diameter by 5 metres depth. Tixophalte was applied by hand to the concrete substrate at a rate of 2 kg/m². The Tixophalte membrane did not flow even under the influence of direct sunlight and was able to follow the thermal dilation of the micro-cracks in the concrete. Where larger cracks were present, a polypropylene geotextile (approximately 140 g/m²) was used to reinforce the sealant and prevent it being extruded into the cracks by water pressure.

	Adhesive strength	
	N/m²	N/m for 4 cm strip
Polyurethane foam on steel	6,700	286
Roofing felt on polyurethane foam	13,000	520

Pulling rate 1mm/min, 3 h cure

Table 9.13 — Initial adhesive strength of Tixophalte

Pulling rate (mm/min)	N/m²	N/m for 4 cm strip
0.1	47,000	1,880
1	70,000	2,800
10	150,000	6,000
50	300,000	120,000

Table 9.14 — Typical ultimate adhesive strength of Tixophalte

9.4.3.3.3.2 Sprayed Tixophalte membrane(16)

Tixophalte has been applied by spray to seal the upstream face of the Dorlay dam in France. Visual inspection had revealed cracks above the waterline which made the structure vulnerable to the effects of solar heating and freeze/thaw cycling. The cracks were seen about one metre below the crest of the dam caused by an imperfect joint between the asphalt mix applied by paver and that applied by hand, a well-known and common fault.

The dam face was repaired in a simple multi-stage operation;

- the main cracks parallel to the crest of the dam were opened,
- the whole of the face of the dam above the waterline was sand-blasted to remove solar reflective paint,
- the face and cracks were cleaned with pressurised water,
- the main cracks (10 cm wide and 10 cm deep) were filled with Tixophalte,
- grey coloured Tixophalte was sprayed over the whole of the dam face above the waterline at a rate of 6 kg/m^2 in order to seal the small cracks in the surface and produce a watertight membrane.

9.4.3.3.3.3 Aqueduct joint sealing(17)

In 1988, the joints in the concrete lining of a water transmission canal near Marseilles in France were sealed using Tixophalte. One kilometre of the canal was restored by an application of reinforced sprayed concrete, leaving two centimetre wide by three centimetre deep expansion joints every five metres. Tixophalte was used in preference to silicone sealants whose adhesive properties are impaired when applied to moist concrete surfaces.

The storage capacity of the reservoir into which water is fed by the canal is equivalent to only one week's supply. The canal was repaired in four days and immediately refilled. The joint sealing operation involved:

- removing polystyrene joint fillers,
- cleaning the joints with oil free compressed air,
- applying sealant to the joint by pneumatic applicator,
- profiling the sealant.

A total of four kilometres of joints were sealed under damp conditions and within the tight time scale imposed by the project.

9.4.3.3.3.4 Crack sealing on an asphalt pavement(17)

Thirty kilometres north of Paris lies the Senlis high speed test track used by the Valeo Company to test motor vehicle equipment such as brake discs and clutches. The surface of the test track comprises 1.6 metre wide asphalt strips in which, over time, the joints had opened, making flying chippings a potential hazard. On the fast sections of the track the road is banked by up to 43 degrees which, in previous maintenance, has excluded the use of conventional hot applied joint sealants.

The joints were prepared by pressurised water to remove all traces of the old sealants and filled with Tixophalte sealant. Each joint was smoothed and a layer of coarse sand applied to the surface of the sealant to prevent pick up on vehicle tyres.

(a) (b)

Photograph 9.2 — Application of Tixophalte as a joint sealant on an aqueduct in France

Photograph 9.3 — Application of Tixophalte on the Senlis high-speed test track in France

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Chapter 10 - Pipe coating

10.1 Introduction

Pipelines are the most efficient means for the transportation of gaseous, liquid and slurried materials over long or short distances with the minimum impact on the environment(1). Long and large diameter pipelines are usually made from carbon steel, an iron based material which is subject to corrosion. The corrosion process (Latin: corrodere, to gnaw away) is a naturally occurring one in which the iron, one of the most reactive elements, reverts to its oxide through the effects of water and oxygen from the air. This process affects nearly all iron structures, above ground, below ground and in water. Structures which are accessible and above ground may be maintained by regular painting or by some other form of coating. Pipelines are, however, rarely accessible and must be protected from their environment for the whole of their service life, which may be as long as 50 years, by a suitable corrosion resistant coating. One commonly used means of corrosion protection for both marine and underground pipelines is the use of a thick bituminous enamel coating reinforced with a glass fibre or polyester wrap. As further insurance against corrosion such a high integrity coating is also supported by the use of cathodic protection.

In the case of offshore pipelines cathodic protection is applied by means of sacrificial anodes of zinc or aluminium connected to the pipeline. On-shore pipelines are usually protected by impressed current applied by means of anodes in ground beds at intervals along the length of the pipeline. The rate of corrosion of an offshore pipeline is determined by sea water velocity, salinity, oxygen content and the influence of marine organisms. As the majority of marine pipelines require to be weight coated with high density (3000 kg/m^3) concrete, any corrosion coating must also resist alkali attack from the concrete. On land, corrosion does not stop at ground level and buried land lines may be subject to attack from soil micro-organisms, together with chemically active ground water.

10.2 Bitumen pipe coating enamel market

Since 1978, most of the offshore steel pipelines constructed in the North Sea have been protected by a bitumen enamel coating(2) and include some major pipeline projects, see table 10.1.

Pipeline	Owner	Length miles (km)	Diameter inches (mm)
Statpipe	Statoil	550 (885)	30 (762)
Fulmar	Shell	260 (420)	20 (508)
SE Indefatigable	Shell	100 (160)	30 (762)
Oseberg	Norske Hydro	100 (160)	24 (610)
Zeepipe	Statoil	850 (1370)	40 (1016)
Europipe	Statoil	375 (600)	40 (1016)

Zeepipe is currently under construction and is the largest ever North Sea pipeline

Table 10.1 — North Sea pipeline projects which have used bitumen coated pipes

Country/area	Length of pipe km	m^2 of 16" pipe (x 1,000)	% of total
USA	12,947	16,520	15
Canada	4,200	4,200	5
Europe	36,345	46,376	43
Middle East	3,712	7,736	4
Africa	3,408	4,348	4
West Pacific	3,376	4,307	4
Southern Asia	11,870	15,146	14
Mexico/C America	708	903	1
South America	8,016	10,228	10
Total	84,582	107,923	100

Table 10.2 — Pipe coating market — five year forecast 1992-1997

In the last decade alone it is estimated that some 2,500 miles (4000 km) of marine transmission pipeline ranging in diameter from 8 inch (203 mm) through to 40 inch (1016 mm) have been laid in the North Sea. The majority of the pipeline has been coated with bitumen enamel, representing some 50,000 tonnes of material. The pipe coating sector of the industrial bitumen market is relatively small (about 3%) but, nevertheless, is an extremely important and demanding area. The pipe coating market as calculated by "Pipeline Industry" in 1992 is given in table 10.2 (3). These data represent a five year time horizon from 1992 giving an average annual market for pipe coatings of some 22 million square metres, of which about 50 per cent is bitumen or coal tar enamel.

The pipe coating industry has the choice of a number of alternative coating materials which include the basic types (based on 1991 statistics) shown in table 10.3.

In Europe, major pipe coating plants exist at Leith in Scotland and Immingham in England, the plants being equipped to coat either coal tar or bitumen enamels at the rate of 150 to 200 twelve metre (forty foot) pipe joints per day. In Germany, coal tar enamel for pipe coating is not permitted and in The Netherlands the last coal tar used was at Delfzijl in Groningen Province in 1977 on an Amoco pipeline. One remaining pipe coating plant at Maasluis near Rotterdam utilises bitumen enamel.

In the USA both bitumen and coal tar enamels continue to be applied, although bitumen now predominates. Coal tar enamel is now prohibited in Canada for health reasons. On-shore and off-shore pipelines in South Africa have for many years been protected by bitumen enamels. In Iran, coal tar enamel coatings have predominated in the pipe coating industry

Coating type	% share
Bitumen enamel	4
Coal tar enamel	38
Extruded polyethylene	20
Fusion bonded epoxy resin	28
Tapes	6
Other systems	4

Table 10.3 — Coating materials used for pipelines, 1991

but, for health, safety and environmental reasons, the industry is moving towards the use of bitumen enamel.

As the use of coal tar enamels declines due to its associated health risks and its environmental unacceptability, it may be expected that bitumen enamels and the new high performance modified bitumen enamels will be suitable cost-effective substitutes.

10.3 Coating requirements

In order to protect a pipeline from the atmosphere it is essential that a strong and effective corrosion proof coating is applied which will keep both water and oxygen away from the vulnerable steel. The majority of line pipe is coated in purpose-built factories in 12 metre (40 foot) "joints" and then shipped to the laying site for welding into a continuous pipeline.

The choice of coating material to protect the steel is dictated both by economics and service requirements. To ensure the integrity of the coating during application, handling and in service it is essential that it possess a number of key properties which include:

- ease of application
- strong adhesion to steel
- resistance to impact at low temperatures
- resistance to flow at high temperatures
- flexibility at low temperature
- negligible water absorption
- electrical resistance
- chemical stability
- resistance to root penetration
- resistance to bacterial attack
- resistance to marine organisms
- resistance to soil stress
- resistance to weathering
- hardness/abrasion resistance
- cathodic disbondment resistance.

10.4 Coating materials

Early carbon steel pipes were protected by dipping in a solution of coal tar, the so called Dr Angus Smith's solution. As this technique produced a coating only a few microns thick, it is unsuitable for today's pipe sections which may weigh in excess of two tonnes.

Today, bitumen is widely used as a cost effective anti-corrosion coating on metal surfaces. Whilst the bitumen itself does not possess any inherent corrosion inhibiting properties, it is effective because of its impermeability, preventing water and oxygen reaching the metal surface. Bitumen is not totally impermeable to water, however, but any desired degree of impermeability can be achieved by applying a sufficiently thick layer of a hard grade of bitumen. The water permeability coefficient of bitumen is about 1.4×10^{-8} g h^{-1} $cm^{-1}mm^{-1}$ Hg.

Bituminous pipeline coatings, commonly known as bitumen enamels or asphalt enamels, are based on oxidised bitumen(4) incorporating a quantity of an inert filler such as talc, slate dust or flyash. In the past micro asbestos was often used but because of the health hazards associated with this material it has now been almost completely replaced by safer alternatives.

10.4.1 Fillers

Fillers are added to the bitumen up to a maximum of 60 per cent by mass, but more normally at 30 to 40 per cent which is equivalent to about 20 per cent by volume depending on filler type.

The effect of the addition of different types of filler on the penetration and softening point of bitumen can be seen in figures 7.4, 7.5 and 7.6(5). Addition of any type of filler will increase the softening point of the bitumen and hence reduce its tendency to flow, as well as improving its resistance to abrasion. Binder viscosity is also increased resulting in the requirement for increased application temperature.

In order to perform satisfactorily a filler must be finely ground and of consistent quality (typically less than 75 microns), have low water absorption, which rules out vegetable based fibres and certain types of clays, and be readily wetted by the bitumen. The filler should be chemically inert and must not settle out easily when the enamel is molten. Fillers with laminar shaped particles and densities close to that of bitumen are best in this respect. The most common filler in use today is slate dust because it is inert and relatively inexpensive.

There is an optimum percentage of filler which gives a coating the required softening point and toughness. Addition of further amounts of filler tends to make application difficult and may impair the water resistance of the enamel. There is always pressure to add the maximum permitted amount of filler on economic grounds since fillers are much cheaper than bitumen.

10.4.2 Pipe enamel

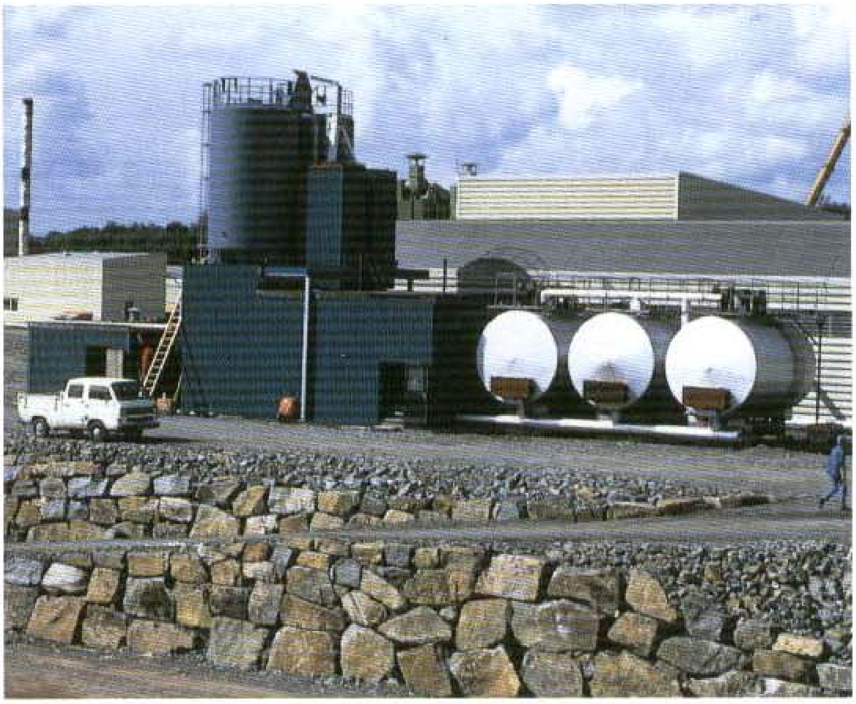
The choice of a pipe coating enamel is a complex matter(6) and several factors need to be considered in the choice of a material. The bitumen coating temperature must not exceed 240°C to avoid thermal degradation. In order to coat efficiently, the enamel viscosity should be in the range 200 to 500 cSt (0.2-0.5 Pa.s) at the coating temperature. The enamel coating must not sag if the pipes are stored in hot sunlight, and must not suffer indentation when the pipes are stacked. The coating must not fracture when the pipe is bent and should withstand a blow struck at low temperature. The in-service temperature of the pipeline is also important as some parts of the line can be at temperatures as high as 90°C.

Mexphalte R115/15 blown bitumen and similar grades are very widely used as the basis for bitumen pipe enamel formulations as described in BS 4147(4). Blown bitumens are preferred

Bitumen grade	25 pen	R95/25
Penetration at 25°C, dmm	25	25
Softening point, °C	57- 69	90-100
Fraass breaking point, °C	-4	-13
Penetration Index (PI)	0.3	4.6

Table 10.4 — Comparison of the properties of a penetration and an oxidised bitumen

for the manufacture of pipe coating because they have a very low temperature susceptibility as indicated by their high penetration index (PI) and their much wider service temperature range, see table 10.4.



Photograph 10.1 — Bituminous enamel production plant (Photograph courtesy of Phønix Pipe Protectors, Denmark)

It should be noted that bitumens are normally supplied to specific bitumen specifications such as British Standard 3690(7) and that other standards such as, for example, British Standard 4147(4) may also contain detailed performance requirements for bitumens. It is not always possible for the performance characteristics required for a pipe coating bitumen, for example, to be met by the standard bitumen specification and the customer is advised always to ascertain that the material received under one specification will actually perform against the requirements of a different specification.

A typical bitumen enamel used for coating steel pipes for use in the North Sea and manufactured to British Standard 4147 : 1987 Type 2b will have properties as illustrated in table 10.5.

Property		Values
Filler content	% by mass	25 - 35
Density at 25°C	g/cm^3	1.2 - 1.4
Softening point (R & B)		115 - 130°C
Penetration at 25°C	dmm	5 - 17
Flash point, °C min	°C	260
Sag at 75°C, 24 hr, max	mm	1.5
Bend at 0°C, min. deflection	mm	15.0
Impact at 25°C, max. disbonded area	mm^2	6 500
Peel, initial and delayed, max 30°C	mm	3.0
40°C	mm	3.0
50°C	mm	3.0
60°C	mm	3.0

Table 10.5 — Typical properties of a bitumen enamel pipe coating

10.5 Wrapping materials

10.5.1 Inner wrap

Wrappings are applied to the pipe enamel to produce a more uniform coating, to allow a thicker application of enamel, and to enhance the coating strength. Early practice involved the use of hessian inner wraps but due to their susceptibility to degradation by water these have now been entirely replaced by glass fibre or polyester materials which are not affected by moisture.

The number of inner wraps specified for a pipe coating is dependent upon the required thickness of the enamel coating. For a typical 6 mm thick bituminous enamel two inner wraps will normally be specified. The wraps are spirally wound onto the pipe so that they overlap by about 25 mm and are pulled into the bitumen enamel such that they are evenly spaced through the enamel without touching either the pipe surface or each other. The wraps may be impregnated with bitumen to ensure strong adhesion of the enamel to the wrap fibres.

10.5.2 Outer wrap

The outer wrap has two functions. It provides a shield against soil penetration of the enamel and provides a line of weakness to prevent soil movements from pulling the enamel off the pipe. The latter requirement can also be achieved by the application of a plastic film or other membrane known as a rock shield.

During application of the outer wrap, which is also spirally wound on to the pipe, it is important that there is some bleed through of the enamel to ensure that the outer wrap is firmly attached to the pipe enamel. The outer wrap is normally much heavier than the reinforcing inner wraps and will normally be bitumen impregnated to improve adhesion.

10.6 The coating process

The essential application technique of the modern pipe coating plant is still one of simply flood coating the hot enamel onto the rotating pipe sections. Tremendous improvements have been made to surface preparation of the line pipe by abrasive blasting, pre-heating and primer spraying, closely followed by controlled application of the bitumen enamel and reinforcing wraps. The coating process is shown in figure 10.1.

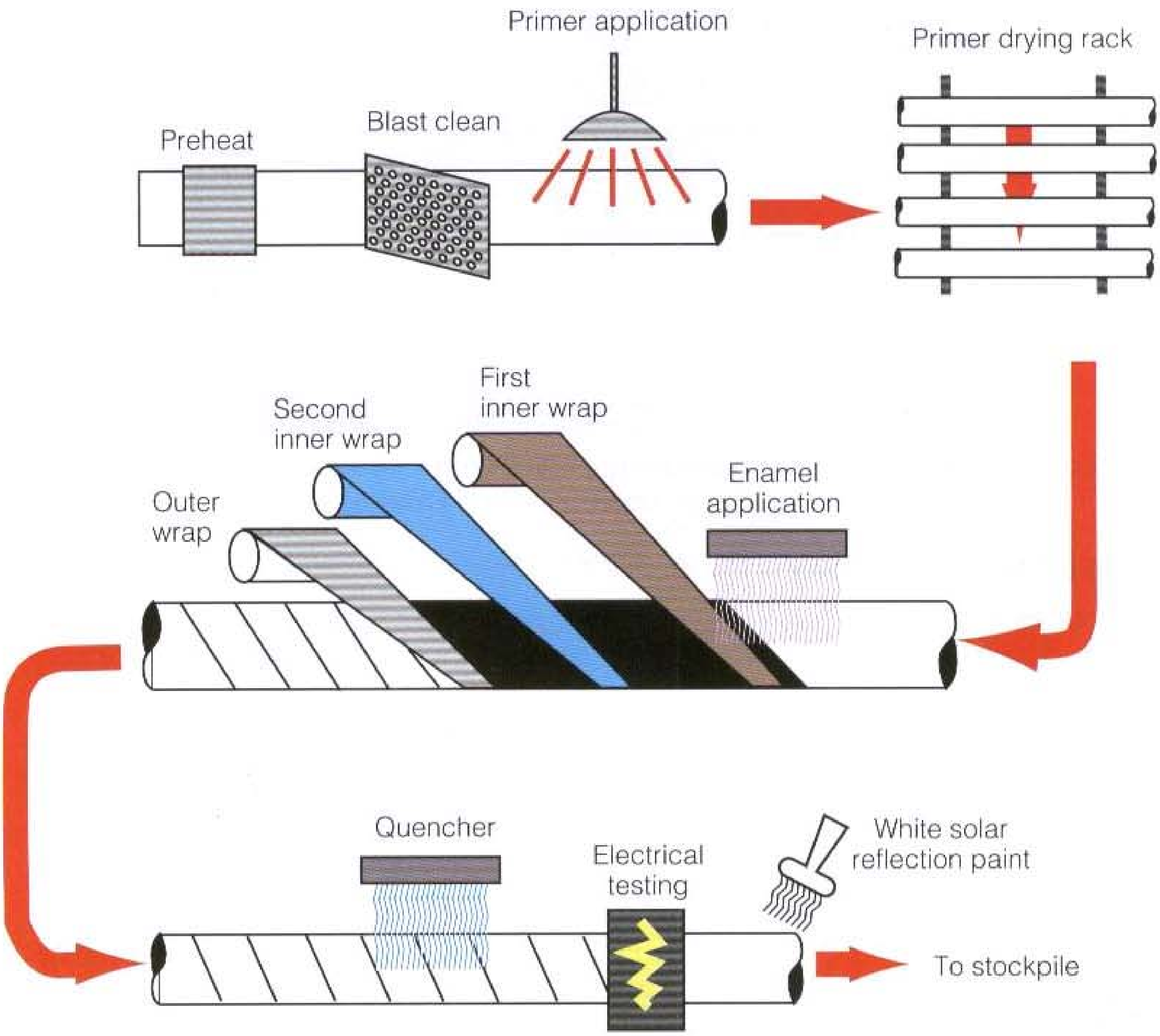


Figure 10.1 — Schematic diagram of the pipe coating process using bitumen enamel

Photograph 10.2 — Steel pipe being prepared for coating (Photograph courtesy of Universal Pipe Coaters, UK)

10.6.1 Pipe preparation

Line pipe is normally preheated either by dipping in hot (80°C) water or by passing through an induction heater prior to cleaning and priming. Preparation of the pipe can be undertaken by:

- wire brushing by hand or machine;
- line travelling mechanical cleaners with cutting knives and brushes;
- sand or grit blasting;
- pickling in sulphuric acid followed by water washing and immersion in phosphoric acid;
- flame cleaning.

One of the most effective methods of cleaning involves pickling the pipe because it leaves a thin phosphate coating which as well as preventing corrosion provides an excellent key for the primer. However, it is not widely used because it is costly and time consuming due to the need to change acid frequently and for the pipes to soak. The most commonly used method for pipe preparation is blasting with grit for factory coated pipes and wire brushing for site coated pipes.

The line pipe should be completely dry before blasting and should be maintained at a temperature at least 3°C above the dew point with a maximum relative humidity of 80 per cent. The blast finish on the external surface of the pipe should be to British Standard 7079 grade Sa $2^{1}/_{2}$ (8) or equivalent.

Following blast cleaning the pipe is inspected for surface irregularities such as weld spatter, slivers, lamination or hackles which would impair the finished coating. Where possible the defects are remedied and the pipe reblasted, otherwise the pipe is rejected.

Photograph 10.3 — Priming of cleaned pipes (Photograph courtesy of British Pipe Coaters)

10.6.2 Priming

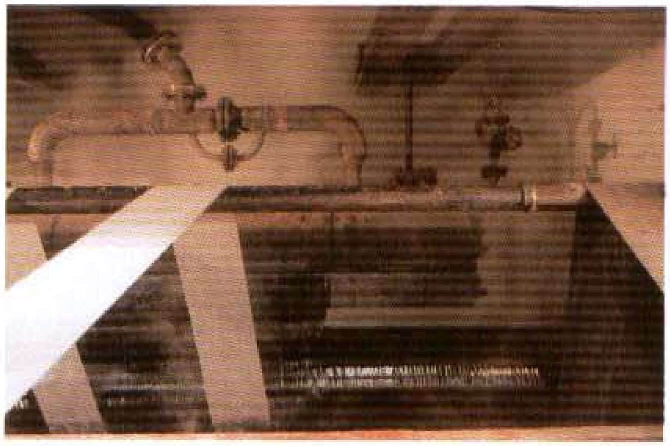
The application of the primer is one of the most important steps of the coating process. The function of the primer is to provide a strong adhesive surface onto which the bituminous enamel can bond. Current primers are based on a solvent borne chlorinated rubber composition and are usually spray or roller applied, with special attention being paid to the longitudinal pipe weld seams.

Priming is normally undertaken when the pipe is at a temperature in the range +10°C to +50°C, although specifications allow priming down to 3°C above the dew point and a maximum relative humidity of 80 per cent. To achieve satisfactory coating temperatures pipes are pre-heated. Synthetic rubber primers dry under normal ventilation conditions in between two and twelve minutes at 25°C. Whilst the primer is drying, a five millimetre thick strip of coating bitumen is applied to the pipe weld seam and allowed to cool and set. The seam is considered to be particularly vulnerable to corrosion if not coated properly and great efforts are made to ensure total protection.

10.6.3 Enamelling

After pre-heating, and before surface preparation and coating, the pipe ends are capped in order to prevent ingress of either blast abrasive or other materials which may damage the pipe bore. The pipe ends are masked for about fifteen centimetres in order to leave them clean for subsequent welding.

The enamel is applied to a rotating pipe by means of a flood box or weir. The bitumen enamel, at a temperature of 215 to 230°C, is flooded onto the pipe surface and the centrifugal force of the rotating pipe distributes the enamel in an even layer over the pipe surface. Simultaneously, the inner wraps and outer wrap are spirally wound into the hot enamel under controlled tension, ensuring a good overlap and in such a way that they are evenly spaced through the enamel coating. The wraps may be bitumen impregnated to ensure good adhesion of the enamel to the reinforcement. Usually two inner wraps are specified with one outer wrap. The tension of the wraps as they are spirally wound onto the pipes is very important. Too little tension and the wraps are not drawn adequately into the



Photograph 10.4 — Flood coating and wrapping bituminous enamel, showing two inner wraps and one outer wrap being applied (Photograph courtesy of British Pipe Coaters)

enamel; too much and they penetrate too deeply into the enamel and do not adequately reinforce it. A scraper may be used to remove excess enamel and a heated plate may be employed to smooth any high spots.

Immediately following coating, the pipe is cooled by water spray to prevent slump of the enamel. Once cooled, every pipe is inspected and tested for electrical defects. Bare spots on pipes caused by poor adhesion of the enamel or bubbles in the coating are called "Holidays". These are located by a high voltage electrical discharge from an electrode using a "Holiday" detector. For pipes a rolling spring electrode set at 10,000 to 20,000 volts is used. In addition, pipes are selected at agreed intervals and tested for impact and peel adhesion resistance, coating thickness, wrap distribution and cut back dimensions.

The peel test involves cutting a piece of the enamel coating to standard dimensions and peeling it away from the pipe surface. The coating is deemed to have failed if base metal is exposed or if the resistance to peel is insufficient. After testing, the defects and test areas are repaired using the same materials and the area is then again Holiday detected. The pipe is passed on to the customer with the repaired area serving to indicate that the pipe has been fully inspected.

The impact test involves a collision between the coated pipe and a large smooth weight which is swung at the pipe and is meant to simulate potential handling impacts. The site of the impact is inspected and the size of any disbonded area measured. Once the coated pipes have been inspected and tested, the pipes are stored in the open prior to use and are exposed to the full effects of weathering. In order to protect the black coated pipes from solar gain (heating caused by the sun) and the degrading effects of ultraviolet radiation, they are protected by an application of a final coating of a water resistant, solar reflective paint usually based on an acrylic medium.

After application of the solar reflective coating the pipes are stored and if required for a marine application, a concrete weight coating is applied either by impingement or by a compressive process. Typical concrete thicknesses are between 25 mm and 115 mm and use either a welded steel mesh or a galvanised wire reinforcement. For a 16 inch (400 mm) pipe the resultant weight coating weighs about 2 to 4 tonnes depending on its thickness. The concrete-coated pipe is then stored for a number of days in a pipe rack to allow the concrete to cure, or alternatively the concrete may be steam cured.

Photograph 10.5 — Coated pipes cooled by water spray prior to inspection (Photograph courtesy of British Pipe Coaters)

Photograph 10.6 — Coated pipes in storage (Photograph courtesy of British Pipe Coaters)

10.7 Jointing and field joints protection

The procedure for jointing the pipeline is essentially the same for both marine and land lines. During the coating process the ends of the pipes are left bare for about fifteen centimetres to allow for the welding operation and the coating is normally tapered towards the joint at the factory to assist the bonding of the mastic over the joint.

When the pipeline is laid, two pipe lengths are held in a line up clamp and their ends are welded. After welding, the field joint is ground smooth, mechanically wire brushed and primed. This is followed by an anti-corrosion coating of cold applied tape. For offshore pipelines the tape is applied in a single wrap around the field joint and on to the enamel cut backs. In land lines the tape is applied by spirally wrapping around the field joint and with an overlap of either 25 mm or 50 per cent as specified.

For offshore pipelines which are concrete coated, it is necessary to use a field joint mastic applied over the pipeline tape and in order to profile the concrete weight coating so that it will pass easily over the lay barge stinger. The field joint mastic, which comprises a mixture of bitumen and limestone filler, is supplied in slabs typically 600 mm by 350 mm by 25 mm thick. These are melted in oil-jacketed kettles and the molten mastic poured around the field joint into a thin steel mould which is strapped around the pipe. The steel mould is left on the joint as the pipe is laid and subsequently corrodes, leaving the mastic to protect the field joint.

When joint moulds are not available several coats of mastic and fibre mat may be hand applied. A more recent practice is to use torch-on, polymer modified roofing felt as a jointing protective. Several layers are applied with the aid of a butane torch until the desired thickness is achieved. The SBS polymer in the bitumen ensures excellent adhesion to the metal and gives superior resistance to flow.

10.8 Internal linings

Bitumen can be used as a lining material for steel and ductile iron pipelines and may be applied either as a thick, hot applied bitumen enamel or as a thin, cold applied (solvent diluted) bituminous system. Hot and cold bituminous materials can be applied by dipping, brushing, spraying or rolling techniques.

Thick, hot applied, bituminous linings are commonly used for raw water and sewage pipelines made in steel(4,9), and cold applied bituminous materials(10,11) are mainly used for lining ductile iron pipes for carrying potable water. The use of hot applied enamel for steel pipes and cold applied bitumen for ductile iron pipes is a matter of tradition and not of any special suitability of one over the other.

Thick, bituminous enamel linings are highly satisfactory in the protection of steel pipelines provided the lining remains intact and is not damaged due to external influences, eg pipe distortion due to ground settlement. Thin cold applied painted or dipped linings for ductile iron pipes generally have a limited life expectancy, usually about five years, due to the relatively thin coating, and are not, today, regarded as satisfactory due to this short service life. Ductile iron potable water pipelines are more commonly lined with cement mortar which affords better corrosion protection of the iron due to the high pH generated by the lime content of the mortar at the iron surface, which inhibits corrosion. However, in those areas where the water supply is particularly soft (usually with a hardness of less than 50 mg/l expressed as calcium carbonate), lime may be leached out of the cement mortar raising the alkalinity of the water. In these areas it is normal practice to coat the cement mortar with a cold applied bitumen layer to shield the lining or to line the pipe with a solvent-free spray coating.

Steel transmission pipelines for carrying oil are not normally coated internally and gas pipelines may be either unlined or lined with epoxy-based paints; however, this is done to improve the flow characteristics of the pipeline and not for the purpose of corrosion protection.

In the hot applied enamel rolling technique, the pipe joint is primed by hot dipping and, while still hot, is mounted in a spinning machine. The requisite amount of enamel is introduced into the pipe to provide a lining of the required thickness. The ends are sealed and the pipe is rotated at a gradually increasing speed to distribute the enamel evenly. Cooling by water spray from the outside is then carried out until the lining has set. Enamel and mastic linings can both be applied by this technique. Internal hot applied enamel coatings can also be applied by a spray lance which travels up the centre of a rotating pipe. This method of application gives a very controlled and even distribution of the enamel through the pipe.

Cold applied bitumen linings are generally applied by dipping or by spraying techniques.

Bituminous linings for steel water pipes have been used for many years and have proved to be effective, reliable and environmentally acceptable providing the lining remains undamaged. For a number of years, in the UK, the water industry(12), and more recently in Europe the European Community Directive 80/778/EEC "The quality of water intended for human consumption"(13,14), has required that all materials and fittings used in conjunction with potable water should be subjected to tests which determine their suitability by measuring:

(a) toxicological properties (to ascertain the extent to which substances are extracted by the water passing through or contained in the fitting or component of a fitting);

(b) organoleptic and physical properties (to ascertain whether the fitting or components of a fitting give rise to taste, odour, colour or turbidity of the water passing through or contained in it);

(c) microbiological growth properties (to ascertain the extent to which the fitting or component of a fitting supports the growth of micro-organisms).

Bitumen coatings generally pass tests represented in (a) and (b) and may also pass test (c). However, it is not uncommon for some bituminous materials to fail the microbiological growth test, which then determines them as unsuitable for lining potable water pipes. That bitumen will support the growth of micro-organisms is not surprising as it is a non-toxic, hydrocarbon, petroleum derivative, see chapter twelve. Where the bituminous enamel lining material has passed all the above tests, it has proved highly satisfactory as a corrosion protection material when applied in thick sections and extensive experience of the use of thick, hot applied, bituminous linings for potable water pipes has highlighted no problems associated with its use.

The UK water industry uses bitumen enamel exclusively for its raw water transmission lines, and, typically, the Yorkshire Water Authority has coated 60 miles (96 km) of 30 inch (762 mm) diameter steel pipeline with bitumen enamel both internally and externally.

10.9 Pipeline laying

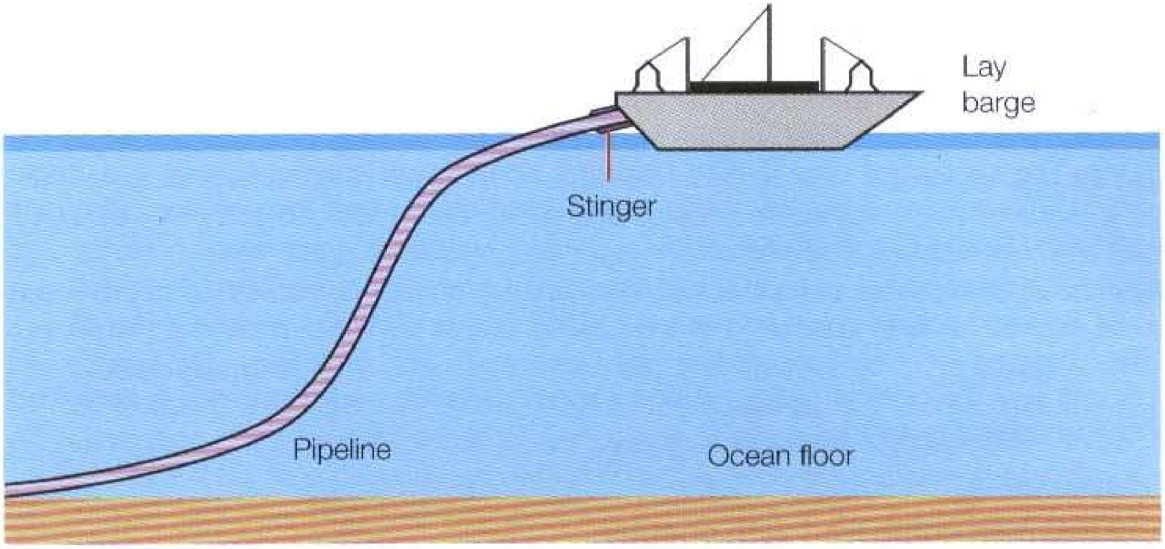
10.9.1 Marine pipelines

For marine pipelines, if the pipeline is to be constructed by the lay barge method, the coated pipe joints are loaded onto a supply boat and shipped to the barge. The joints are stored until required and then welded together and conveyed via a track tensioner and laid over the stinger (the hydraulic ramp located at the stern of the vessel), see figure 10.2a.

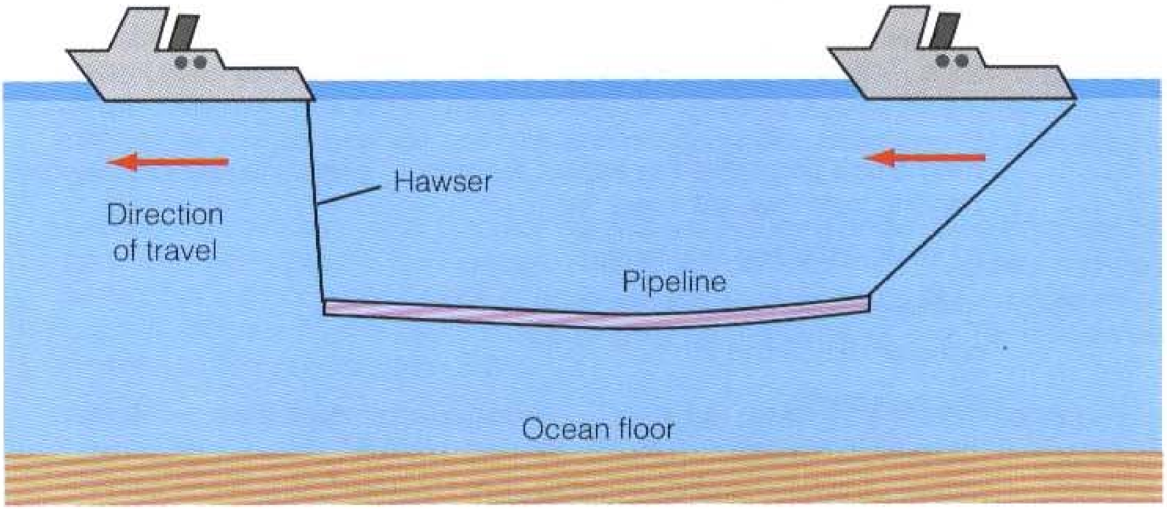
An alternative method of laying pipelines offshore is that of bottom (or mid depth or submerged) tow. Individual factory coated joints are welded into a continuous pipeline which is "strung out" on a series of rollers at the land site. Laying is achieved by pulling the string down the beach and then between two tugs to the off-shore location, see figure 10.2b. The pipeline is suspended some distance from the sea bed. In both the above methods it will be appreciated that accurate control of the submerged weight is vitally important. Equally important is that the integrity of corrosion protection is maintained during storage and installation.

The major difference between marine and land pipelines is that the marine pipelines need to be concrete coated to act as a counter buoyancy measure and to act as a mechanical protection for the vulnerable enamel coating from dragging anchor chains, trawl gear of fishing vessels and such similar hazards.

Photograph 10.7 — Marine pipeline being laid from a lay barge



10.2a — Laying pipes from the stern of a lay barge



10.2b — Laying pipes by the submerged tow method

Figure 10.2 — Techniques for laying pipes at sea

10.9.2 Land pipelines

For land lines the individual coated pipe joints, typically eight to fourteen metres long, are strung out along the "right of way" (the area adjacent to the pipeline trench) until required. The pipes are welded together and then the bare steel areas adjacent to the weld are prepared by mechanical wire brushing and application of pipeline tape. Tracked vehicles support the weight of the pipe as well as the welding line-up clamps, allowing the pipe to be placed carefully in position.

In the Middle East, for lines coated "over the ditch", the pipe is first welded into a continuous length and then at some time, maybe weeks later, the coating train is attached to the pipeline. The bare steel pipe is then brushed, primed and enamel coated in a single operation. This process is typically conducted in desert areas where there are long pipe runs uninterrupted by roads or other obstacles.

Where the pipeline passes through soil containing sharp angular fill material, extra protection may be needed to avoid puncturing of the coating. Large sheets of protective membrane, similar to roofing felt, may be specified, often referred to as rock shield. This can be laid under and over the pipeline. After the land line has been "ditched" the trench is back filled and the landscape restored.

10.10 Bitumen compared with coal tar

Early pipelines were buried without corrosion protection, but coatings of coal tar and bitumen were rapidly adopted to reduce the incidence of leaks due to corrosion of the steel. Bitumen enamel was one of the original pipe coating materials, dating back to the 1920s. However, for many years coal tar has been the predominant "thick" corrosion protection for steel pipes and there is still much debate about which gives the better protection. Regardless of the merits of the two materials, the use of coal tar is diminishing as it becomes increasingly undesirable to use it with its unacceptably high content of carcinogenic polycyclic aromatic compounds (PCAs)(15,16).

Comparison of bitumen and coal tar enamels in practice is very difficult as operational circumstances may vary widely, therefore most comparisons tend to be made under laboratory conditions. Aspects of pipe coating performance commonly examined include:

- mechanical properties (eg impact resistance, indentation resistance, cold bending, cold flow, soil stress, etc);
- adhesion, initial and long term;
- water absorption and permeability;
- cathodic disbonding;
- root penetration;
- micro-biological attack;
- health, safety and environmental effects.

Some of the differences between coal tar and bitumen are examined below:

Mechanical properties. Coal tar enamels have very low penetration indexes (see section 5.8), are very hard and consequently very much more brittle than bitumen, resulting in restrictions on handling and cold bending to prevent coating failures. In contrast, bitumen enamels are relatively tough and flexible but tend to be rather soft, sometimes leading to indentation and flattening at the supports in hot weather, although this can be overcome by the use of a strong outer wrap. Coal tar enamels tend to suffer from cold flow and are very vulnerable to soil stresses, in contrast to bitumen enamels.

Adhesion. When a steel surface is not entirely clean and dry, coal tar is believed to give better adhesion, due, probably, to its generally higher polarity. Coal tars were for many years added to bitumens used for surface dressing roads specifically to improve their adhesion under damp conditions. With clean surfaces free from moisture there is little difference in adhesion between bitumen and coal tar. Long term adhesion is affected by water absorption and the permeability characteristics of the coating.

Water absorption. It is generally believed that coal tar enamel is more suitable for the protection of underground pipelines than bitumen because it is claimed that the water absorption characteristics of coal tar are lower than for bitumen. In fact, this is incorrect, as water absorption depends upon various factors, including the type of filler, exposure to light, temperature, material consistency, salt content of the enamel and the type of water. The amount of water absorbed by a hard blown bitumen in grammes per square metre per year is approximately equal to the numerical penetration value of the material. That is, Mexphalte R115/15 with a penetration value of fifteen would absorb fifteen grammes of water per square metre per year which is equivalent to a film 1.5 microns deep, which is for all practical purposes negligible. The value for coal tar would be the same, but a coal tar of equivalent softening point would have a penetration of about five to ten and would on this basis absorb about half the amount of water. Furthermore, coal tar contains water soluble, leachable constituents and some techniques used for the evaluation of the water absorption of coal tars do not take into account the loss in weight due to these materials.

Results obtained using the Shell Research "aerated brine test" in which coated steel panels are exposed to aerated brine under cathodic protection conditions shows the effect of enamel hardness on performance, see figure 10.3. Coal tar enamels appear to perform as well as bitumen enamels with no systematic difference between the two generic types of coating.

Cathodic disbonding. The practical significance of the cathodic disbonding test has been widely discussed in the literature, with US authors believing it to be very important, while other authors prove it to be of significance only where stress corrosion conditions prevail. In general, the cathodic disbonding performance of coal tar enamel and bitumen tends to be about the same.

Attack by roots and micro-organisms. Roots will penetrate an unprotected bitumen pipe coating enamel, whereas the toxic nature of coal tar inhibits attack by roots. The addition of a suitable herbicide to bitumen enamel can render it resistant to attack, see chapter twelve.

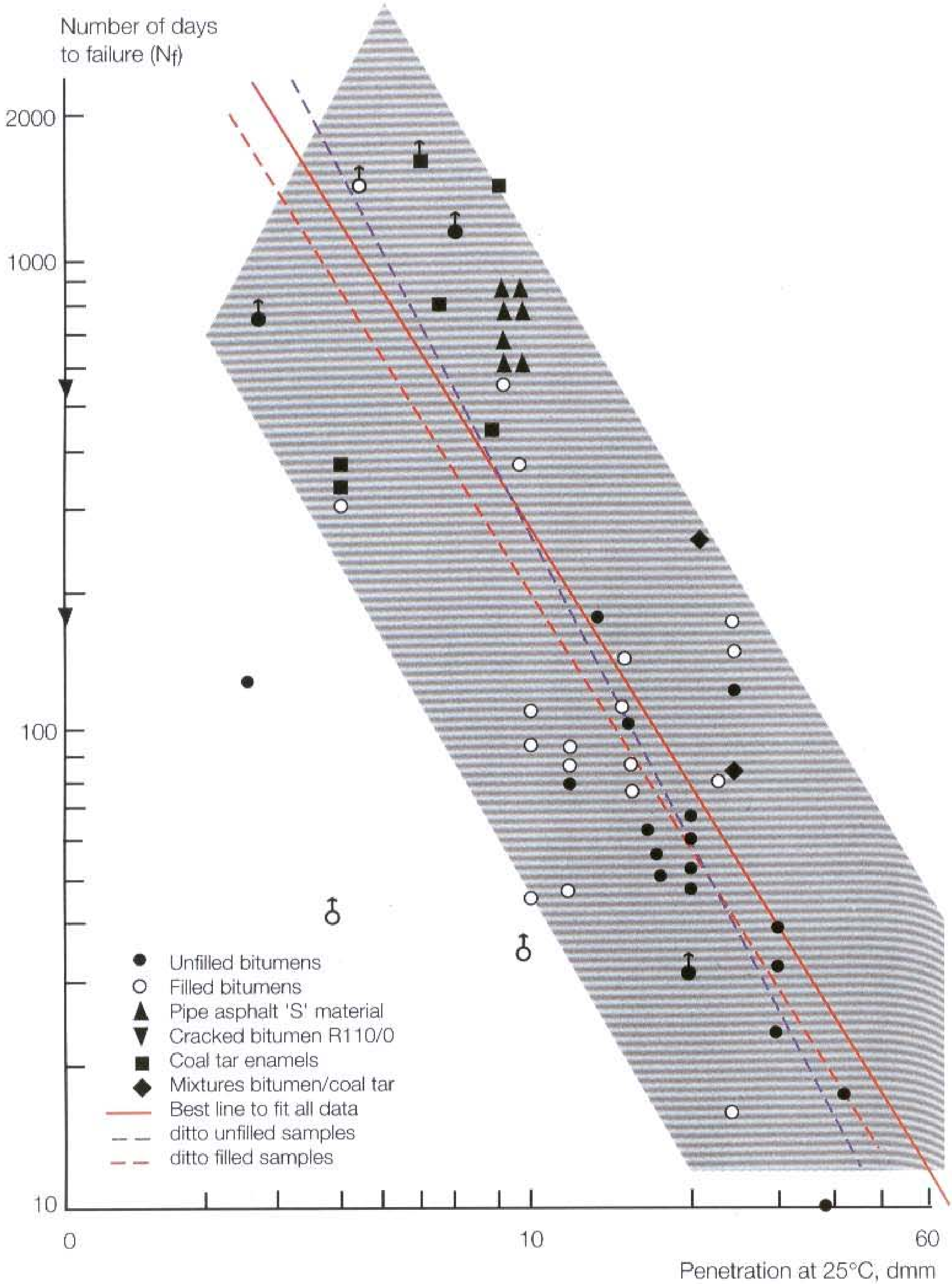


Figure 10.3 — Relationship between number of days to failure and penetration at 25°C in the Shell "aerated brine test"

International standards

American Asphalt Institute Specification SS-7. Asphalt protective coating for pipelines. 3rd edition,1972.

American Water Works Association Standard AWWA C203. Coal tar protective coatings and linings for water pipelines — enamel and tape — hot applied.

Swedish Standard SIS 05 5900. Pictorial surface preparation standards for painting steel surfaces.

German Standard DIN 30672. Coatings of corrosion protection tapes and heat shrinkable material for pipelines for operational temperatures up to 50°C.

German Standard DIN 30673. Bitumen coatings and linings for steel pipes, fittings and vessels.

Netherlands Corrosion Committee II. Communication 13. Specifications for the protection with asphaltic bitumen of cast-iron and steel pipes and vessels to be laid underground.

British Gas Specifications

BGC PS/CW1	Hot applied coal tar coatings for pipeline protection
BGC PS/CW2	Cold applied wrapping tapes and tape systems.
BGC PS/CW3	External wrap operations for steel line pipe (using hot applied bitumen)

British Standards

BS 534: 1990	Specification for steel pipes, joints and specials for water and sewage.
BS 903	Methods of testing vulcanised rubber.
BS 1134	Assessment of surface texture.
BS 2752	Specification for chloroprene rubber compounds.
BS 3900	Methods of tests for paints.
BS 3900 F10	Determination of resistance to cathodic disbonding of coatings for marine structures.
BS 3900 F11	Determination of resistance to cathodic disbonding of coatings for on-land based structures.
BS 4147: 1987	Specification for bitumen based hot applied coatings for protecting iron and steel.
BS 4164	Specification for coal tar based hot applied coating materials for iron and steel.
BS 7079	Preparation of steel substrates before application of paints and related products.
BS 4508	Thermally insulated underground pipelines.
BS 5375	Methods of test for raw general purpose chloroprene rubbers.
BS 5493	Code of practice for protective coating of iron and steel structures against corrosion.
BS 8010	Code of practice for pipelines.

The standards and specifications listed frequently form the basis for pipeline operating company specifications for surface preparation and pipeline coating. In addition some standards for testing and assessing raw materials and their performance on buried or submerged pipelines are listed.

Table 10.6 — Coating standards and specifications(17)

It is possible to grow bacteria on bitumen enamels but it is unlikely that this will ever cause more than superficial damage to the pipe coating.

Toxicity. Coal tars are known to contain very high levels of polycyclic aromatic compounds (PCAs) which are known to be responsible for producing cancer in humans. The fumes from coal tar are also known to be a serious health hazard and comparisons of bitumen with coal tar are well documented(15,16). By contrast, bitumen contains extremely low levels of PCAs and is not considered to be a health risk.

Solubility in oil. Coal tar is less soluble in mineral oil than bitumen and is preferable where pipes are laid in oil soaked ground. Coal tar coatings are commonly used where oil or fuel resistance is required, as in some types of asphalt surfacing (eg aircraft refuelling areas).

The influence of the properties of these two materials can be seen by the different practices in Europe and the USA. In the USA it is common to coat pipes on site "over the ditch" so that they are not subject to great handling and therefore brittleness is not so important. For this reason, and for their superior oil resistance, coal tar coatings are preferred in the USA. In Europe, however, it is more common for pipes to be coated in specialised factories and then transported to site. It is, therefore, more important that the enamel should have good handling properties and superior flexibility. Thus, bitumen tends to be preferred, especially in colder areas.

10.11 Criteria for defining pipe coating properties(6)

Many pipe coating specifications exist, eg those of the British Standards Institution BS 4147, the Asphalt Institute SS-7, and the Dutch Corrosion Committee Communication 13 (DCCC 13), which lay down qualitatively the requirements for a satisfactory pipe coating, see table 10.6.

In selecting a pipe coating material it is usually necessary to compromise between the mechanical requirements of the enamel and the corrosion protection requirements of the steel pipe.

10.11.1 Mechanical and rheological requirements for a bituminous pipe enamel

The visco-elastic properties of bitumen are related to temperature, loading time, penetration index (temperature susceptibility) and softening point, see chapter five. Utilising Van Der Poel's nomograph and the above mentioned parameters, the stiffness modulus of the bitumen can be obtained and subsequently the strain at break of the bitumen can be determined(5). It is thus apparent that the determination of the practical performance requirements for a pipe enamel should be based on an assessment of the expected loading time and strain in specific practical circumstances, more particularly because these are the parameters which define the breaking limits of the bitumen.

Schellekens(6) examined each stage of the pipelaying process and estimated the strains and loading times to be found in the coating due to handling, testing and laying operations. Estimated values of the strain and loading times experienced by the pipe enamel, and determined during the full-scale field trials in the Netherlands, are summarised in table 10.7.

Process	Requirement	Limits
1 Coating	Viscosity at 240°C	<200 cSt
2 Handling	Typical strain Loading time	0.018% 0.155 seconds
3 Transportation	Typical strain Loading time	0.045% 0.01 seconds
4 Storage	Indentation at 250 kN/m^2	< 1 mm
5 Field bending (see table 10.5)	Maximum strain Loading time	3.2% 20 seconds
6 Ditching	Maximum strain Loading time	0.25% 70 seconds
7 High pressure testing	Maximum strain Loading time Maximum strain Loading time	3% 3 hours at compression 0.5% 2 minutes at decompression
8 Offshore application	Maximum strain Loading time	0.5% 70 seconds
9 In-service	Low permeability for corrosion agents High electrical resistance	

Table 10.7 — Practical requirements for pipe coating properties as determined during pipe laying field trials in the Netherlands

During storage of coated pipes, compressive loads on the pipe enamel can be as high as 250 kN/m^2 when the pipes are stored two high. Under these storage conditions the pipes should not develop indentations greater than 1 mm since this necessitates repairs.

Field bending of pipes imposes the greatest demands in terms of flexibility of the coating. Maximum deformation is usually dictated by national standards(18,19,20,21). However, in the field strains may locally exceed those calculated from national codes. Measurement of actual strain was made during full scale field bending trials in which twelve metre pipe joints of 91 cm (36 inch) and 107 cm (42 inch) diameter were bent through eight degrees. Maximum strains experienced in practice were found to be 0.2 per cent greater than those strains given in table 10.8. The loading time estimated during the above field trials was twenty seconds.

After bending, the pipe bends are welded into the pipe string and the whole section is lifted and lowered into the ditch. The strain in this operation is estimated to be limited to the elastic strain of the steel (0.25 per cent) with a loading time of about one minute.

Prior to service the pipeline is pressure tested to about 90 per cent of the yield stress value of the steel, resulting in a maximum strain of 0.3 per cent with a loading time of three hours. The decompression (0.5 per cent), however, is accomplished in a few minutes. In service the pipe coating is required to withstand soil stresses and stone indentation as well as requiring a high level of electrical resistance and low permeability to water. The strain

Pipe size, o d (inches)	Radius	Maximum strain (plastic + elastic) (%)
<12¾	18 D	3.0
14	21 D	2.6
16	24 D	2.3
18	27 D	2.0
>20	30 D	1.9

Table 10.8 — Minimum radius of curvature allowed by the American code for oil pipes

induced in the pipe during laying offshore, for example, is again limited by the elastic limit of the steel. However, Schellekens defined the requirements such that the coating should be capable of withstanding strains of 0.5 per cent at a loading time of 70 seconds. The loading time was estimated from observations made during an off-shore pipe laying operation.

10.11.2 Corrosion protection requirements

A corrosion protection coating on steel pipes is required to provide a continuous film of electrically insulating material over the metal surface. The function of the coating is to prevent direct contact between the metal and the surrounding soil and to interpose such a high electrical resistance in the corrosion cell circuitry that there will be no significant corrosion current.

Two basic requirements are necessary from the coating to satisfy the electrical criteria:

- the coating must have a high electrical resistance,
- this resistance must be maintained throughout the anticipated life of the pipeline.

Bitumen normally has a high electrical resistance and therefore the first criteria can be met provided that the bitumen coating is applied without defects such as pinholes, cracks and wrinkles. The electrical conductivity of bitumen is approximately 5 to 20 x 10^{-11} ohm^{-1} m^{-1} and increases with temperature.

The second requirement is subject to the resistance of the coating to water absorption which can affect the long term electrical conductivity of the enamel. Accumulation of water at the interface may cause disbonding of the coating, which will affect the mechanical resistance of the coating to soil stresses, possibly resulting in the exposure of bare steel. Bituminous coatings tend to be very thick (in the range three to seven millimetres) and consequently provide a good barrier to water.

Comparisons have been made between the water absorption of coal tar and bitumen with the aid of gravimetric methods. However, the solubility in water of many coal tar constituents is often not taken into account and it is erroneously concluded that coal tar is better than bitumen in this respect. Considering the large proportion of polar constituents in coal tar by comparison with bitumen it is more probable that water absorption is greater for coal tar than for bitumen. Experiments conducted by Shell Research using radioactively labelled water (T_2O) have shown no differences between coal tar and bitumen. However, these investigations have shown that in principle harder grades of bitumen (and also coal tar) generally give better corrosion protection than softer grades and that the use of filler in bitumen enamel (eg slate dust) has no significant effect on corrosion protection properties.

10.11.3 Practical requirements and existing specifications

Many pipe coating specifications exist throughout the world(22) and often comprise combinations of mechanical and non-mechanical specification parameters. The purpose of the specifications is to translate the mechanical, electrical or other performance requirements under consideration into a test which can be performed and quantified on some or all of the pipe coating system, eg bitumen, bitumen enamel or coated pipe.

For example, application viscosity may be reflected in an equiviscous temperature at about 200 cSt (0.2 Pa.s) or as a maximum softening point. Deformation during stacking at elevated temperatures can be simulated by flow and sag tests. The behaviour of a pipe asphalt at normal temperatures during storage, handling, transportation and bending is associated with indentation tests, shatter or ball drop tests and low temperature bending tests.

Sometimes a minimum penetration at 25°C is specified, which may be based either on practical experience or on a theoretical or experimental correlation with bending or shatter tests.

Pipe ditching or high pressure testing can be simulated by bending and ring expansion. Soil stressing and stone indentation are reflected in flow and indentation tests.

Service requirements exist for many other aspects of pipe enamel formulation and use. For example, the use of filler may require a specification for settlement and sieve residue. Special applications such as the internal coating of water pipes may require tests for odour and taste. Adhesion tests may be specified and reinforcement fabrics must possess certain properties to ensure good performance.

Following the establishment of the qualitative relationships between the practical requirements and specification parameters, Schellekens(6) examined the validity of some of the specification limits.

The flow and sag tests as specified by the DCCC 13 and the Asphalt Institute require the enamel to resist a compressive loading as high as 250 kN/m^2. The test limits, when described in terms of the required stiffness modulus (40 N/m^2), are in surprisingly good agreement with each other. The practical service requirements, however, are far more severe and therefore the deformations in practice will largely be dependent upon the quality of the fabric reinforcement. Nevertheless, practical experience provides confidence in the validity of the specification limit.

In respect of the shatter or ball drop test, Schellekens challenges its veracity in quantifying the brittleness of the enamel in relation to practical performance, as the test is characterised by a combination of point loading, high strains and short loading time. A low temperature bending test will give a better indication of brittleness under practical circumstances in respect of pipe bending. The shatter test is still valuable, however, in simulating the effects of impact loads on an unprotected pipe enamel.

Process	Requirement
Coating process	Maximum softening point Equiviscous temperature
Handling, transportation	Brittleness tests, eg ball drop or shatter tests (adapted ball weight)
Storage	Flow or sag tests Indentation tests
Field bending	Low temperature bending test
Ditching	Low temperature bending test
High pressure test	Ring expansion test
Service	Water absorption Permeability tests

Table 10.9 — Practical requirements and related specification tests

The low temperature bending test of the American Water Works Association (AWWA) showed that at the specification limit of 20 mm deflection, the strain in the coating amounts to about ten percent. When the deflection rate of this test is adjusted to one millimetre per second, the loading time of 20 seconds comes into line with the practical loading time found during cold bending trials, see table 10.7. For pipe bending operations this appears to be better related to practical circumstances.

A summary of the practical requirements for pipe coating materials and the best related specification test is given in table 10.9.

10.11.4 Relationship between practical requirements, specification limits and bitumen properties

A relationship between the flow test values, according to the DCCC 13, and the softening point of the asphalt as a function of penetration index (PI) was established by Schellekens who found that the test requirement of six millimetres maximum is satisfied if the bitumen has a softening point of at least 105°C. Furthermore, as a rule of thumb for the PI range under consideration, the 200 cSt (0.2 Pa.s) application viscosity is normally reached at 100 to 110°C above the softening point.

A relationship between the indentation value according to DCCC 13 and the penetration of the bitumen enamel at 25°C was found by statistical interpretation of about 150 experimental results, see figure 10.4. An indentation requirement of less than 17 mm corresponds roughly to a penetration of 25 dmm maximum at 25°C.

The evaluation of strains and loading times and their conversion to minimum penetration limits is mainly based on the work of Heukelom(23) who established a link between strain at break and stiffness modulus, see figure 10.5. In this figure a distinction has been made between the different bending modes of steel and for this case the second possibility was chosen, ie, linear bending on steel. However, Heukelom's diagram was developed for road

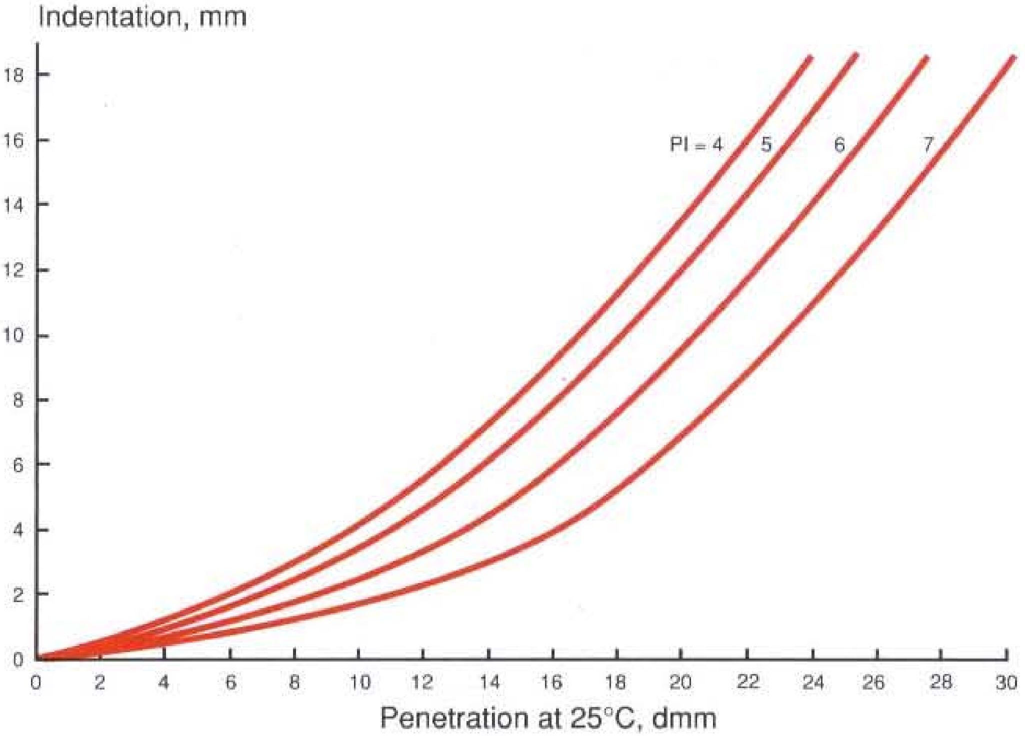


Figure 10.4 — Correlation between the penetration at 25°C and indentation according to DCCC 13

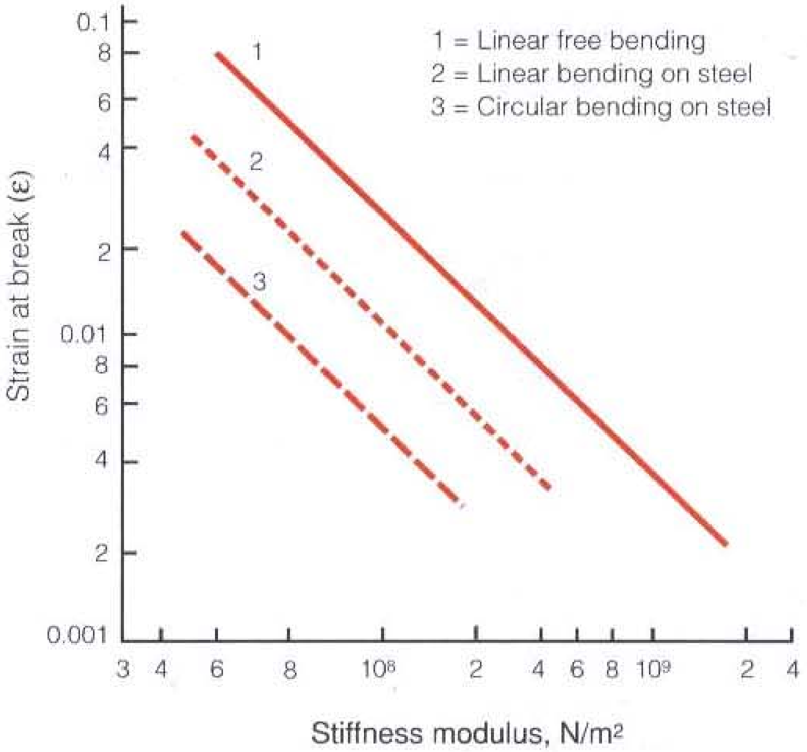


Figure 10.5 — Strain at break (ε) as a function of the stiffness modulus (s)

Handling step	Strain %	Loading time seconds	Temperature °C	Min penetration @ 25°C dmm
Yard handling	0.018	0.155	-10	3
Transportation	0.045	0.01	-10	7
			0	5
Ditching	0.25	70	0	4
High pressure testing	0.5	10,800	0	4
	3.0	10,800	0	8
	0.2	120	0	4
Field bending	1.7	20	0	12
			10	8
	2.1	20	0	14
			10	10
	2.2	20	0	14
			10	10
	2.5	20	0	15
			10	11
	2.8	20	0	16
			10	11
	3.2	20	0	17
			10	12
Offshore application	0.5	70	0	6
	0.25	70	0	4

Table 10.10 — Fracture limits (without safety factor) for bitumen pipe enamel during handling

grade bitumens with PI values ranging between +1 and -1. High PI oxidised grades deviate from this diagram which was suitably modified, resulting in a number of parallel lines whose position is dependent on PI.

Thus, for a given PI and strain it is possible to assess the stiffness modulus of the pipe enamel at break. The stiffness modulus, PI and practical loading times when entered into Van der Poel's nomograph give the temperature difference between the softening point (equivalent to T_{800pen}) and the test temperature, see chapter five. This subsequently yields the softening point at the specific test temperature. From this softening point and the required PI, the minimum penetration value can be derived with the aid of the PI nomograph.

Schellekens utilised this method to scan the PI scale from +3 to +7 to cover the normal range of coating grades and found almost identical penetration limits. The highest value was then taken as the minimum penetration value for a given set of strain, loading time and temperature requirements. Resulting lower penetration limits (without a safety factor) were determined for the strains and loading times exerted during handling, transportation, cold bending, high-pressure testing and offshore application and are detailed in table 10.10.

The accuracy of Van der Poel's nomograph governs the accuracy of the calculations, which is estimated as a factor of two for the stiffness modulus. This factor corresponds to about 5°C in the temperature parameter or about 25 per cent in the derived penetration value, which is considered to be sufficiently accurate for all practical purposes.

10.11.5 Selection of the appropriate grade of bitumen pipe enamel

A rational specification is one which is directly or indirectly derived from practical requirements. The choice of pipe asphalt, therefore, should be governed by the total set of practical requirements that the enamel should satisfy. Within the framework of the required mechanical properties, the bitumen grade chosen should be the one which possesses the best corrosion protection qualities.

The required properties of a bitumen enamel for use on a land pipeline carrying gas, for example, can be calculated, as indicated below, where the cold bending is limited to 1.5 per cent strain (40 D) at a temperature not lower than +10°C.

10.11.5.1 Determination of softening point range of enamel

Maximum softening point is derived from application conditions - typically 200 cSt (0.2 Pa.s) at a maximum temperature of 240°C - and is set at 130°C. Minimum softening point is governed by flow properties which will be adequate if, for example, the DCCC 13 flow test is satisfied - the softening point will then be 105°C.

10.11.5.2 Determination of penetration range of enamel

The maximum penetration for the bitumen enamel is determined by the allowable deformation during storage. It is assumed that deformation is satisfactory if, for example, the DCCC 13 indentation test is satisfied. The maximum penetration value at 25°C will then be 25 dmm. The minimum penetration at 25°C is dictated by the cold bending requirements. A strain of 1.7 per cent in 20 seconds at 10°C gives a minimum penetration at 25°C of about 8 dmm. With the addition of a margin for error, the minimum penetration at 25°C would be 10 dmm. This gives a penetration range at 25°C of 10 to 25 dmm.

Therefore, for the above defined application the pipe enamel specification would be:

softening point	105 - 130°C
penetration at 25°C	10 - 25 dmm.

Given that the corrosion protection of a bitumen is better for harder grades, and allowing for some variations in bitumen properties, R115/15 bitumen would be the most appropriate choice. An R120/20 filled with 30 per cent of slate dust might also be considered suitable.

10.12 Specification tests for bitumen and bitumen enamel for pipe coating

The quality assurance of pipe line coatings is dependent upon the schedules of tests and specifications set out by the various national and international standards bodies with an interest in pipe line operations, see table 10.6. Quality assurance of pipeline coatings therefore depends on a series of tests on raw materials, on materials tests during coating and tests on coated pipe joints before they are transported from the coating plant. This section examines some of the more important pipe coating performance tests as applied to bitumen enamels.

10.12.1 Coating thickness

Bitumen, coal tar and polyethylene coatings for pipelines are thick, usually three to seven millimetres compared to the much thinner layers associated with epoxy coatings. Coating thickness is an important factor in corrosion protection and thick coatings are a distinct advantage, allowing excess material for biological consumption, abrasion, and chemical and physical degradation in addition to providing a large barrier to water absorption. Coating thickness is normally measured using a magnetic or electromagnetic thickness gauge. These are usually satisfactory up to a thickness of about six millimetres. For greater thicknesses, instruments are used which incorporate magnetic resistor probes.

10.12.2 Peel test

The adhesion of the pipe coating to the steel substrate is of paramount importance for good corrosion protection and a wide variety of tests exists to measure this property. The adhesion of the coating to the steel is related to the ease with which the enamel coating wets the steel which is itself a function of the enamel viscosity. All standards include a measure of the viscosity of the enamel. In the case of a bituminous coating, viscosity can be defined by softening point and penetration, both of which are measurements related to viscosity under very low rates of shear.

Adhesion tests are always carried out on the coated pipe and always by a method involving peel resistance. For the AWWA C203 test or variations of this test, a strip of the coating of a pre-cut width is peeled from the steel pipe after cooling. The objective of the peel test is to determine the strength of the bond of the coating to the steel plate. Differences in adhesion found in practice are mainly caused by improper application of primer and coating, and/or the use of an unsuitable combination of primer and coating material.

10.12.3 Impact test

The impact test is intended to simulate the effects of damage to a pipe coating received during transport, handling, pipe laying, trenching, back filling, soil stressing, etc of pipe joints. For on-shore pipelines impact results may have more significance than for off-shore pipelines which usually incorporate a heavy concrete weight coating.

In general, a known mass is dropped from a standard height at 25°C onto an unreinforced bituminous enamel coating on a thick steel plate which has been grit blasted, primed and flood coated with the enamel. In BS 4147, the height is 2.45 metres and the steel ball weighs 650 g. After the mass has been dropped onto the bituminous coating, the panel is immediately tested using a Holiday detector with a voltage of 15 kV. The Holiday detection delineates any cracking in the enamel. This is followed by removal of disbonded enamel and the estimation of the disbonded area. The specification limit for BS 4147 impact resistance is a maximum of 6500 mm^2 of disbonded area at 25°C.

10.12.4 Bend tests

Pipe joints are commonly required to be bent in the field and consequently the corrosion coating must be able to withstand the stresses that this bending imposes on it. The bend test needs to simulate the degree of bending that the pipe will experience in practice and should be conducted at temperatures which will be experienced during field bending. Most standards specify the amount of bending allowable per pipe diameter.

Bituminous pipe enamel tests involve a three point bending test on steel strips coated with enamel. The deflection at which the first cracks are observed is noted, while at the maximum deflection the amount of disbonded area is measured. In fact this is linear bending on steel and according to Heukelom(23) the strain at break is half that of a freely bending beam. At 35 mm this amounts to a strain of two per cent at a loading time of 83 seconds, the stiffness at break being 1.1 x 10^8 N/m^2. The bend test may be considered as a large Fraass test in which the temperature is constant but the strain may vary and fracture occurs at a temperature at which the stiffness has about the same value as the Fraass test.

10.12.5 High temperature performance

10.12.5.1 Sag and flow tests

The high temperature performance of an enamel pipe coating is quantified by the sag test or the flow test. Upper service temperature limits for pipeline coatings are difficult to define and those given in table 10.11 are based on generally acceptable limits(17), although these may not be the absolute upper limits. The effect of elevated temperature on pipe coatings is of great importance as it places greater demands on other properties. There is, in general, no demand for any type of ageing test on bituminous enamel coating materials.

In the sag test, a steel test plate typically three millimetres thick is primed and coated with 1.5 to 5 mm of enamel, depending upon the particular test method employed. The coating may be scored by parallel lines at 75 mm spacings to give a number of replicates on the same panel. Most often, the plate is placed vertically in an oven at the test temperature (typically 70 to 75°C) for up to 24 hours. At the end of the test the amount by which the enamel coating has flowed down the plate is recorded. Table 10.19 shows the typical requirements for filled bitumen enamel coatings.

10.12.6 Low temperature performance

The low temperature performance of enamel pipe coating is quantified by impact and bending tests at low temperature. It is becoming increasingly necessary for coatings to be

Coating system	Temperature, °C
Bitumen	70
Coal tar*	80-95
Fusion-bonded epoxy resin*	90-110
Polyethylene	80
Polyurethane	115
Polypropylene	125

* dependent on grade

Table 10.11 — Upper temperature resistance of coatings

Material	Standard	Bend test °C	Impact test °C
Bitumen enamel	BS 4147	0	0
Coal tar	BS 4164	0	25
Fusion-bonded epoxy resin (FBE)	CAN/CSA Z245 20-M86	-30	-30
Polyurethane	DIN 30671	23 +/- 2	23 +/- 2
Polyethylene	DIN 30671	23 +/- 2	23 +/- 2

Table 10.12 — Low temperature impact and bending requirements

able to be handled, laid and operated at temperatures as low as -40°C. The low temperature requirements for various coatings are given in table 10.12. From these specification values it can be surmised that bending and impact should not be allowed to occur at temperatures much lower than the test temperature.

10.12.7 Cathodic disbonding

Steel pipelines are susceptible to corrosion either in sub-sea or in buried locations. The rate of corrosion is dependent upon, amongst other things, the steel, temperature and the availability of oxygen, water and chemical salts to the metal surface. To protect the steel and to minimise the degree of corrosion, special coatings, which include thick bitumen enamel coatings, are applied to the external pipe surface. Enamel coatings are applied under controlled conditions, often in factories, and great efforts are made to ensure that they are free from defects caused during the coating operation, as well as by transport, handling and laying stresses. Nevertheless, defects can occur and for this reason pipelines nearly always utilise additional corrosion prevention measures such as cathodic protection.

Cathodic protection current is applied to a steel pipeline or structure to polarise the steel at the site of damage to the corrosion protective coating to a sufficiently negative potential to reduce the corrosion rate at these sites to a negligible amount. This is achieved by forcing an electric current to flow through the electrolyte towards the surface of the metal to be protected, thereby eliminating the anodic areas. However, it is known that coating adhesion loss can occur at the edge of the defect in the coating under the influence of the negative polarisation. This adhesion loss which is known as cathodic disbonding is one of the most frequently discussed parameters of pipe corrosion protection. Some authorities believe that it is not a serious problem with thick coatings such as bitumen(24), whilst American user opinion(25) suggests that good resistance to cathodic disbonding is one of the most desirable properties of a corrosion protection coating. Lundt et al(26) concluded from a study for the Statpipe pipeline system in the North Sea that bituminous coatings were by far the type with the longest off-shore record and with no serious reported corrosion problems.

The effectiveness of all cathodic protection systems is assessed by measuring the potential between the surface of the protected metal and the surrounding electrolyte. The potential is measured before and after the application of the cathodic protection current and the effectiveness of the corrosion protection coating is taken as the difference in the readings before and after the potential is applied. The cathodic disbonding test can be conducted by a number of similar methods including ASTM G8, BGC/PS/CW6, BS 3900 : F10 and F11, and BS 4164. Eden and Woolf(2) have reviewed the various methods available for assessing cathodic disbonding and have presented a new method for the measuring the degree of disbonding at the end of the test.

The cathodic disbonding (CD) test involves the following procedure:

- A steel plate, or section of pipe, is coated with the complete corrosion protection system under examination (ie primer plus enamel).
- A defect is made in the coating (usually a drilled hole).
- A plastic cylinder is sealed centrally around the defect with an anode above (normally platinum).
- The cylinder is filled with electrolyte, usually a sodium chloride solution, and polarised via a potentiostat capable of providing up to 1 ampere at -1.5 volts referenced against a $Cu/CuSO_4$ electrode.

The test is normally allowed to run for 28 days, after which the coating sample is removed from the apparatus and the degree of disbonding is measured from the point of the original defect.

10.13 New developments in bituminous pipe coating enamels

Bitumen coatings for steel pipes have been used for many years and have proved to be easy to apply and to give good service at an economic cost. It is expected that bituminous coatings will continue to be specified for long and large diameter marine pipelines(22), as well as for on-shore installations. The gradual decrease in the use of coal tar products on health, safety and environmental grounds(15,16,27) will almost certainly lead to the increased use of bituminous materials.

The principal limitation of a bitumen enamel coating is its relatively narrow service temperature range, see table 10.13. In its favour the main advantages of bitumen enamel are that it is a thick, reinforced coating (about three to seven millimetres), hence providing a substantial barrier to water, it is relatively easy to apply and still relatively inexpensive(17). However, for many years there has been a demand for higher performance, particularly at extremes of temperature, which has led to the development of other types of coating systems such as polyethylene, polypropylene, epoxy resin, and many others. None of these alternatives has proven to be totally satisfactory, see Askheim and Eliassen(17).

Coating type	Working temperature °C		
	Askheim & Eliassen (17)		Woolf (22)
	Upper	Lower	Upper
Bitumen enamel	60-80 (90?)	-25?	70
Coal tar enamel	60-80 (90?)	-30?	80-95
Polyethylene	60-70	-40?	80
Fusion bonded epoxy resin	90-100 (120?)	-40?	90-110

(? - sic)

Table 10.13 — Service temperature range of pipe coatings

	Handling	Installation	Testing	Operations
Conditions:	Impact Abrasion	Bending Backfilling (impact)	Hydostatic expansion	Soil stressing Temperature changes Corrosive environment Disbonding
Requirements:	Impact strength Abrasion resistance Compression strength Penetration resistance Corrosion resistance	Extensibility Tensile strength Fatigue strength Impact strength	Extensibility Tensile strength Notch sensitivity Adhesive strength	Shear strength Tensile strength Coefficient of expansion Notch sensitivity Chemical, corrosion resistance. Adhesive strength

Table 10.14 — Conditions and related engineering properties after Gray(28)

Enamel type	Standard	Bend test	Impact test	Cathodic disbonding	Sag test
		mm, min	mm2	8 days, mm max	24 hrs, mm
Bitumen	BS 4147, type 2, grade	15 @ 0°C	<6500 @ 25°C	No specification	<1.5 @ 75°C
Coal tar	BS 4164, grade 105/8	15 @ 0°C	<10 000 @ 25°C	5 @ 20°C	<1.5 @ 70°C
Bituseal	Results achieved	70 @ -20°C	5027 @ -20°C	3 @ 25°C	0.5 @ 80°C

Table 10.15 — Comparison of performance requirements for high performance pipe coating enamel

With the slow demise of coal tar and the continuing demand for improved quality(6,29) and cost-effective solutions to pipe protection, a polymer modified bitumen enamel of improved service temperature range, flexibility and durability (Bituseal) has been developed(29) jointly by Phønix Pipe Protectors, a Danish company, and Shell International Petroleum Co Ltd.

Chapter seven has detailed the improvements that can be made to the properties and performance of bitumen by the addition of a thermoplastic rubber (TR) polymer. Improved flexibility at low temperature (illustrated by the improved Fraass value, modified ductility behaviour and ductility recovery tests), improved high temperature performance (causing increased viscosity at higher temperatures and higher softening point values) and increased adhesive strength (shown by the tensile test results) have indicated the potential for improving the properties of bituminous pipe coating enamels.

Gray(30) has indicated the particular engineering properties of a pipe coating enamel which have the greatest relevance to in-service performance, see table 10.14. From this table it is clear that all the major performance parameters required of a pipe coating system are either met by the properties of conventional oxidised bitumen or can be enhanced by the incorporation of a thermoplastic rubber modifier. Improvements in the performance of a pipe coating incorporating this type of high performance bitumen enamel can be reflected in the results obtained from standard pipe enamel tests.

10.13.1 Improved performance of a modified bitumen pipe coating enamel

In setting target limits for the development of a high performance bituminous pipe enamel, the basic requirements for bitumen and coal tar were determined from current enamel standards(4,31) and performance criteria were set which were considered to be desirable and achievable using bitumen/TR technology. Particular attention was paid to the "secondary" performance properties of the enamel, such as bend, sag, impact and cathodic disbonding properties, rather than the "primary" binder properties. Typical performance data is detailed in table 10.15.

The "secondary" performance properties of the enamel and the standards against which they were evaluated were:

- Low temperature bend test	BS 4147 Appendix F/BS 4164 Appendix J
- Low temperature impact test	BS 4147 Appendix G/BS 4164 Appendix K
- High temperature sag test	BS 4147 Appendix E/BS 4164 Appendix G
- Cathodic disbonding	BS 3900 Part F11

These tests evaluated comparatively the corrosion protection and mechanical properties of a pipe coating enamel formulated using a bitumen/TR binder and were tested in parallel with conventional bitumen and coal tar enamel in order to rank the three systems.

Evaluation of bitumen, coal tar and bitumen/TR pipe enamel formulations was undertaken on test plates which had been blast cleaned to Sa 21/2(8) and primed using a type 'B' synthetic primer. The bitumen/TR formulation was applied over a special synthetic primer designed specifically for compatibility with the modified bitumen. The enhanced properties of the bitumen/TR high performance pipe coating enamel are briefly described below.

> **Bend test.** This test simulates the in-service exposure of coated steel pipes to bending stresses during field bending of straight pipe joints. The modified bitumen enamel was tested in accordance with the method described in BS 4147 Appendix F at 0, -10 and -20°C.
>
> The coal tar enamel failed to meet the test requirements at 0°C and below. The bitumen enamel failed at -10°C and below, while the modified bitumen still performed at -20°C. The modified bitumen test panels were bent well beyond the test limit (15 or 20 mm deflection depending on the standard) with no cracking, demonstrating the superior flexibility and adhesion of the bitumen/TR enamel down to -20°C, see table 10.16. The absolute lower temperature limit for this material has not yet been determined .

Coating	Temperature °C	Deflection mm	Comment
Coal tar	0	7.25	Cracked
Bitumen	0	70	No cracking
Modified bitumen	0	70	No cracking
Coal tar	-10	13.25	Cracked
Bitumen	-10	18.75	Cracked
Modified bitumen	-10	70	No cracking
Coal tar	-20	6	Cracked
Bitumen	-20	4.25	Cracked
Modified bitumen	-20	70	No cracking

Table 10.16 — Bend test results at 0, -10 and -20°C

Impact test. Impact resistance of coated pipes is an important parameter and relates to handling, transport, pipe laying, trenching, back filling, etc. The impact test is normally conducted at 25°C; however, in order to assess the low temperature performance of the modified enamel, tests were conducted at 0, -10 and -20°C, see table 10.17. The bitumen/TR enamel is superior to both bitumen and coal tar enamel at all temperatures, illustrating the greatly improved low temperature flexibility of the modified bitumen.

Cathodic disbonding. Both on-shore and off-shore pipelines require supplementary corrosion protection (in addition to the waterproof enamel itself) to safeguard the steel against the effects of corrosion at defects in the enamel coating. The resistance of the pipe coating enamel to detachment due to electrical effects at the pipe surface resulting from coating defects is simulated in the cathodic disbonding test. Cathodic disbonding tests were carried out at ambient temperature (25°C) for 28 days and the coatings were examined and the disbonded areas measured, see table 10.18.

Coating	Temperature °C	Crack radius mm	Disbonded area mm^2
Coal tar	0	15	2830
Bitumen	0	shattered	—
Modified bitumen	0	no cracks	0
Coal tar	-10	35 to 40	3850
Bitumen	-10	shattered	—
Modified bitumen	-10	12	3850
Coal tar	-20	30	6360
Bitumen	-20	30	13275
Modified bitumen	-20	25	5027

Table 10.17 — Impact test results

Sample	Average disbonded length, mm
Coal tar	10.0
Bitumen	11.5
Modified bitumen	3.0

Table 10.18 — Cathodic disbonding test results at 25°C

The test results obtained at 25°C clearly demonstrate the superior performance of the bitumen/TR enamel in the cathodic disbonding test compared to both conventional bitumen and coal tar enamel giving a level of performance more appropriate to fusion bonded epoxy resin coatings. The improved adhesion of the bitumen/TR enamel and the development of a special compatible primer have made a very significant contribution to the improvement of the cathodic bonding performance for the modified bitumen enamel.

Sag test. One of the primary requirements of a pipe coating enamel is that it will resist creep and sag while in service, especially where the operating temperature of the pipe is high, and also during storage in hot weather where the pipe may be subjected to significant solar gain. The addition of TR to bitumen improves its high temperature performance, as shown by the increase in softening point, see chapter seven.

The sag test is the generally accepted method for quantifying the resistance of a pipe enamel to flow. In this test, conducted according to BS 4147 Appendix E, the enamel is subjected to heating in a vertical position in a controlled oven at 80°C for 24 hours. The results of this test are shown in table 10.19 where it can be seen that the modified bitumen enamel has far greater resistance to sag at 80°C than either coal tar or bitumen enamel. From these results it may be surmised that the modified bitumen enamel could resist sag up to 90°C, although this has not yet been determined experimentally.

Sample	Sag test (mm)
Coal tar	1.0
Bitumen	1.5
Modified bitumen	0.5

Table 10.19 — Sag test results at 80°C

10.13.2 Summary of the modified-bitumen enamel test properties

In summary, the TR modification of the bitumen can be shown to improve the working temperature range of a bitumen pipe coating enamel from typically 0 to 70°C (delta T=70°C) for an R115/15 bitumen to -20 to +80°C (delta T=100°C) for the bitumen/TR system. The improvements to the bitumen properties brought about through modification by TR also bring about beneficial changes to the key pipe coating properties. These improvements have been quantified on a laboratory scale and have subsequently been investigated on full scale pipes(32). The reported performance properties of the bitumen/TR pipe coating enamel show clearly that the new generation of thick high performance bituminous coatings have the potential to perform at the same level as higher performance materials such as polyethylene and fusion-bonded epoxy resin, but at a lower cost.

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Chapter 11 - Other uses of bitumen

11.1 Sound insulation

Bitumen is used not as a sound insulator but as a vibration damper. It is used in two sound damping applications; sound deadening panels and sound insulation panels in motor vehicles, and sound damping in buildings.

11.1.1 Motor vehicles

11.1.1.1 Sound deadening panels

Bitumen is used to damp vibration and stop the 'boom' caused by large areas of sheet vibrating at relatively low frequencies. Rigid panels are applied to the inside of motor vehicles and household appliances such as washing machines, dishwashers, tumble dryers, etc. The panels are manufactured with a heat activated adhesive on one side and a non-tacky finish on the other. Paper is often used for this latter purpose.

Experience has shown that penetration grades give better damping characteristics than oxidised grades for the same test conditions. However, 15 pen is too brittle whereas 50 pen is too soft, producing panels which flow during storage. Panels are positioned by hand onto a body panel and then subjected to heat (typically 140°C) whereupon they must conform to the shape of the body panel under their own weight and adhere strongly. The bitumen panels must allow air to escape and are usually either grooved or perforated and must also be capable of bridging holes. Fibres are added to give the bitumen sufficient 'body' for this purpose. A typical composition is shown in table 11.1.

Component		% by mass
Bitumen	(25 pen)	25 - 30
Polymer	(APP, EVA etc)	0 -5
Fibre		3 - 5
Filler	(limestone, clay, mica, etc)	60 - 70

Table 11.11 — Typical composition of a sound deadening panel

Magnetic panels are produced for areas where gravity does not hold the panel prior to adhesion, eg roof and door panels. In this case a magnetic filler is incorporated. Panels are manufactured in thicknesses of two to three millimetres.

11.1.1.2 Sound insulation panels

These are used almost exclusively in cars and are usually placed between the engine and the occupants, eg behind the instrument panel. The panels are slightly flexible and consist of a layer of bitumen backed with compressed fibre, felt or foam 'rubber'. Large boards are stamped out to produce panels specific to a particular vehicle.

Panels may be shaped by heating over a former for areas such as footwells. The bitumen used here needs to be fairly flexible to withstand cracking during handling and installation. Penetration grades between 50 and 100 pen are used,

11.1.2 Sound damping in buildings

There are several systems available in Europe for the reduction of noise transmission in buildings. In France building regulations dictate the use of floor and wall damping measures in residential buildings to keep external noise down to a standard level.

There are two types of treatment:

- Floors
  Flooring systems usually consist of tiles bonded onto a bituminous layer similar to a heavy roofing felt. Because of the thickness of the system it is only suitable for new house construction.
- Walls
  Internal partition walls are particularly suitable for treatment. Panels, similar to carpet tiles but heavier, are bonded to the wall. The panels may be cork faced and can be painted or wall papered over.

11.2 Carpet tiles

11.2.1 Required properties of the binder

To resist indentation in service, a hard bitumen is required but it should also have a sufficiently high PI to prevent cracking during laying. Also, to resist deformation and flow at higher temperatures, eg where it may be close to a central heating radiator or in hot climates, a high softening point is required. Suitable grades have softening points in the range 90 to 120°C and penetrations of 10 to 20 dmm. Mexphalte R115/15 is commonly used for carpet tiles although Mexphalte 15 and 25 have also been used.

11.2.2 Manufacture

Bitumen is used as a backing for loose-laid carpet tiles. The process will vary depending on the quality of the tile being produced but generally consists of three stages. Long fibres are spread evenly onto a loose woven hessian or polypropylene backing. The fibres are partially pushed through the backing with barbed spikes to form a loop on the underside. This passes over a lick-roller which coats the underside with a bitumen layer about two millimetres thick. In the last step a backing of jute felt or similar is applied to the still hot bitumen. As well as providing further dimensional stability this also acts to stop the underside of the felt being tacky. For the very highest quality tiles which contain looped pile or short pile fibres the woven backing and pile may be prepared at a different site and transported in large rolls to the coating factory. Large sheets, approximately 2 metres by 1.5 metres, are produced which are rough trimmed, stacked and allowed to cool before being cut to size.

11.2.3 Filler

Filler is frequently incorporated into the binder to increase stiffness, to reduce cost and to increase the weight of the tile. Limestone filler with a particle size of less than 75 microns is very commonly used.

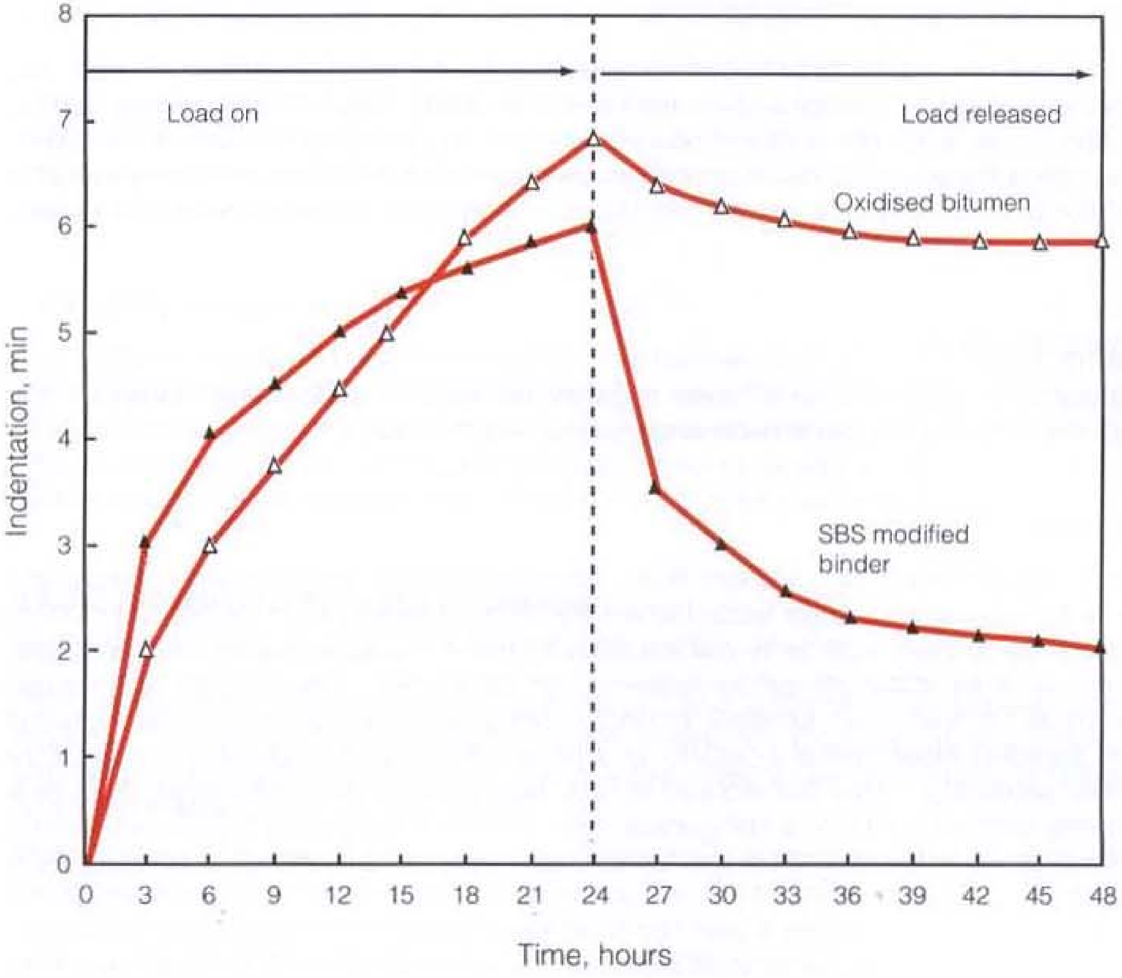


Figure 11.1 — Indentation resistance in bitumens used for carpet tile backing

11.2.4 Polymers

Polymers are increasingly being used in bituminous backings to improve low temperature flexibility during laying and to reduce permanent set in service. Styrene-butadiene-styrene (SBS) block copolymers are the major type although polyethylene and polypropylene plastomers are also used. Since the polymer is not fundamentally essential for satisfactory performance in normal circumstances low grade polymers are sometimes incorporated. Figure 11.1 shows elastic recovery results on carpet tile backing compound for SBS modified and oxidised bitumens.

11.2.5 Problems

There are very few problems associated with the manufacture and use of bitumen carpet tiles although some aspects are worthy of mention:

11.2.5.1 Cut-edge effect

When the bulk tile is trimmed into individual square tiles of side 0.5 metres, bitumen can sometimes smear the cut edge and leave a black stain, particularly with light colours. This is a function of the temperature of the bitumen and the sharpness/cleanliness of the blade. Where cooling is carried out under controlled conditions and the cutter is well maintained it should not be a problem. It is known that bitumens containing some polymers give cleaner cuts.

11.2.5.2 Cut-edge staining

During laying the bitumen edge will mark surfaces, eg walls, if insufficient care is taken. It is not a problem if fully trained and experienced operatives are used.

11.2.5.3 Static electricity

All carpet tiles which contain synthetic fibres will generate static electricity when walked on. In the past this could be a major hazard where sensitive computers were located but modern computers are generally sufficiently well insulated for this not to be a problem. Nevertheless, standards exist for static generation/dissipation on carpet tiles. The problem is not easily overcome as bitumen is an excellent insulator. Many additives have been tried including carbon powder, coke, metal powders and polar chemicals but all have proved only marginally successful. They are required at fairly high concentrations and either produce a conductive pathway, which is dangerous if an electrical fault should arise, or have a deleterious effect on the bitumen properties before any appreciable change in conductivity is observed.

11.2.5.4 Dimensional stability

Some polymeric carpet tiles have poor dimensional stability and can shrink in service. As well as this, the polymer can suffer from 'memory effect' and cause the tiles to lift away from the floor. Bitumen backed tiles are rarely a problem in this respect.

Polymer modified bitumens are increasing being used, especially for indentation resistance where they reduce permanent set considerably.

11.3 Electrical insulation

11.3.1 General

Bitumen has been widely used in the electrical industry because of its excellent electrical properties, resistance to water and chemicals and its thermoplastic properties which make it easily workable for manufacture. Applications include filling and sealing compounds for dry batteries, capacitors, cable junctions and terminal boxes, insulation tape, and the insulation of cables, motors, transformers, etc. A few applications are discussed here:

11.3.1.1 Dry battery sealing

Dry battery cells are sealed with hot bitumen in order to retain the contents, exclude contamination and in some cases to strengthen the assembly. Preferred grades are Mexphalte R85/25, R85/40 and R115/15. Mexphalte 25 pen or H80/90 (with ten per cent by mass of wax) may also be used. If required, up to 50 per cent by mass of an acid resistant filler can be incorporated.

11.3.1.2 Electric cable protection

The cable is wrapped in successive layers of a bitumen impregnated carrier such as jute, hessian, paper or synthetic mat and metal tape or wires. The various layers are coated with bitumen, softer grades such as 200 pen on the inside and harder grades such as 15 pen or R85/25 on the outside. The outermost layer may have wax added to reduce surface tackiness and may be whitewashed. Alternatively it may be coated with plastic.

11.3.2 Electrical properties of bitumen

11.3.2.1 Conductivity/resistivity

Bitumen has a high resistance (low conductivity) and is therefore an excellent insulating material. Harder grades have slightly higher resistance than soft grades although the difference is not important in practice. The resistance decreases with increasing temperature as shown in table 11.2.

The influence of fillers on resistance is negligible, provided that the filler is not conductive. Large quantities of conductive fillers can reduce the resistance markedly, eg mastic asphalt containing coke, graphite or metal powder fillers can have a resistance of 10^3 to 10^6 ohm/cm and may be used as flooring where some conductivity is required to avoid electrostatic hazards.

Temperature, °C	Resistance, ohm/cm
30	10^{14}
50	10^{13}
80	10^{12}

Table 11.2 — Variation of bitumen electrical resistance with temperature

11.3.2.2 Dielectric strength

The dielectric strength (or breakdown voltage), a measure of the resistance of a dielectric to electrical breakdown, is measured in kV/mm and depends on the conditions of the test and the shape of the electrodes.

Dielectric strength increases with bitumen hardness and decreases with increasing temperature as shown in table 11.3. The effect of fillers on these values is not known precisely but they will tend to decrease dielectric strength.

Temperature, °C	Dielectric strength (kV/mm), flat electrodes
20	20-30
50	10

Table 11.3 — Variation of dielectric strength with temperature

11.3.2.3 Dielectric constant and dielectric loss

The dielectric constant of bitumen is approximately 2.7 at 20°C increasing to 3.0 at 90°C. Dielectric loss increases with increasing temperature and decreases with increasing frequency, see tables 11.4 and 11.5.

11.3.3 BS 1858 Bitumen based filling compounds for electrical purposes

British Standard BS 1858 gives specifications for five classes of bitumen compounds and one natural asphalt or bitumen/filler compound. The compounds are classified by their softening point range and the standard sets out minimum values for penetration. The actual value of penetration and softening point which can be used is a matter of agreement between the purchaser and supplier although the standard lays down tolerances on the agreed values. The tolerances are extremely tight, much tighter than BS 3690 which is the specification for bitumen manufacturers, and in some case is narrower than the reproducibility of the test method. Hence most bitumens will only meet the requirements of a particular class of compound in BS 1858 when their properties are at around the mid-point of their respective specifications in BS 3690. Manufacturers of these materials usually blend two grades of bitumen to make a product with the desired properties.

Temperature, °C	Dielectric loss, tan δ (50H_Z)
20	0.015
50	0.017
80	0.029
100	0.045

where δ = angle of phase distortion

Table 11.4 — Variation of dielectric loss with temperature

Frequency, (H_Z)	Dielectric loss, tan δ (20°C)
50	0.015
10^5	0.006
10^6	0.003
10^7	0.001

where δ = angle of phase distortion

Table 11.5 — Variation of dielectric loss with frequency

			Suitable grades															
Class	S.Pt °C	Pen (min)	Penetration grades								Oxidised grades						Hard grades	
I	40 max	—	450	300	200													
II	41-70	20				100	70	50	35	25								
III	71-90	20												85/40	85/25	75/30		
IV	91-120	10									115/15	105/35	95/25					
V	121 min	7																
VI	—	7	450	300	200	100	70	50	35	25	115/15	105/35	95/25	85/40	85/25	75/30	80/90*	100/120*

* H80/90 and H100/120 would need to be at the soft end of their respective specifications

Table 11.6 — Penetration and softening point requirements for electical filling compounds specified in BS 1858

Table 11.6 shows the penetration and softening point limits contained in BS 1858 and which bitumen grades meet the requirements of the six classifications. There are no bitumens manufactured to BS 3690 which have a softening point sufficiently high for a class V compound. In this case either a special bitumen would have to be manufactured or polymers could be used to raise the softening point.

As well as penetration and softening point the standard contains requirements for:

Viscosity	BS4693 Limits by agreement between purchaser and supplier
Pour point	
Solubility	BS 4690
Electrical strength	IEC 243
Flash point	BS 4688
Ash (mineral matter)	BS 4450
Acidity	BS 4694
Copper corrosion (injurious sulphur)	
Adhesion	
Shrinkage on cooling	
Filler settlement (class VI only).	

In general most bitumen grades would meet all the requirements (subject to agreement).

It should be noted that the presence of foreign matter such as rust or coke particles will have a deleterious effect on electrical strength. To minimise this risk it is important that storage tanks are well maintained, utilise filters and that bitumen is not heated excessively during storage.

11.4 Waste material encapsulation

All human activity creates waste by-products of one type or another. Our increasingly complex society is often in danger of poisoning itself with the toxic residues of the many industrial processes which sustain our wealth creating economies. The threat from some

Inactivition of fly ash	Encapsulation in bitumen	Class 1 waste* thresholds
Structural integrity test (NF. EN. 196.1)		
Compressive strength	17 MPa	>1 MPa
Fall in compressive strength after moisture/exudation test (6 cycles immersion for 24 h exudation for 24 h)	13%	<30%
Leaching test (3 successive leachings each of 16 h duration)		
Soluble fraction as percentage of the dried mass of stabilised waste	8%**	<10%
Metals in mg/kg of dried stabilised waste material		
Leached Hg	<0.1***	<5
Leached Cd	<0.1***	<25
Leached As	<0.5***	<5
Leached Pb	28	<50
Leached OCD (Oxygen chemical demand)	250	<2000
Leached TOC (Total organic carbon)	82	—

* Acceptance criteria for inactivated waste according to EC Directive.

** Soluble fraction for ash with high soluble fraction before inactivation: 15%.

*** Represents detectable limits for the analytical techniques.

Table 11.7 — Effectiveness of the encapsulation of waste materials using a hard grade of bitumen

types of waste products such as radioactive residues, spent refinery catalysts, residues from water treatment plants and from waste incinerators is so great that legislation has proved to be essential in the management, disposal and control of them.

In Europe, the Directive EEC 91/689 of 12th December 1991(1,2,3) on the disposal of Class 1 discharges defines the characteristics of inactivated waste which will be the only materials acceptable for disposal with effect from 1995. Table 11.7 shows the acceptance criteria imposed by the regulations for the inactivation of residues from the purification of smoke from household waste incinerators. This regulation covers the most dangerous industrial waste which is currently buried in Class 1 disposal sites or in on-site dumps. This category of waste totals some several hundred thousand tonnes per annum in France alone. By 1995 such hazardous waste will be required to be stabilised before disposal at controlled dumping sites to eliminate any possibility of the contamination of ground water and aquifers by run-off water from the tip. This Directive will also apply to on-site dumps at factories and chemical plants. All dumping sites will be required to incorporate an impermeable geomembrane at the bottom of the tip and a drainage circuit to control effluent. In addition, the dumps will only be permitted to accommodate stabilised wastes.

In France, in order to comply with the Directive and where recycling of the materials is neither practicable nor economically feasible, the waste materials will be encapsulated in bitumen or cement. A stabilisation technique has been developed by Shell Bitumen for the treatment of hazardous waste materials based on the traditional process of asphalt manufacture. The waste materials are stirred with 30 to 50 per cent of hot bitumen in an asphalt mixer for several hours to ensure complete coating. The resultant bitumen-rich mastic material can be packed into drums at a factory or poured directly into moulds at the waste storage site.

The French CEA (Atomic Energy Commission) has approved the use of bitumen for the encapsulation of certain types of radioactive waste for the last thirty years. As an encapsulant, bitumen has a number of special advantages:

- good resistance to the effects of radiation;
- chemical inertness;
- impermeability to water;
- resistance to cracking (flexibility);
- physical, chemical and biological stability;
- easy to process (thermoplastic hydrocarbon);
- many grades of bitumen;
- ready availability;
- reasonable cost.

Radioactive waste by its very nature has a limited life span. The life span of toxic or corrosive chemical waste is, however, infinite so its encapsulation must be efficient. Experience with the encapsulation and management of radioactive waste has indicated potential for the treatment of chemical wastes such as spent industrial catalysts.

11.4.1 Reduction in leaching of dangerous ions

The petrochemical industry uses catalysts in the form of extruded pellets several millimetres long, comprising an aluminium medium coated with a metal (particularly nickel). Spent catalyst has been used to study the leaching behaviour of waste materials encapsulated in bitumen.

A mastic asphalt compound comprising 47 per cent of a hard penetration grade bitumen (Mexphalte 85/2) and 53 per cent of spent catalyst produce a dense material with a continuous bitumen phase having no interconnecting voids and a bulk density of about 1.41 g/cm^3.

Shell and the CEA, at the Effluent and Waste Analysis Laboratory at Cadarache (SAED), have investigated the encapsulation of spent catalyst waste, adapting the techniques developed and used by CEA since 1960 for treating radioactive waste. The bitumen coated spent catalyst waste has been studied carefully to ascertain the risk of dangerous nickel and molybdenum ions leaching from the encapsulated material. Typical data from these leaching experiments is shown in table 11.7. Using the data from these leaching experiments, a physico-chemical study was undertaken by Shell and Intakta[3,4] to develop a mathematical model for the behaviour of an encapsulating bitumen coating over time.

Using Fick's 2nd Law applied to a pure, diffuse system in a semi-infinite medium and taking account of a zero concentration of ions at the limits of the system, the quantity of ions released per unit area as a function of time, M(t) is given by:

$$M(t) = \frac{-2\,Ao}{V\,\varepsilon\,R} \sqrt{\frac{D_e\,\varepsilon\,Rt}{\pi}}$$

Ao	initial content of Ni or Mo (g)
V	volume of leaching residue sample (m^3)
ε	porosity
R	delay factor
De	actual diffusion (m^2/s)
t	time (s).

The fact that molybdenum has a solubility limit alters this equation which was taken into account in the model. For pure diffusion, the quantity released is thus proportionate to the square root of the time of exposure.

The effective diffusion coefficient (D_e) for the ions can be calculated from the gradient obtained in a nomogram for $\sqrt{t}$ after surface leaching (day three). The adjustment of the model to the experimental data was very effective in producing the following regression coefficients.

Ni catalyst (not encapsulated)	0.825
Mo catalyst (not encapsulated)	0.979
Ni catalyst (encapsulated)	0.996
Mo catalyst (encapsulated)	0.989.

The diffusion coefficients for the Ni ion are thus equivalent to:

D_e Ni = 4.25×10^{-12} (m^2/s)	for the spent catalyst without encapsulation
D_e Ni = 5.8×10^{-18} (m^2/s)	for the spent catalyst with encapsulation.

As the diffusion coefficients are calibrated using the data from the experiments, it is possible, if scaling factors are applied, to calculate the quantities released for larger samples such as a drum and over very long periods of time, provided that the hypotheses upon which the model is based remain valid. Figures 11.2 and 11.3 show the quantities calculated for the release of nickel and molybdenum from a corroded drum containing spent catalyst and encapsulated spent catalyst respectively.

The hypothesis for the corroded drum is somewhat pessimistic for the first few years in a controlled disposal site, but very soon becomes realistic. The comparison of figures 11.2 and 11.3 shows that a drum of non-encapsulated catalyst would release about 1,400 g of nickel into the environment in 150 days. A calculation shows that it would take over seven million years for the same quantity of nickel to be released by a drum of encapsulated catalyst under similar environmental conditions.

Photograph 11.1 — Spent catalyst before encapsulation

Photograph 11.2 — Encapsulated spent catalyst being packed into metal drums

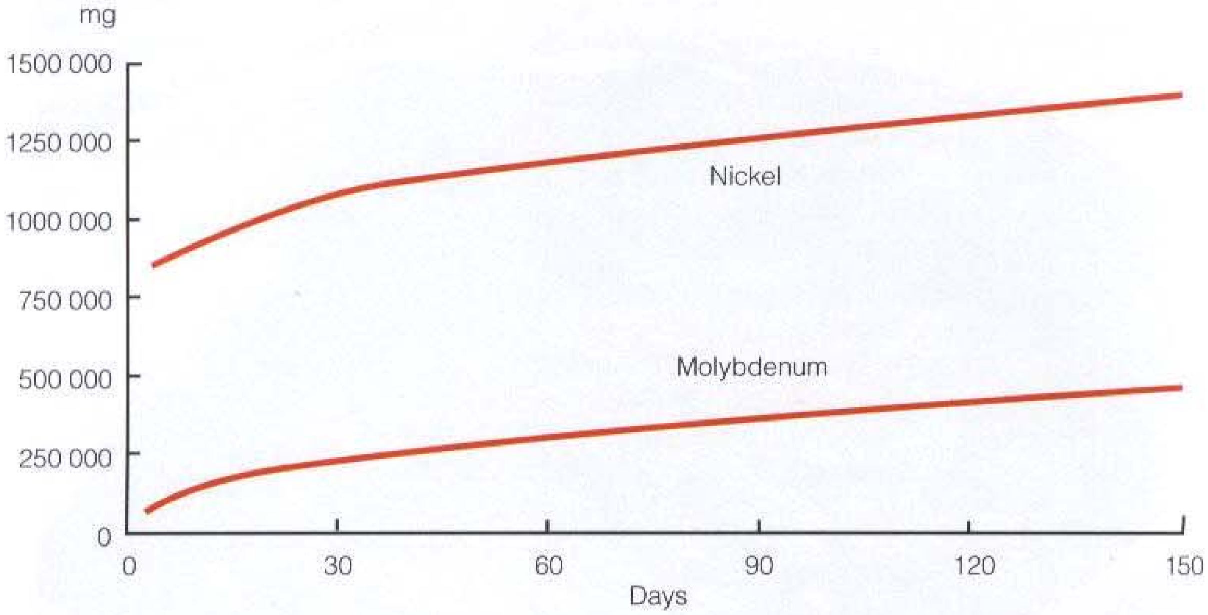


Figure 11.2 — Quantities of nickel and molydenum leached out of a corroded drum of spent catalyst

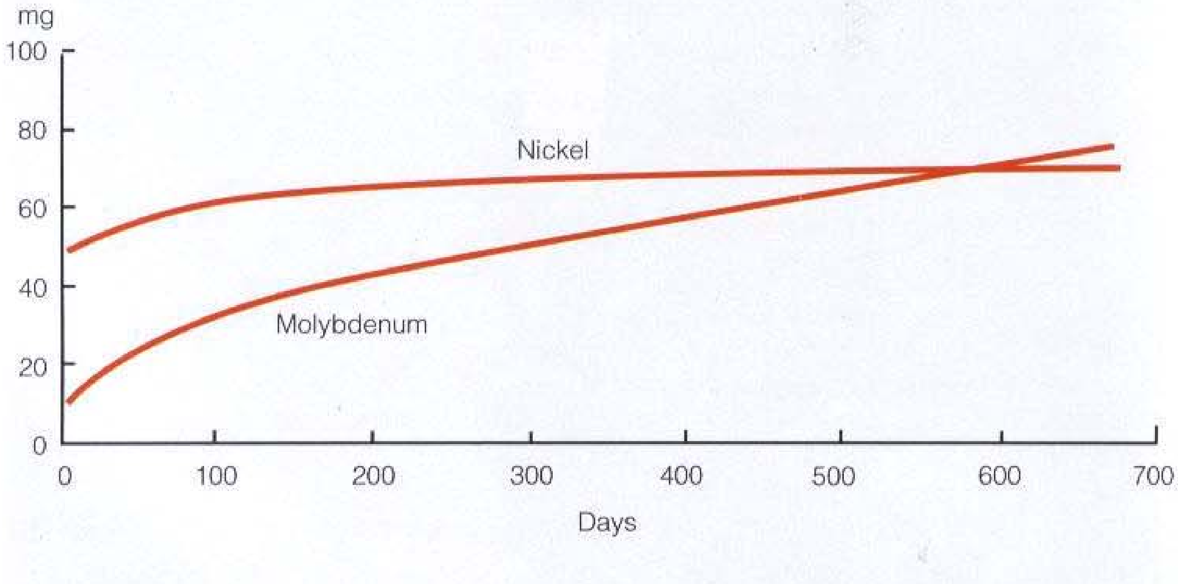


Figure 11.3 — Quantities of nickel and molydenum leached out of a corroded drum of spent catalyst encapsulated in bitumen

11.4.2 Application

The process for the encapsulation of the spent catalyst uses a conventional mastic asphalt mixer. Pilot trials using a charge of three tonnes of hard penetration grade bitumen (Mexphalte 85/2) and three tonnes of spent catalyst (stored under nitrogen because it is pyrophoric) required mixing for three hours after which the resultant mastic was poured into steel 200 litre drums for transportation to the waste disposal site. During a six month period the Shell refinery at Petit-Couronne in France encapsulated some 2,000 tonnes of spent catalyst, see photograph 11.1.

A hard bitumen, Mexphalte 85/2, is used for the encapsulation process because it ensures that the stabilised waste preserves its structural integrity over time. The contact surface area between the encapsulated waste and run-off water should be kept as small as possible to minimise the risk of leaching of soluble salts. The hard bitumen makes it possible to meet all the requirements for compressive strength and leaching tests laid down in the regulations, see table 11.7. It should be noted that the bituminous encapsulant must not be allowed to come into contact with effluent which contains petroleum solvents which may soften the bitumen and expose the waste products. In the overwhelming majority of cases exposure to solvents in controlled waste dumps is unlikely.

The ease of application and efficiency of the bitumen encapsulation process make it an economic process which can be readily adapted to encapsulate other types of hazardous waste. Already in France, this process is being used for the treatment of "REFIOMs" - residue from the purification of smoke from household waste incineration plants.

REFIOMs account for an enormous quantity of toxic waste. An average household waste incinerator produces some 3,000 tonnes per year of fly ash. Around 18 million tonnes of household waste are produced each year in France, 4.1 million tonnes of which are incinerated using energy recovery systems and 2.4 million tonnes without energy recovery, producing some 300,000 tonnes of fly ash. Once encapsulated in bitumen this residue, which contains heavy metal ions, presents no risk to the environment.

One further advantage of the encapsulation of REFIOMs is that it reduces the volume of this very powdery waste quite considerably. Before encapsulation the bulk density of the fly ash is around 600 kg/m^3 - after encapsulation in bitumen it is around 1600 kg/m^3.

11.4.3 Advantages of the process

The encapsulation of waste products using bitumen can be undertaken with a wide range of materials, without the necessity to change the formulation of the encapsulating medium, as bitumen is inert to all but the most aggressive chemical agents. Encapsulated waste can be poured directly into a specially designed pit or skip or into 200 litre steel drums which are readily available and cheap. This is possible because the bitumen solidifies rapidly on cooling. After a few hours it is possible to conduct the leaching conformity test on the material. The encapsulation process utilises a standard mastic asphalt mixer which is mobile, simple and inexpensive. Investment is low and can be scaled up as the volume increases.

The intrinsic properties of bitumen, such as durability, resistance to micro-organisms and to many chemical substances makes it a stable and effective treatment for neutralising hazardous waste.

11.4.4 Encapsulation of radioactive waste

In France, more than 70 per cent of electricity is produced by nuclear power stations which generate radioactive waste products that cannot be made safe by either chemical, physical or biological processes. Only time depletes the hazardous nuclear radiation from this type of waste and, as a consequence, the contaminated materials need to be specially treated to isolate them from the environment. Radioactive waste exists in a number of forms which include:

- **High-level or long-lived wastes.** These materials must be stored in underground sealed cavities at great depth. By the year 2000, in France for example, this type of waste will amount to some 83,000 m^3. No underground storage repositories are yet available in France; however, some deep mines in Germany meet the necessary geological conditions and are used for this purpose.
- **Low-level and short-lived wastes.** "Short-lived" waste is defined as that in which the effects of radioactivity become negligible after about 300 years. This type of waste is stored in surface repositories and represents some 30,000 m^3 per year. In France, a surface site, the La Manche Centre, has been in existence near La Hague since 1969, and another, at Soulaines (Aube) has been operational since 1991.

In order to store radioactive waste safely, two important constraints govern its handling. Firstly, the waste needs to be reduced in volume, and secondly, precautions have to be taken to protect it against natural forces, particularly water. Surface storage sites are always provided with meticulously designed waterproofing, although the possibility of water seepage into and out of a repository cannot be excluded. This risk is also present with underground storage where water could dissolve radioactive elements from the waste material and carry them outside the storage area. This phenomenon, known as leaching, is more extensive the greater the surface area exposed to the action of water.

Before being stored, nuclear wastes are subjected to treatment designed to reduce their volume and bind them so that the surface area potentially coming into contact with water is minimised. Non-powderous solid wastes are simply compacted at the storage site, and, at Soulaines in France, a 1000-tonne press is used for this purpose.

Liquid waste, however, is more difficult to handle and is first concentrated at source to form a sludge which is then bound with a binding agent for ease of handling and subsequent storage. Three processes have been developed to effect this binding:

- vitrification,
- cement encapsulation,
- bitumen encapsulation.

Vitrification is a very expensive process and is reserved for high-level radioactive wastes.

Cement encapsulation is not commonly used because:

- the volume of sludges to be stored cannot be reduced and the cement fixes the water in the sludge
- not all liquid wastes can be treated; when treated with cement, sludges with high salt contents produce encapsulates which are too friable.

Bitumen encapsulation is the most widely used method in France for the safe and efficient encapsulation of low and medium level radioactive waste.

This process was developed in France by the Atomic Energy Commission (CEA) in the 1960s and its first industrial application was at Marcoule (Gard) in 1967. The encapsulation process has subsequently been investigated in the USA, UK, Belgium, the countries of the former USSR, Germany, India, Pakistan and Japan. In France, it has been adopted for use in the new nuclear fuels reprocessing plant constructed at La Hague.

The excellent adhesion of bitumen to many materials and its insensitivity to many chemical agents mean that it can be used to bind many types of radioactive waste, including, in particular:

- solid waste of small particle size, such as ion exchange resins and incinerator ash;
- chemical co-precipitation sludges, the residues from the radiochemical purification of plant waste water; the radio elements present in this water are concentrated by co-precipitation and are collected in crystalline sludges containing approximately 50 per cent of water (after filtration), and colloidal sludges with 80 per cent of water,
- evaporation concentrates, resulting from the processing of irradiated fuel rods; every year one third of fuel in a reactor is renewed, the rods used to charge the nuclear reactors are removed and their contents are dissolved in nitric acid in order to recover the residual fuels (uranium and plutonium); liquid wastes from this processing essentially consist of nitrates which can only be concentrated by evaporation; the free nitric acid in the sludges obtained in this way is neutralised before bitumen encapsulation.

Bitumen encapsulation of waste is achieved by mixing hot bitumen and hot sludge in the presence of a surfactant in a double screw extruder. The water in the sludge evaporates during mixing. A five metre long extruder can produce of the order of 50 kg/hour of bitumen mastic.

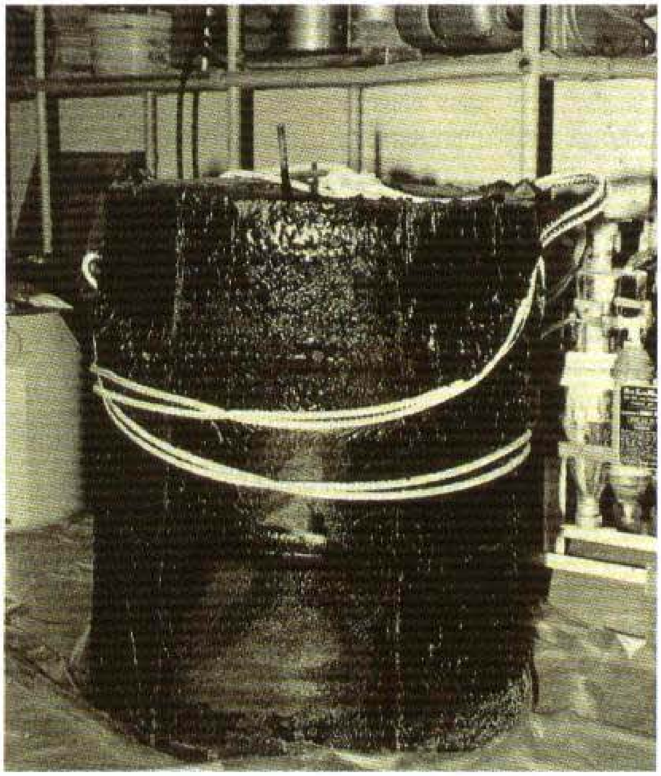
A sludge which contains 50 to 70 per cent of water is processed to give a bituminous mastic containing 40 to 50 per cent of bitumen and 0.5 per cent of water. The mastic is manufactured and cast at 130°C into metal drums which are then stored.

A wide range of bitumens of various consistencies (penetration, and softening point) are available for the encapsulation of radioactive waste, and consequently, the bitumen most appropriate for the sludge requiring treatment and the desired mechanical properties of the bituminous mastic can be selected.

Using this method the volume of the waste to be stored can be reduced by between ten and twenty per cent. However, more importantly, the mastic obtained in this process does not deteriorate over time as bitumen is unaffected by water and most chemical agents and is only slowly affected by micro-organisms, see chapter twelve.

The bituminous mastic obtained by binding radioactive wastes has the same properties as bitumen itself, does not crack over time, and has excellent impact resistance. The leaching of radioactive particles by water therefore remains very limited, and is predicted to remain so even for several centuries.

The use of bitumen as an encapsulation medium for radioactive waste has prompted studies on the effects of radiation on various grades of bitumen considered to be suitable for this use, see photograph 11.3. The studies have examined the bitumen compositions produced during the encapsulation process using both active and inactive mineral materials. A summary of some of the work is given here(5).



Photograph 11.3 — Drum of agglomerated radioactive waste used for leaching studies (note completely corroded drum)

11.4.4.1 Effect of gamma radiation on bitumen(5)

It is known from studies conducted by the Atomic Energy Research Establishment at Harwell in the UK that gamma irradiation of bitumen compositions can cause swelling due to nucleation and the growth of gas bubbles within the material. The degree of swelling depends upon the radiation dose rate and the size of the sample.

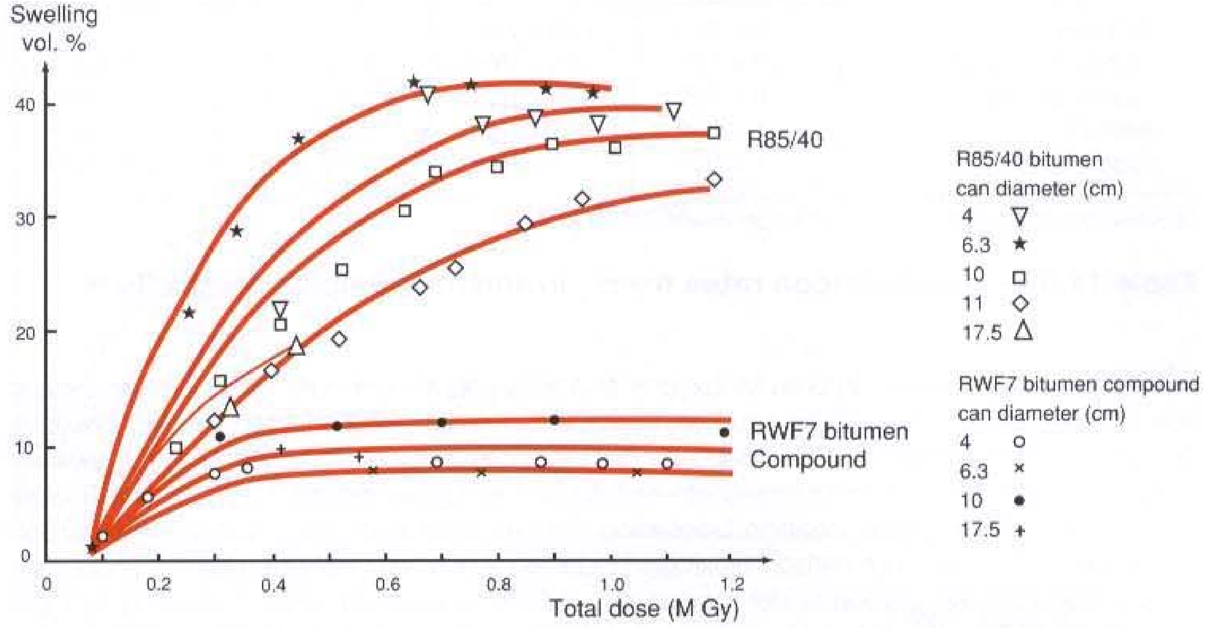


Figure 11.4 — Irradiation swelling of bitumen R85/40 and RWF 7 waste/simulate for different sample diameters(5)

Figure 11.4 shows the degree of swelling for Mexphalte R85/40 bitumen and a bitumen composition in containers of various sizes and at dose rates from 0.25 kGy/h in a Co cell at 22°C. The dose rates for the various samples approximated to the conditions experienced by a 200 litre drum of waste containing about 1 Ci/l activity. On irradiation, swelling of the material commences at about 50 kGy and saturates at about 300 kGy. The unfilled bitumen (R85/40) swells by 40 per cent of its volume but the bitumen composition swells by only about ten per cent.

Other experiments to determine the saturation swelling of filled and unfilled bitumens are summarised in table 11.8. It is apparent that some oxidised bitumens are more suitable for the encapsulation of radioactive waste than the penetration grades.

Bitumen type	Waste content (mass%)		
	0	24	40 to 51
Mexphalte 25	—	>80	20-40
Mexphalte 35	40-70	—	12
Mexphalte R85/40	30-40	—	8-11
Mexphalte R90/40	5-15	—	1-3 or 7-8

Table — 11.8 Bitumen saturation swelling (volume %)(5)

Gas evolved	Oxygen atmoshere		Argon atmosphere	
	0.6 MGy	3 MGy	0.5 MGy	2.6 MG
Hydrogen	3.9×10^{-4}	3.9×10^{-4}	1.5×10^{-4}	2.2×10^{-4}
Carbon monoxide	1.3×10^{-5}	3.5×10^{-5}	2.1×10^{-4}	1.8×10^{-5}
Carbon dioxide	2.6×10^{-5}	3.0×10^{-4}	1.1×10^{-5}	6.7×10^{-6}
Methane	$<1 \times 10^{-6}$	1×10^{-6}	5.2×10^{-6}	7.5×10^{-6}
Hydrocarbons ($C \geq 2$)	$<1 \times 10^{-6}$	5×10^{-6}	1×10^{-6}	2.2×10^{-6}

Samples comprised inactive simulated bitumen/waste compositions

Table 11.9 — Gas evolution rates from γ irradiated samples ml/g/kGy (5)

During gamma irradiation, in both an oxygen and an argon atmosphere, gases are generated due to the decomposition of the bitumen. Samples of an oxidised bitumen R85/40 generate 95 per cent of hydrogen with some carbon monoxide, carbon dioxide and low molecular weight hydrocarbons at total doses of ~0.5 MGy. At higher doses ~3 MGy, the relative proportions of the gases change becoming 50 per cent hydrogen, 5 per cent carbon monoxide, and 4 per cent carbon dioxide. Under an argon atmosphere a higher proportion of hydrocarbons are evolved under irradiation, ~4.5 per cent at 0.5 MGy increasing to 7 per cent at 2.5 MGy. The rates of gas evolution for the main constituents are summarised in table 11.9 for both oxygen and argon atmospheric irradiations.

11.4.4.2 Effect of alpha radiation on bitumen(5)

Accelerated alpha irradiation of compositions of R85/40 plus 30 per cent by mass of inactive filler was undertaken by incorporating ^{241}Am at a level of approximately 1 Ci/l providing a dose rate of 0.1 kGy/h, a factor of 10^3 greater than the proposed real waste form. The swelling data is shown in figure 11.5 for samples of different thickness. At the dose rate of 90 Gy/h and with samples of the size tested, gamma irradiation causes no swelling. However, alpha irradiation can cause significant swelling, the amount of swelling being dependent on the depth of compound in the sample cans.

11.4.4.3 Effect of radiation on the mechanical properties of bitumen(5)

11.4.4.3.1 Effect on penetration and softening point

Mexphalte R90/40 bitumen and compositions with dried sludges irradiated with a ^{60}Co source at a dose rate of 5.7×10^3 Gy/h (1st series of tests) and 3.6×10^3 Gy/h (2nd series of tests) are shown to harden the bitumen by about one grade from R90/40 to R115/15, see table 11.10.

11.4.4.4 Gas evolution through bitumen

The gaseous evolution from pure R90/40, mainly hydrogen, is higher than that from the simulated bitumen/waste composition (RWF9) by a factor of 6 to 7. Irradiation in the presence of air shows that oxygen is rapidly absorbed, probably by strong reactivity with oxygen radicals present in the bitumen.

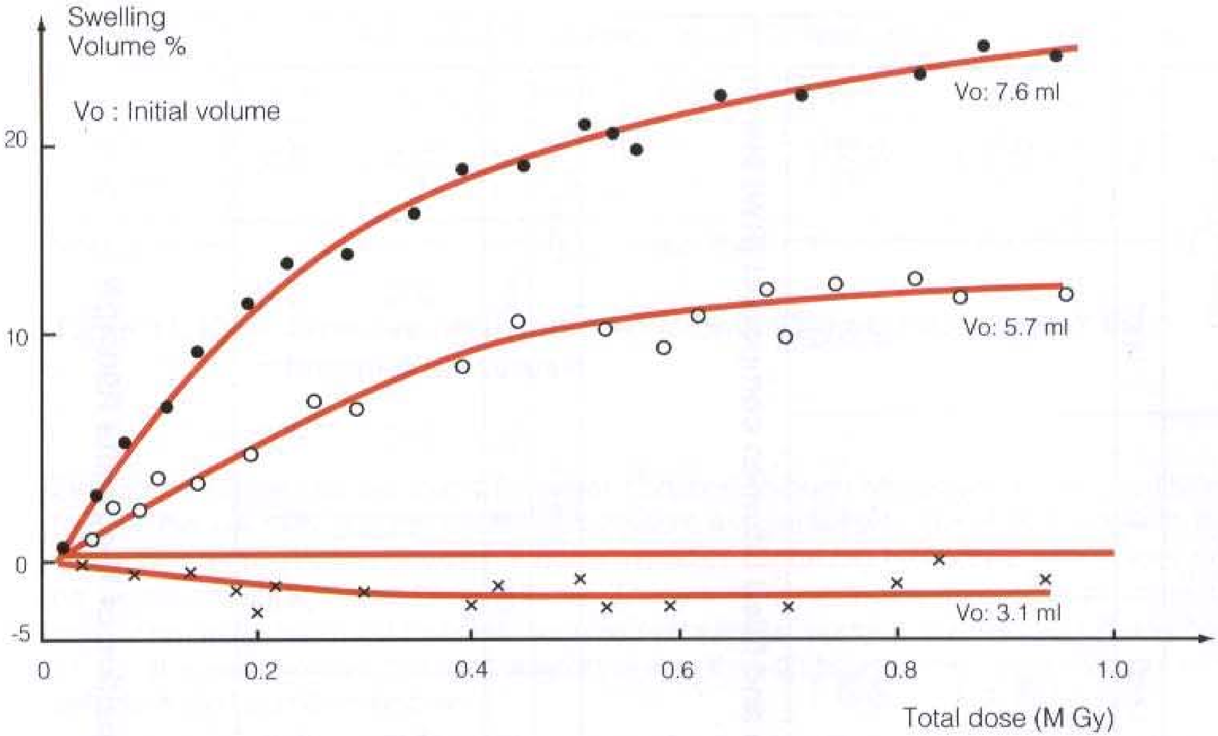


Figure 11.5 — Alpha irradiation swelling of RWF7 bitumen/waste simulate(5) (dose rate 90 Gy/h)

The rate of gas permeation through a membrane thickness of 4 mm of Mexphalte R90/40 bitumen at 500 to 1500 mbars and 25°C was measured as:

diffusion coefficient of hydrogen in bitumen	1.9×10^{-6} cm^2/s
hydrogen permeability in bitumen	0.18×10^{-6} cm^2/s (10^5/Pa)
solubility coefficient of hydrogen in bitumen	0.1×10^{-5} Pa.

11.4.4.5 Effect of radiation on the chemical composition of bitumen

Irradiation can produce changes to the penetration and softening point of a bitumen, see table 11.10. SARA analysis conducted on samples of Mexphalte R90/40 bitumen show that the irradiation decreases the proportion of saturates in the bitumen while the resins generally increase and the asphaltenes remain relatively unchanged, see table 11.11. The effect on the aromatics in the bitumen is unclear.

11.4.4.6 Water solubility and diffusion in bitumen

Radioactive waste may occur as a slurry in water which is subsequently encapsulated in bitumen. Bitumen is known to be able to take up small quantities of water and the water uptake of the encapsulation bitumen is illustrated in figure 11.6. From measurements of the weight increase of bitumen due to water uptake and from diffusion experiments with tritiated water through thin membranes, see figure 11.7, the water solubility of bitumen can be shown to lie in the range 0.2 to 0.5 per cent and the diffusion coefficient about 2 to 3×10^{-8} cm^2/s.

Sample	Apparent density		Swelling %	Penetration dmm		Softening point °C	
	Unirr*	Irr*		Unirr*	Irr*	Unirr*	Irr*
1st Series							
R90/40 Helium	1.00	0.83	17	—	—	—	—
R90/40 Air	1.00	0.80	20	34	20	95	113
RWF9 Helium	1.33	1.17	12	—	—	—	—
RWF9 Air	1.33	1.17	12	—	—	—	—
2nd Series							
R90/40 Helium	1.00	0.91	10	34	—	95	120
R90/40 Air	—	—	—	32	—	98	119
RWF9 Helium	1.33	1.33	—	—	—	149	—

Table 11.10 — Physical properties of irradiated bitumen and filled bitumen compound (RWF9)(5)

Sample	Asphaltenes		Saturates		Aromatics		Resins	
	Unirr*	Irr*	Unirr*	Irr*	Unirr*	Irr*	Unirr*	Irr*
1st Series								
Helium	29	29	28	16	19	19	20	31
Air	29	31	28	18	19	25	20	31
2nd Series								
Helium	29	31	28	23	19	16	20	28
Air	29	30	28	20	21	13	20	33

* Unirr = unirradiated
* Irr = irradiated   1st series 10.4 MGy   2nd series 8.2 MGy

Table 11.11 — Effect of radiation on the chemical composition of Mexphalte R90/40(5)

	Ratio of $NaNO_3$: bitumen				Ratio of $NaNO_3$: bitumen: sludges		
	60:40	40:60	20:80	0:100	40:20:40	20:20:60	0:20:80
D_e H_2O	220	80	60	0.5	360	240	1.4
D_e Na^+	9	10	1.3	—	1500	11	—

$NaN0_3$ as crystals <0.1 mm, bitumen Mexphalte 40/50, sludges $BaS0_4$ + Ni Fe $(CN)_6$ precipitate, 20°C

Table 11.12 — Effective diffusion coefficients (D_e) of H_2O and Na^+ in bitumen mixtures(5)

Only minor differences are found for water transport through Mexphalte 40/50 and R90/4. Neither the solubility nor the diffusion coefficient are particularly low which suggests that some long term diffusion of water into the materials containing hydrophilic substances may be expected under humid conditions. The water uptake rate increases for bitumen containing finely dispersed particles, such as precipitation sludges, see figure 11.6 and table 11.12. It is also believed that the transport of ions through bitumen can occur through micro defects in the bitumen membrane.

The use of bitumen and other materials for the encapsulation of radioactive waste is the subject of much investigation by the Commission of the European Communities and other bodies. Bitumen appears to possess many of the required attributes for an efficient encapsulating medium, ie ease of processing, good adhesion, water resistance, chemical inertness and stability to irradiation.

11.5 Bituminous geomembranes in water pollution control

Bituminous materials have been used satisfactorily for many decades to seal various types of surface. The materials used have included asphaltic concrete, mastic asphalt, sprayed bitumen membranes and prefabricated bitumen membranes. Prefabricated bituminous geomembranes have been used for some 20 years in many types of hydraulic projects but are normally used to waterproof basins, dams or canals containing clear water. Occasionally an impervious construction may be required to contain polluted water. The base and upper surface sealing of these types of domestic and industrial waste reservoirs pose particular problems which can be readily overcome by the use of prefabricated geomembranes that can compete with locally available natural sealants such as loam or clay. This is particularly the case when the sealant is required to protect ground water from contamination. Under these conditions, according to Friesecke(6) "the limited permeability of clay cannot justify its use". The impermeability of bitumen and its excellent resistance to numerous chemicals and micro-organisms makes it an ideal material for this application.

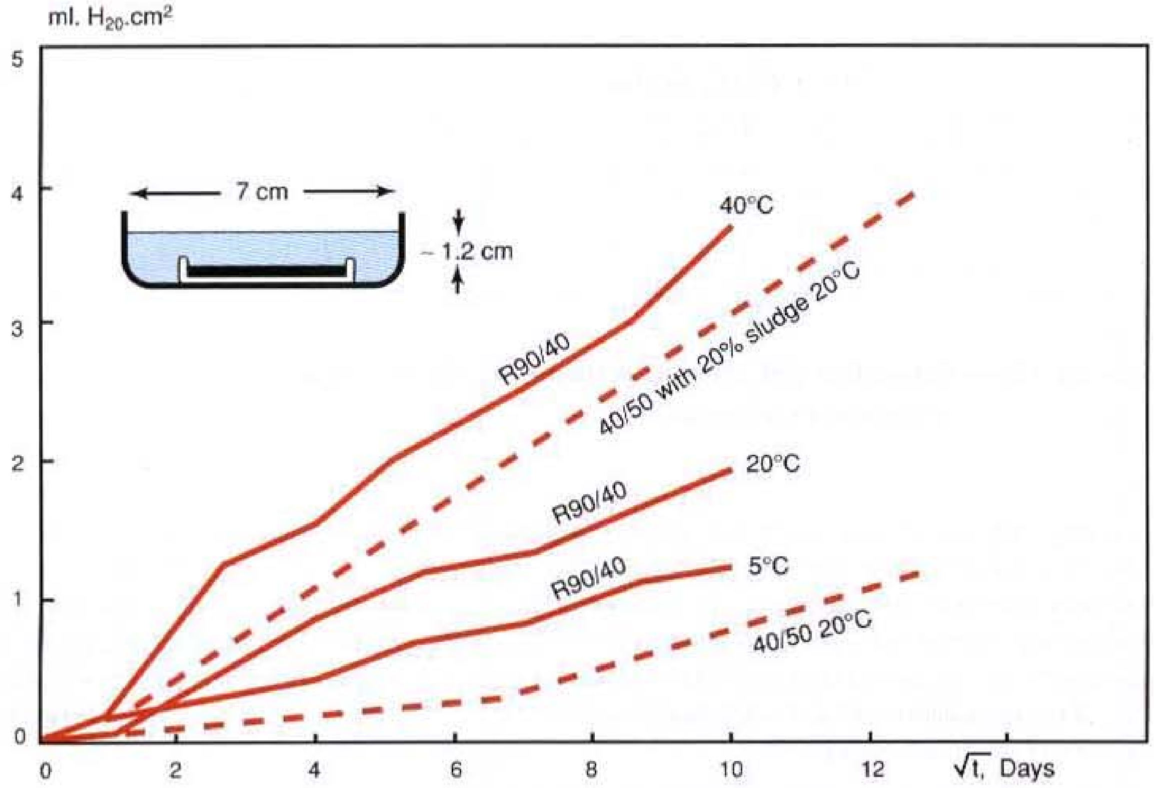


Figure 11.6 — Water absorption in pure bitumen (Mexphalte R90/40 and 40/50) and 20% loaded 40/50(5)

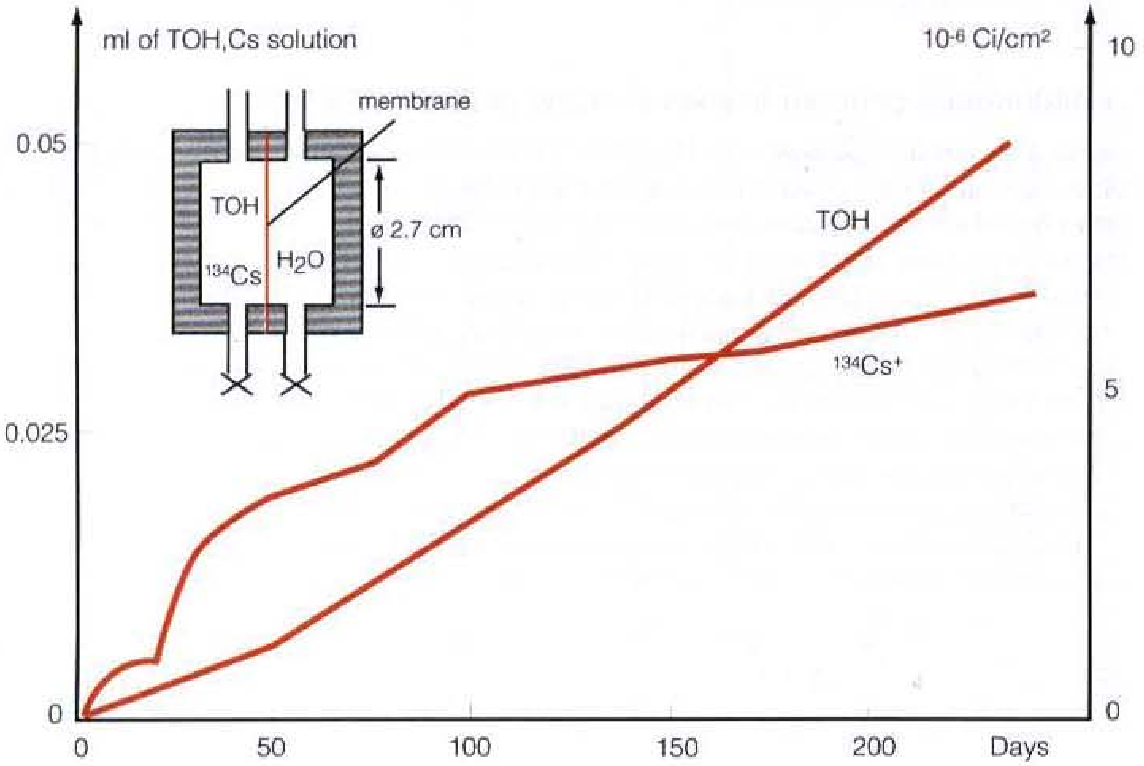


Figure 11.7 — Transport of tritiated water and ^{134}Cs through 0.59mm thick membrane of Mexphalte 40/50 (20°C)(5)

11.5.1 Requirements for a bituminous geomembrane(7)

A bituminous geomembrane is required to have a number of important attributes which contribute to its effectiveness in containing water. These attributes include:

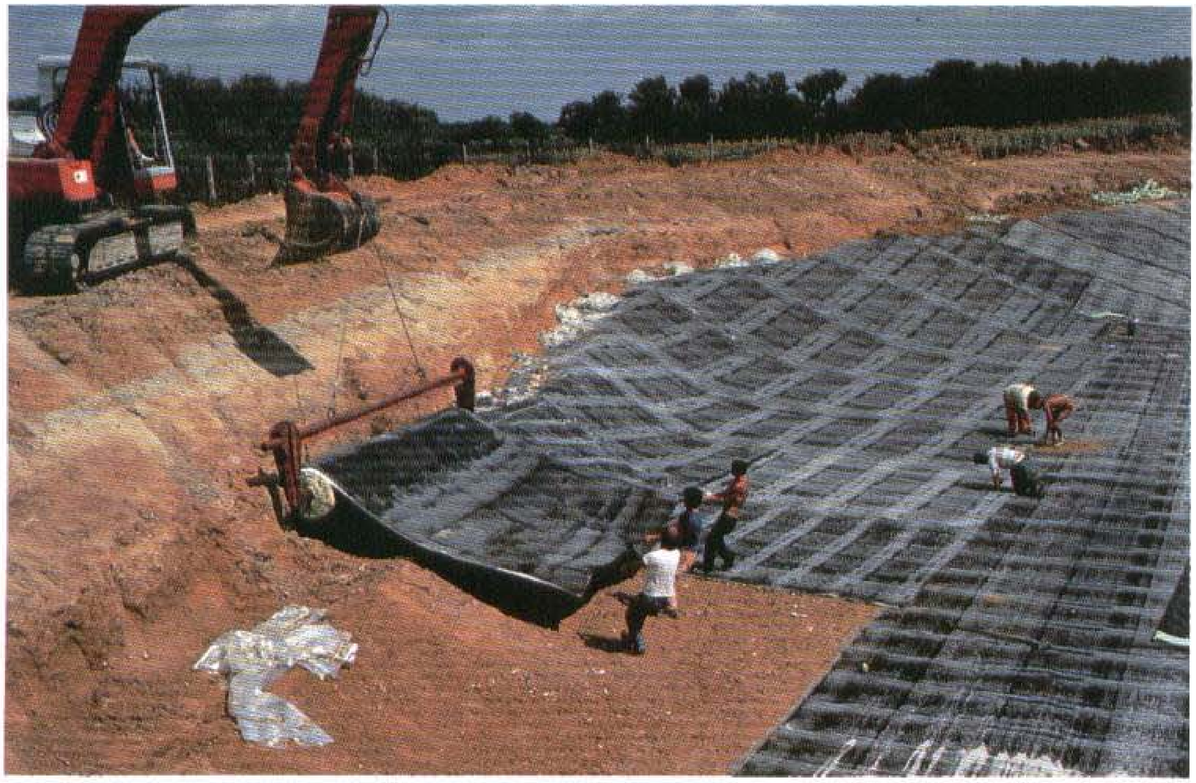
Base sealing	- to facilitate the collection and removal of seepage water.
Surface sealing	- to remove surface water and to collect and remove waste gases.
Effective sheet jointing	- to efficiently and reliably join adjacent membrane sheets with a reliable method of testing joint integrity.
Long effective life	- to ensure a long and safe operating lifetime for the membrane particularly with respect to its waterproofing integrity.
Enhanced physical properties	- to resist stresses and strains arising from installation, subsidence, load applications, heat and ultra-violet radiation.
Chemical resistance	- to resist the effects of aggressive liquid and gaseous chemicals.
Biological resistance	- to resist soil micro-organisms, plant organisms, growth penetration from roots, etc., and the effects of small animal life (eg rodents).

11.5.2 Membrane composition

Several types of bituminous geomembrane are available of which the most commonly used comprises a high tensile strength, bitumen impregnated, woven or non-woven, rot resistant synthetic fabric, such as Colas Coletanche(8). A bituminous geomembrane is very similar in structure to a bituminous roofing felt but is manufactured in much larger rolls than those typically used in roofing applications.

The underside of a membrane can be protected from penetrating plant growth by coating with a plastic or metal foil. If special chemical protection is required the upper surface can be coated with a film of material having appropriate chemical resistance. To minimise the number of longitudinal and lateral joints, the membranes are manufactured in rolls normally 4 to 5 metres wide and 80 to 100 metres long. Typically, a four metre wide roll of geomembrane will weigh about one and a half tonnes. Conventional membranes for roofing work are typically one metre wide by ten metres long. When delivered to the construction site (see photograph 11.4), they are unrolled in parallel bands. Overlapping membranes are jointed on-site by helt welding of the overlaps (see photograph 11.5).

A typical membrane is produced by impregnating a non-woven long-fibre polyester geotextile with a filled R100/40 oxidised bitumen. For application of the geomembrane at temperatures below 0°C it is preferable to use a filled bitumen-elastomer blend which is more flexible and less likely to crack during unrolling and laying. The membrane may be sanded either on both sides, or on one side only, with an anti-root polyester film affixed to the reversed side. The geomembrane, which has been specially designed for waterproofing civil engineering works, is thin (between three and six mm), flexible, and remains watertight even after quite major deformations of the supporting soil, providing it is cleared of sharp stones, chippings, building materials and other debris which could puncture the membrane.



Photograph 11.4 — Unrolling geomembrane

Photograph 11.5 — Heat welding of geomembrane overlaps

Tensile properties	Tensile strength, kN/5cm		Elongation at break, %	
	Initial	2 months at 50°C	Initial	2 months at 50°C
Lateral	1.1	1.2	35	42
Longitidinal	1.4	1.4	36	32
Non recoverable tensile strain (24 hours at 25% of maximum strain) 54% at 20°C, 68% at 70°C.				

Fatigue properties	Tensile strength kN/5cm	Elongation at break %
Initial	0.41	30
After 5000 cycles at 0°C, max strain 10% elongation at break	0.28	30

Low temperature	Bend test: 20 seconds, 2cm diameter mandrel, no cracks at 0°C
Water resistance	Absoption: 0.6% volume increase after 28 days immersion Permeability: Darcey's co-efficient < 10-12 m/s (1 bar, 8 days) Pressure: No cracks on a free surface of 1x 8 cm after incremental pressure increase of 1 bar/15 minutes up to 30 bar
Mechanical strength	No damage inflicted by a steel rod, contact surface 10 cm x 10 cm, falling 75cm
UV resistance	No cracks or blisters, no effect on tensile strength after 500 hours exposure
Chemical resistance	Resists low acid concentrations, phenols, lyes and salts
Weight of carrier	Mass per unit area — typically 210 g/m^2

Table 11.13 — Typical properties of bituminous geomembranes

11.5.3 Advantages and properties of bituminous membranes

Bituminous geomembranes have a number of advantages when compared with naturally available sealants and include:

Consistent quality	- geomembranes are manufactured to a consistent high standard in a factory and their properties and performance can be readily tested and evaluated before installation.
Water resistance	- bituminous materials remain resistant to water during the whole life of the installation and do not present any "drying out" problems experienced with some types of naturally occurring materials.
Rapid application	- modern application techniques and working practices allow rapid application of the geomembranes.
Economy	- the use of a geomembrane does not require the importation of large quantities of material such as loam or clay with obvious cost implications.
Membrane integrity	- geomembranes can be readily checked for impermeability and can be rapidly and effectively repaired.

Typical properties for bituminous membranes are shown in table 11.13.

	Length (m)	Width (m)	Depth (m)
Basin 1	100	28	1
Basin 2	88	50	0.4

Table 11.14 — Dimensions of treatment basin

11.5.4 Some applications of geomembranes

11.5.4.1 Waste water basins

In small communities of about 1000 inhabitants waste water basins are the most cost-effective way of pre-treating the water. If clay is available locally, and there is no danger of pollution to ground water used for domestic purposes, it will always be the cheapest material out of which to construct impervious basins, but if not, bituminous geomembranes provide an alternative solution. Figure 11.8 shows how a geomembrane has been used to waterproof two basins, the geomembrane of the second basin having been covered with 20 cm of earth to allow water plants to grow (photograph 11.6).

The dimensions of these two basins, installed in a village of 600 inhabitants are shown in table 11.14.

11.5.4.2 Industrial and municipal refuse landfill

Municipal refuse can be incinerated, but in some circumstances a dangerous gas (dioxin) can form during the combustion process. An alternative solution for the disposal of such refuse is to dump it in waterproof landfill sites. The decomposition of the refuse generates gases (mainly methane), which must be collected and burnt, and liquids which must be channelled into a drain installed over the membrane for subsequent treatment in basins.

Since 1981, a landfill site of about 400,000 m² near Rouen in France, has progressively been waterproofed with a bituminous geomembrane and filled with non-toxic industrial and municipal waste, see photograph 11.7. When full, this site will store seven million cubic metres of such refuse.

Photograph 11.6 — Geomembrane in water basin covered with 20 cm of soil to support plant growth

Photograph 11.7 — Aerial view of a landfill site, Fosse Marmitaine in France

11.5.4.3 Reduction of leaching from a spoil heap

A common problem with spoil heaps containing ore treatment residue is prevention of contamination of rivers and ground water by water soluble salts leaching out of the site. One such problem in France was solved by the use of a geomembrane in the following manner:

- The top of the heap was flattened, and a 2.4 per cent incline created, to channel the rain water into a collecting basin dug into the side of the spoil heap.
- A geomembrane was applied over the top of the spoil heap, including the basin, to cap the site and render it impervious to water. The result is that rain water no longer penetrates the ore residue to leach out salts and the water which collects in the basin is safely diverted unpolluted into the river, see figure 11.9.
- Top soil was applied to the steep slopes of the spoil heap, and the area grassed over. Rain water running down the slopes of the spoil heap is not in contact with the ore-treatment residue and is collected unpolluted in a gutter.
- An encircling drain, at a depth of 1.2 metres, collects any polluted water from the inside of the spoil heap. This is now easier to treat as it is no longer diluted by rain water.

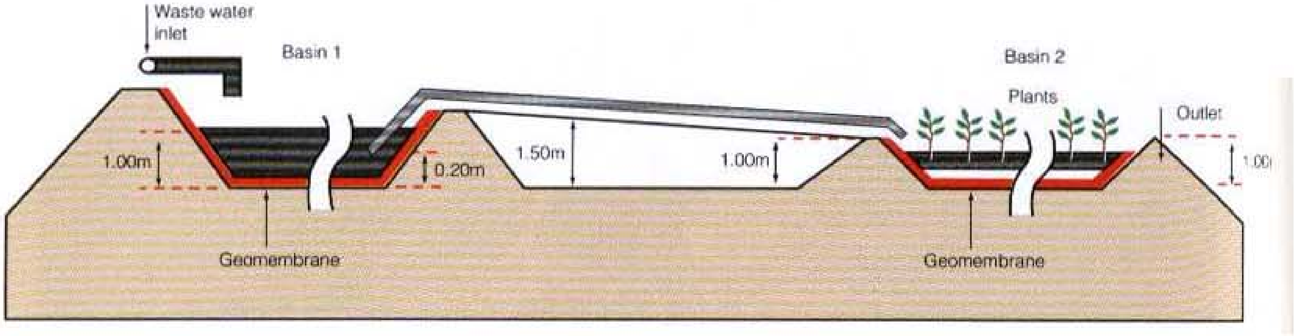


Figure 11.8 — Geomembrane used to line a waste water basin

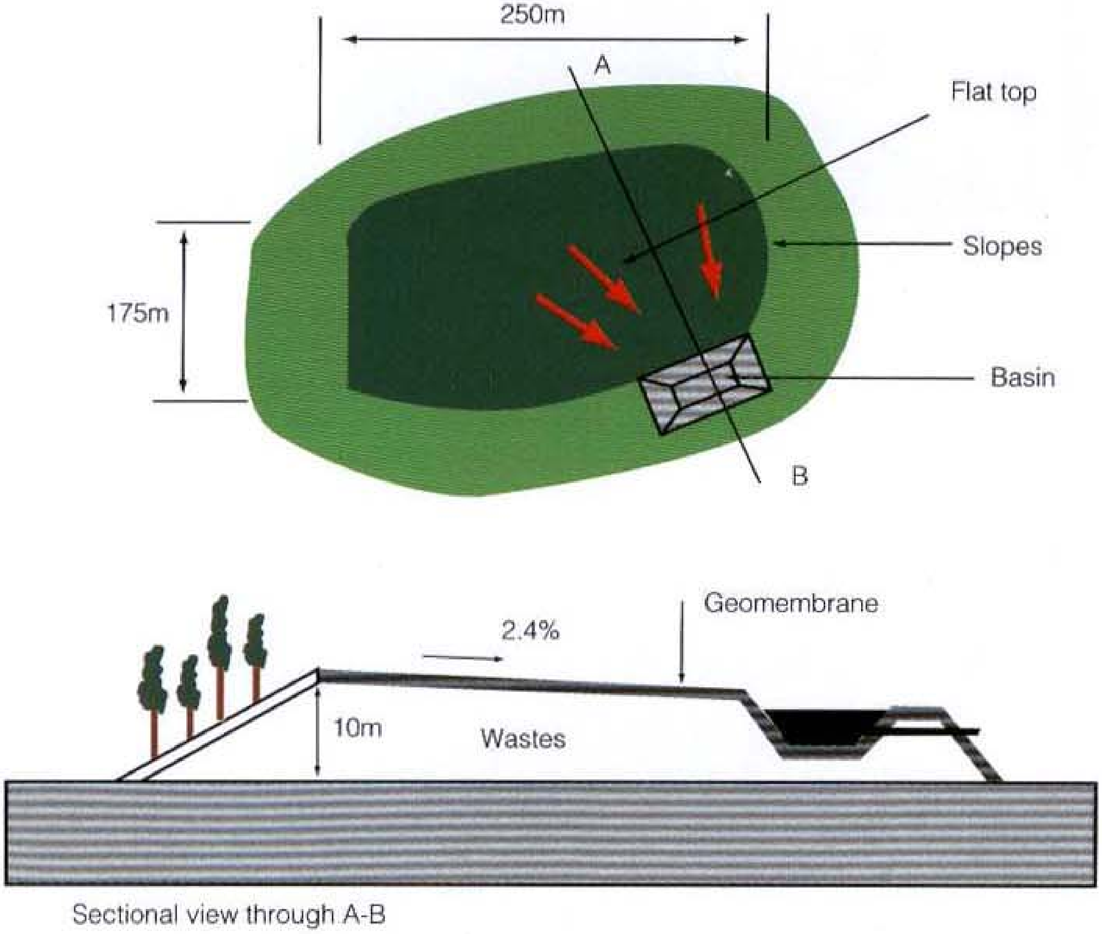


Figure 11.9 — Geomembrane used to seal a spoil heap

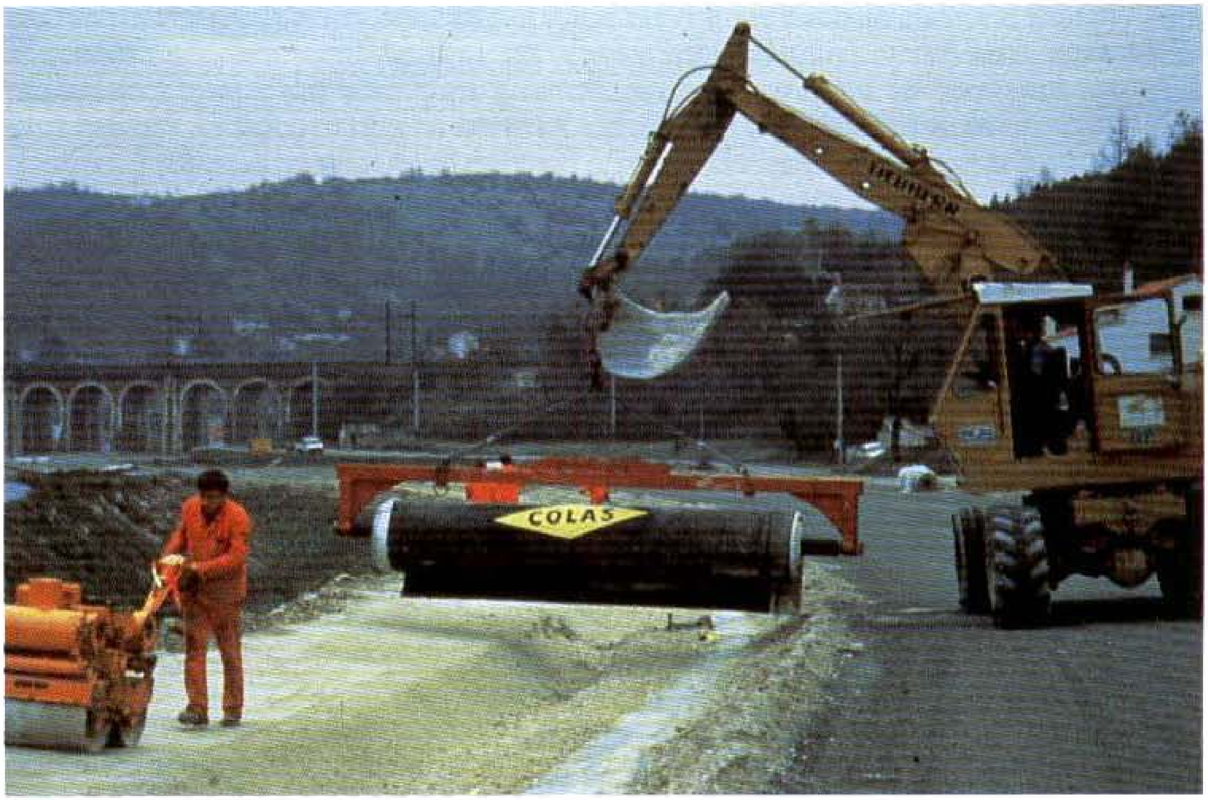
11.5.4.4 Protection of ground water from pollution by road traffic

The road and motorway networks of all countries are an essential feature of our modern industrial civilisation. Without an efficient and effective means to transport manufactured goods the impact on both rural and industrial economies would be enormous. However, the presence of a road system or the construction of a new motorway over a porous soil can significantly increase the risk of ground water pollution due to the effects of winter treatments, accidental spillage of chemicals and leaching of residues associated with vehicles. The pollution of ground water may arise from a number of sources which include:

- de-icing chemicals spread on the road in winter,
- rain water which collects combustion residues, dust, lubricants and greases generated by traffic,
- accidental spillage of chemicals and fuels from vehicles.

In France, legislation demands that new road projects include protective measures to eliminate these pollution risks, as is demonstrated by the use of a protective bituminous geomembrane on the Cahors bypass which opened in 1987, see photograph 11.8.

This road was constructed on a porous and severely fissured, chalky soil which supplied rain water to an aquifer from which water for the town of Cahors is drawn. The slope of the asphalt pavement was such that any rain water falling on it would rapidly be directed to the drainage ditches at the side of the road. As the asphalt pavement was considered to be adequately impervious to water, the pollution control measures were applied only to the hard shoulders and the earth verges, as shown in figure 11.10.



Photograph 11.8 — Positioning geomembrane over the drainage ditch

The road was constructed with a W-shaped profile, including the pavement, hard shoulders and neighbouring earth banks, which ensures that there is a sufficiently large impermeable area to retain the entire contents of a road tank vehicle. Gutters and drains were installed to channel away any pollutants to a collecting basin further downhill, which was also sealed with a geomembrane.

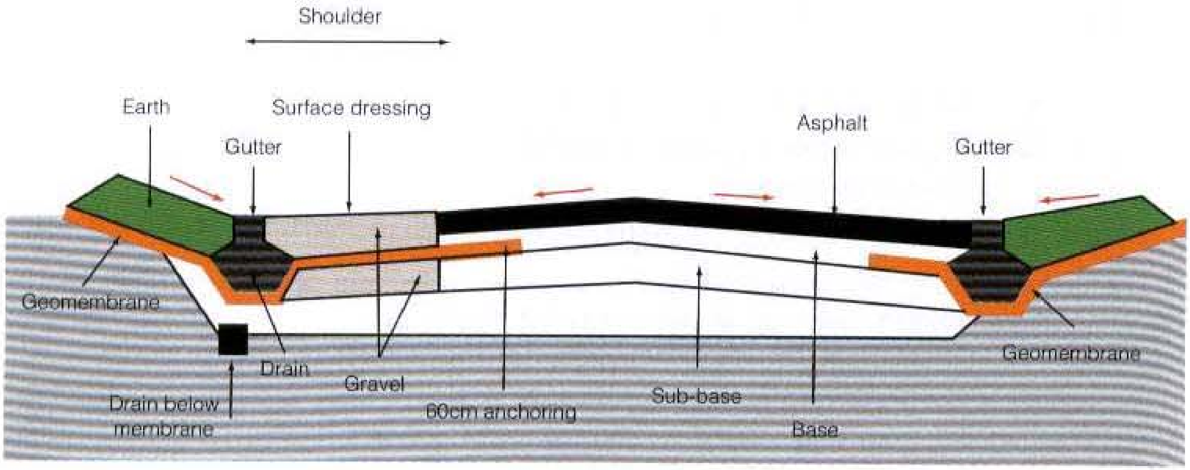


Figure 11.10 — Geomembrane used to seal a drainage ditch alongside the Cahors road

11.6 Clay pigeons

Clay pigeons are manufactured on a huge scale amounting to to many millions per year world-wide. The disc is prepared from a highly filled binder and hot-pressed to shape. Because they may be exported and require long shelf lives the binder must resist deformation, to allow the disc to fly straight, but be brittle enough to break on impact. Coal tar pitch has been used in the past but its use is declining because of its toxicity.

Bitumens with a softening point greater than 100°C, eg Mexphalte R115/15 or H100/120 are used with up to 30 per cent by mass of limestone filler.

11.7 Agricultural applications

The good management of agricultural land serves the joint interests of the environment and agricultural production. In some areas the destructive effects of natural forces, such as floods and high winds, have been combated by the construction of flood defences and wind breaks. However, on a local scale environmental damage by effects such as soil erosion is still a serious problem. Wind drift, causing erosion to top soil, is damaging to agricultural production and the erosion of top soil by rain can rapidly destroy the fertility of soil. Besides damage to crops, effects can be seen on roads and in rivers where silt can be a serious problem. Bitumen in different forms has found a number of applications in agricultural and related used including:

- Mulching,
- Dune stabilisation,
- Jiffy pot manufacture.

11.7.1 Agricultural mulching

Mulches have been used in agriculture and horticulture for many decades to promote crop growth(9). Materials as varied as stubble, straw, banana stems and even sand and stones have been found to be effective. In more recent years paper and polyethylene have been used to great effect. The positive benefits of applying a very thin bituminous coating to field cultures has been known since the 1930s and during World War II bitumen mulches were commonly applied to airfields in the UK to promote the rapid germination of grass.

The bituminous material used for agricultural mulching is essentially the same as the bitumen emulsions used in road surfacing technology. The bitumen emulsion is sprayed on to the soil surface where it breaks, leaving a thin, dark brown or black film of bitumen which will remain on the soil surface for several months. The bitumen mulch affects plant growth by changing certain soil characteristics including soil temperature, soil moisture and soil structure, although the magnitude of the effect will be determined by the type of crop and the nature of the soil from location to location.

As long ago as the 1960s(9,10,11,12,13,14) trials with vegetable crops demonstrated that additional yields could be obtained. However, at that time there were difficulties associated with the efficient application of the bitumen to the soil.

Those important beneficial effects which have a direct influence on the development of young plants and which can be enhanced by the use of a bituminous mulch include:

- Soil temperature increase.
- Soil moisture retention.
- Soil structure improvement.

11.7.1.1 Soil temperature

The normal effect of applying a bituminous mulch to a soil is to increase its temperature. This effect is created by the increased absorption of solar radiation by the black surface as compared with the bare soil. The magnitude of the effect is determined by the intensity of the sunlight incident on the soil. For example, in England the maximum temperature increase can be expected to be about 1° to 2°C. In Trinidad, by comparison, the temperature increase can be up to 8°C, and trials under Mediterranean conditions, in Italy, for example, recorded maximum increases of 5° to 7°C(9).

Under Italian conditions(9), see figure 11.11, relatively large increases in soil temperature are experienced for most of the day and only at night does the soil temperature under the bitumen mulch and the bare soil come close together. Even though the black soil surface might be expected to lose heat more quickly at night than the light coloured soil, when the soil is moist, the temperature of the mulched plots is always higher. In dry soil, however, the temperature of the mulched plots falls by as much as 2°C below that in the bare soil. The above illustrates that very considerable temperature increases can be obtained by the use of bituminous mulches. Figure 11.12 shows the superior effect on soil temperature of bitumen as a mulch compared to black polyethylene as a mulch. This same effect has been noted by other work conducted in England, the USA and Australia(10,11,12,13).

The influence of the bitumen film thickness in experiments conducted in the 1960s(9) appeared to be unimportant as films of 150 µm thickness were as effective in increasing soil temperature as those twice as thick.

11.7.1.2 Soil moisture retention

Laboratory experiments have demonstrated that the use of a bitumen mulch can dramatically reduce the amount of moisture lost to the atmosphere by evaporation, see figure 11.13. Bitumen films as thin as 0.2 mm deposited from an emulsion on a smooth soil surface retained up to 50 per cent of its initial moisture content after ten to fifteen days while a similar untreated specimen lost half its moisture content in one day.

This effect can also be seen in the field but is dependent upon good seedbed conditions, the coarseness of the seedbed being the critical factor. The bitumen mulch has been shown to be of most value when the seeds are germinating and the plants are young. However, once the plants have formed a fair amount of leaf, the loss of water vapour by transpiration can far outweigh any saving due to the mulch.

Under arid Middle Eastern conditions water savings of up to 30 per cent have been recorded by the use of bituminous mulches.

11.7.1.3 Soil structure improvements

The use of a mulch can influence the soil structure in two ways. Firstly, by eliminating or reducing the effects of wind erosion, by stabilising the soil and protecting seedlings from sand damage, and, secondly, by protecting the soil from rain damage. Photograph 11.9 shows the beneficial influence of the use of a bitumen mulch on the growth of carrots. The mulched plot on the left shows much improved growth and yield due to the protection from wind erosion allowing a greater number of seedlings to develop.

Experiments conducted by Woodstock Agricultural Research Centre(9) have shown that soil treated with a film of bitumen only 200 µm thick withstood as much as four times more rain than the bare soil before the surface became compacted.

Photograph 11.9 — Carrot trial 1965. Plot on left was mulched using bitumen. The difference was due to reduced wind erosion resulting in more seedlings

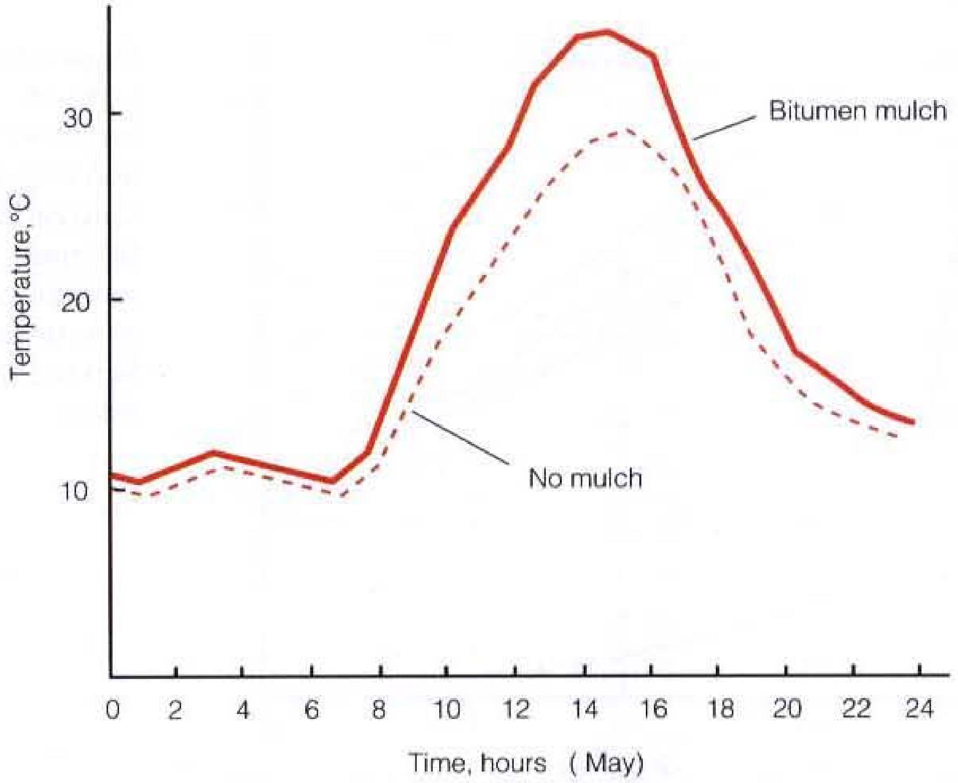


Figure 11.11 — Diurnal soil temperature under a bitumen mulch compared with unmulched soil. Recorded at a depth of 5 cm

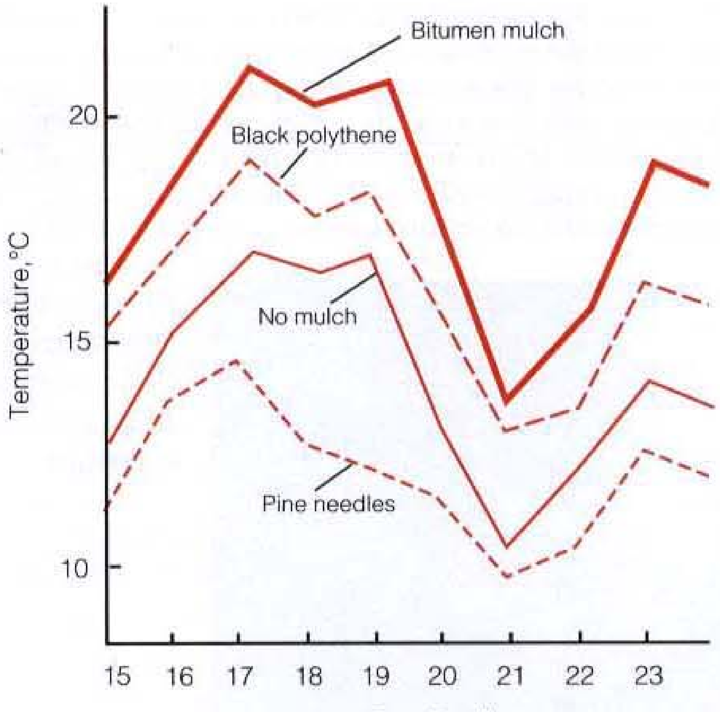


Figure 11.12 — Diurnal soil temperature under a bitumen mulch compared with unmulched soil. Mean day soil temperature under various types of mulch. Recorded at a depth of 10 cm

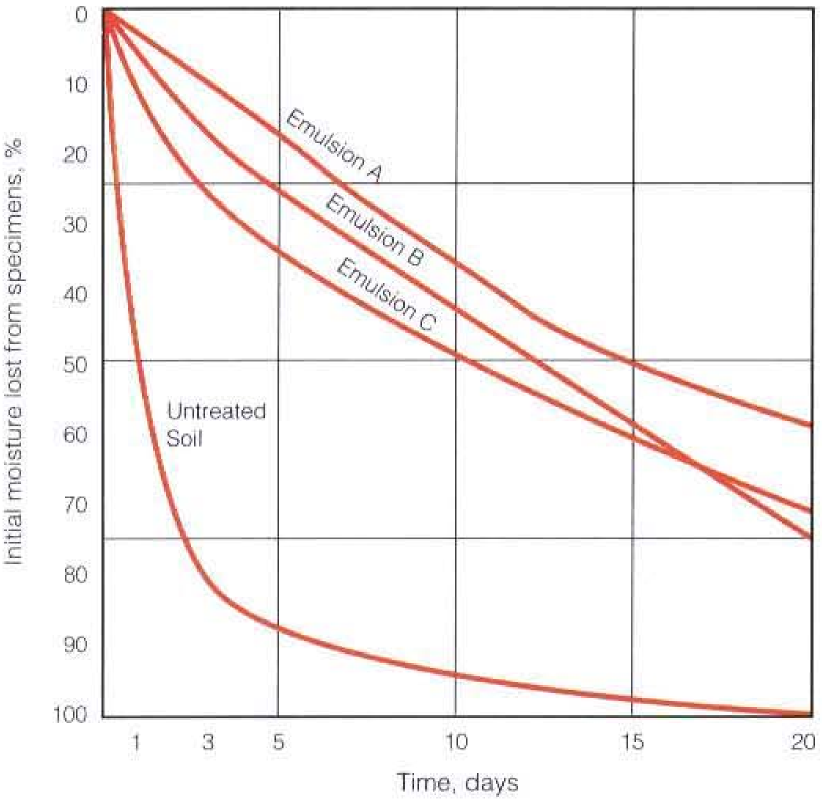


Figure 11.13 — Loss of moisture from soil specimens sprayed with bitumen emulsion to give bitumen film 0.2 mm thick

11.7.1.4 Improvement of crop yields

Increased vigour in the early stages of crop growth is a universal result of mulching and is reflected in early germination and a higher percentage of growing seedlings(9,11), see photograph 11.10. However, it has been questioned whether this early improvement is ultimately reflected in increased yields because other agronomic factors interact as the plants grow. Table 11.15 shows some results obtained on various crops grown in Italy(9). In general, increased vegetative growth was almost always noted on treated plots and with short term crops (those shown above the line in table 11.15), usually followed by an increased yield. Longer term crops (those shown below the line in table 11.15), however, often showed no advantage.

Photograph 11.10 — Potato trial 1965. Enhanced early growth of a mulched plot on the right

Crop	Time of treatment	No. of weeks to harvest	Increase in yield, %
Asparagus	March 1964	3 - 10	+ 45
	March 1964	5 - 9	+ 81
	February 1965	6 - 14	+ 22
	February 1965	8 -15	+ 32
Bean	Mid April 1964	9 - 11	+ 50
	Mid April 1964	10 - 13	- 9
	Late April 1965	8 - 18	+ 10
	Late April 1965	12 -16	+ 23*
	August 1965	10	+7
Melon	April 1965	10 - 15	+ 35
Pea	April 1964	7 - 9	+ 24
	March 1965	9 - 10	+ 1
	Late April 1965	10 - 12	-16
Strawberry	March 1965	9 - 14	+ 170
Zucchini	April 1965	9 - 18	+ 28
	May 1965	8 - 12	+10
Cotton	April 1965	28 - 36	
Aubergine	April 1965	15 - 24	-8
	April 1965	13 - 25	-9
Groundnut	April 1964	24 - 34	
Melon	April 1965	16 - 22	-22
	May 1965	14 - 18	+18
Sweet pepper	May 1965	12 - 19	-2
	April 1965	14 - 24	+ 2
	April 1965	14 - 27	- 10
Tomato	April 1965	14 - 19	0

* Mountain site — equivalent to early spring sowing

Table 11.15 — The effect of bitumen mulch on the yield of various crops in Italy(9)

In 1979, early trials of Terrafix(14), a specially developed bituminous emulsion for agricultural purposes which could be easily applied by spraying, were conducted on onions and other vegetables. This emulsion produces a very thin topsoil coating which interacts with the soil in such a way that, at a critical thickness (about 0.1 mm average), neither water nor wind affects the germinating crops. The outcome of the trials showed very promising results in terms of crop yield but also highlighted a full range of problems. Terrafix not only encouraged the growth of crops but also that of the weeds with which they were in competition.

Further trials in 1980 and 1981 were conducted on maize, potatoes, fruit and various vegetables such as pumpkin, beans, peas, tomatoes, cabbage and paprika. These trials generated important information about the emulsion application rate for each type of crop and the special requirements for different soil types to prevent soil erosion and soil crusting. The incorporation of herbicides and insecticides and the protocol for spraying and protecting germinating crops were also developed.

Treatment	Yield	Yield		Usable carrots		Yield
	Stalks and carrots	Carrot		Size 20 to 35mm		Increase
l/ha	kg/ha	kg/ha	%	kg/ha	%	%
Untreated	58.000	28,062	48.4	13,722	48.9	100
900 in strips	94,000	41,994	44.7	27,438	65.3	200
1,310	95,000	43,210	45.5	28,637	66.3	209

Table 11.16 — Parisian carrots treated by spraying Terrafix, 1983

In 1982, Terrafix was applied in a trial on a commercial scale in Austria where 100 hectares of sugar beet and 20 hectares of maize were experimentally treated. With the equipment available at the time, up to 25 hectares per day could be spray treated depending on the topography of the ground. The crop yields achieved in this trial of Terrafix showed a remarkable increase as well as successfully combating wind and water erosion. Yields of sugar beet and maize were increased by up to 25 per cent in Austria.

Photograph 11.11 — Cradle-mounted sprayer

The results of trials using the Terrafix emulsion lasted several years and demonstrated remarkable increases in crop yields with additional factors such as the size grading adding greater significance to the results. For example, the proportion of usable carrots produced in the size range 20 to 35 mm from a trial in Austria in 1983 was increased by over 100 per cent, see table 11.16.

Initial trials of Terrafix involved spraying the whole of the field area with Terrafix. However, driven by economic considerations, tests were conducted in which the field was treated in strips. The results of these trials were equally surprising in that very considerable increases in yield were achieved despite the significantly lower coverage of the field area with bitumen. Bitumen mulching is a relatively expensive operation and the expedient of spraying strips helps to reduce the overall cost of the treatment without apparently adversely affecting the advantages gained.

Further developments of the Terrafix process have included the simultaneous sowing of crops, spraying of bitumen emulsion and application of herbicides and insecticides to improve the efficiency of the process.

During the course of the experiments, the effects of the bitumen emulsion on the soil were carefully monitored. Extensive examination of the soil fauna, soil structure, possible ground water contamination and longer term effects on cultures showed no damaging effects.

11.7.1.5 Bitumen/straw mulch

An alternative method for the mulching of crops commonly used in the USA comprises the use of a bitumen emulsion for anchoring straw or hay(15) to a seeded area.

It is possible to use two approaches to the use of this type of mulch. In one method, straw or hay is spread over the area in question which is then blanketed with a fog spray of bitumen emulsion. In the alternative method, straw or hay is ejected from a special blower simultaneously with the bitumen emulsion and the two constituents are mixed in flight. Both methods give excellent results if applied properly.

In the first method, the ground is prepared for planting and seed, mixed with water and liquid fertiliser, is spread with a hydraulic seeder. Straw or hay is spread over the prepared area at a rate of 3.3 to 4.5 tonnes per hectare and bitumen emulsion is then sprayed over the area, shortly after, at a rate of 0.45 litres per square metre. This effectively locks the straw or hay mulch in position preventing it from being blown about by wind. Continuous coverage of the soil by the bitumen emulsion is the most effective way of application especially under windy conditions. However, it is possible to use a variety of stripes and chequered patterns to achieve economies in materials and application time. The rate of application of the bitumen emulsion must be increased if the amount of straw or hay is increased over 4.5 tonnes per hectare.

In the second method, after the area has been prepared, the mulch and bitumen are simultaneously applied to the area by blower. This method has the advantage that it applies the two materials in one single operation so reducing cost and reducing application time. It also achieves a more complete interlock of the hay straw mulch. The same type of emulsified bitumen used for mulching is also suitable for use in the above procedures.

11.7.2 Greening the desert

The use of bitumen emulsions for mulching crops in Europe has led to experiments in the Middle East to "turn the desert green". The application of a bitumen emulsion mulch to conserve ground water and encourage the growth of hardy vegetation has been shown to be possible even under arid Middle Eastern conditions.

The use of bitumen emulsion mulches in a hot and arid environment has several aims including:

- Water conservation
- Increased crop yield
- Re-cultivation of the desert
- Desalination of soils
- Sand stabilisation.

11.7.2.1 Water conservation

From work conducted in the Middle East it has been found that savings of up to 30 per cent of irrigation water can be achieved by the application of a suitable bitumen emulsion formulation. Less irrigation is required on areas sprayed with bitumen emulsion than for unsprayed areas. The thin film of bitumen, 0.075 mm to 0.1 mm thick, is semi-permeable thus allowing water to pass through it during irrigation but trapping moisture in the soil below. In arid regions, the saving on water demand of up to 30 per cent represents a significant strategic advantage in farming.

11.7.2.2 Increased yield

Very big increases in crop yields have been reported in trials conducted in the Middle East. Cotton yields have been shown to increase by 250 per cent, while sugar beet, maize, Sudan grass, potatoes, Soya bean and cereal crop yields increased by 20 to 30 per cent. This magnitude of yield enhancement is similar to that obtained in trials in Europe and again represents a major improvement in productivity.

11.7.2.3 Re-cultivation of the desert

The use of bitumen emulsion to encourage the formation of soil humus has been successfully undertaken in Egypt. Grass seed from a hardy variety is sown, the soil irrigated and bitumen emulsion mulch sprayed. The mulched grass grows strongly and rapidly and is then allowed to die back. This process is repeated several times until a self sustaining humus develops. The bitumen emulsion prevents humus erosion by wind, thus accelerating its decay. The time needed for re-cultivation may be reduced from five years to under three years by the adoption of this process.

It is also possible to regenerate desert areas without the necessity to irrigate using special emulsions to prevent the evaporation of water from the soil.

11.7.2.4 Desalination of soils

The concentration of salts in the soil surface is a common problem in areas which rely heavily on soil irrigation to maintain fertility. Irrigation frequently results in the degradation of the soil and in extreme cases renders it unfit for cultivation. By the prevention of evaporation of moisture from the soil the water table in the soil is improved and subsequently salts are shifted to lower soil levels, thus preventing the degradation of soil quality by salt concentration at the surface.

11.7.2.5 Sand stabilisation

Prevention of wind erosion by the use of bitumen emulsions is a positive benefit in the process of establishing soil humus. Sand dunes can be stabilised to prevent sand drifting along roads and into housing areas, see section 11.7.3.

11.7.3 Dune stabilisation

The movement of sand causes many problems on construction sites, in commercial and agricultural developments and in coastal dune erosion. This is especially so in semi-arid regions, but also in construction works involving the use of large quantities of sand. Sand is easily blown about by the wind resulting in sandstorms and sand encroachment.

One technique to deal with this problem utilises a form of mulching to promote or sustain the growth of suitable grasses or other vegetation. This can involve the erection of a wind break, combined with pegged-down brushwood or dried grasses, preventing movement of the sand and assisting grass growth. Another method is the petroleum mulch process which consists of applying a mixture of seed, chopped straw or cellulose and water, bound together with bitumen emulsion or cutback.

In recent years there has been increasing interest in lower cost methods for treating large areas with petroleum products to obtain temporary stabilisation of wind blown sands until vegetation can be firmly established, giving permanent stabilisation by root growth. In the Netherlands, a specially prepared cutback bitumen, called Shell Sandfix, has been developed for this purpose.

Sandfix has been used on areas of land reclaimed from the sea using the hydraulic sand fill method. After levelling, a special composition of seeds is put down at an application rate of 100 kg/ha, followed by calcium nitrate fertiliser at 300 kg/ha. Finally, Sandfix at a rate of 5000 l/ha (0.5 l/m^2) is applied through atomising jets on a 25 metre long spraybar, see photograph 11.12. Because this layer absorbs heat radiation from the sun, and retains moisture in the soil, rapid germination of the seeds is promoted.

When sprayed, this cold bituminous product penetrates three to ten millimetres into the soil and coats the sand particles. As the solvent evaporates, the sand particles stick together at their contact points. A stable coherent sand layer results which resists erosion by wind and rain until the grass and vegetation is able to stabilise it.

For temporary projects, such as sand stockpiles, a Sandfix treatment can be applied without seeding. The sand stabilisation effect will last for six to twelve months depending upon the application rate and the climate following treatment.

Photograph 11.12 — Unimog sprayer with 10 m spraybar

11.7.4 Mining reinstatement

Australia is a vast resource for the heavy minerals rutile and zircon. The mining of these minerals takes place close to heavily populated areas and consequently there has been considerable pressure from environmentalist groups to restore the mined areas to their original condition(16).

Prior to mining the area is surveyed to record soil types and vegetation, and the topsoil is then stockpiled in strategic positions. After mining is completed, the area is back filled with processed sand and contoured to restore the landscape to its previous shape. Top soil, which is usually rich in viable seed of native species of shrubs, is replaced to a depth of about 150 mm thickness. As an additional measure, seed or seed bearing brush is also spread over the reinstated area.

Once the soil has been prepared and any new seed has been sown, a fast growing, high fertility crop is planted to protect the native species until they become established. This usually comprises short lived annuals such as hybrid sorghums or millets. After a while, due to the leaching of applied nutrients from the sandy top soil, the grasses die out and the native plants, which survive in a low fertility soil, take over. After about two years the regeneration of the area is very well advanced.

In order to encourage the growth of the protective crop of grasses, and to reduce the wind drift which is common in exposed areas and which damages young seedlings, a number of techniques have been used including:

- spreading native brush,
- erecting sand trap fences,
- spreading straw mulches,
- using Terolas emulsion.

Terolas is applied at the rate of 1500 to 3000 litres/hectare depending upon the severity of the exposure of the site. The emulsion is sprayed from a spray bar drawn by a caterpillar-type tractor to create as little disturbance of the soil as possible. The treatment of the area is relatively quick and the results are very effective. Thus, even after major disruption, an area can be returned to a condition similar to its undisturbed state.

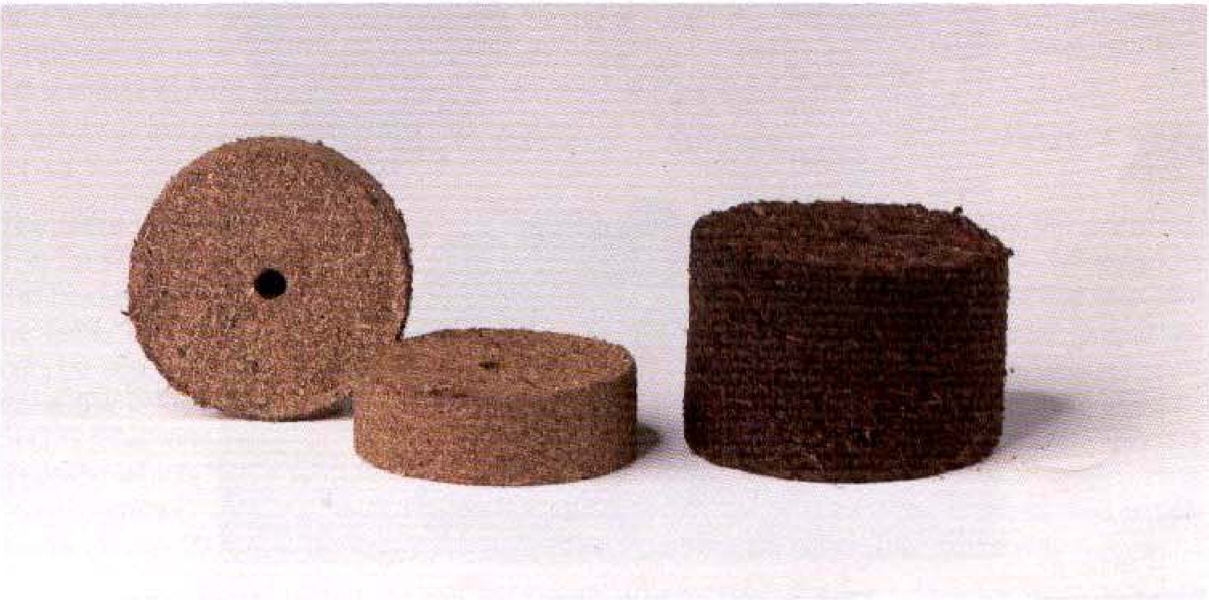
11.7.5 Jiffy pot manufacture[17]

Peat flower pots, which are filled with a growing medium, are well known in horticulture. One of their attractions is that roots of plants grown in them penetrate readily through the walls so that no check is suffered when potting on or planting out.

Jiffy Pots Ltd, prominent manufacturers of these pots, simplified the method when they introduced the Jiffy 7 which combines pot and growing medium, see photograph 11.13. This is a peat briquette containing nutrients which, when soaked in water, swells to form a cylinder about 50 mm high. The briquette is enclosed in a plastic mesh which allows expansion in contact with water but preserves the final shape and permits subsequent handling without disintegration. Jiffy pots are now used in very large quantities, some nurseries counting their consumption in millions per year, and they have been found to have several advantages over the use of hollow pots filled with a growing medium.

The most recent development has been the replacement of the external plastic mesh by an integral bitumen binder. Bitumen was an obvious choice for this work because it is non toxic, has no harmful effects upon growing plants and is not attacked by fertilisers. The primary function of the bitumen is to weld adjacent peat fibres together, and selection of the correct quantity of binder is very important in order to balance the conflicting requirements of strength and expansion of the briquette. Because completely dried peat is unable to swell in the presence of water and because the binder must be very finely dispersed with the fibres, hot binders were found to be unsuitable and bitumen emulsions were selected for experiment.

Firstly the mechanics of obtaining a uniform distribution of the bitumen emulsion throughout the peat were resolved. Work was then directed to find the best bitumen to use and a special emulsion was developed, care being taken to ensure that the emulsifiers used were also non-toxic to plant growth. Finally the rate of addition of the emulsion was determined at the level to give briquettes which swelled to five times their height in water but yet remained sufficiently strong to withstand subsequent handling and root growth.



Photograph 11.13 — Peat flower pot bound using bitumen. (Photograph courtesy Jiffy Pots Ltd)

Jiffy pots are expanded in the nursery by standing them on a moist underlayer under a moist installation until uniform distribution of the dissolved nutrients has been achieved, and the structure and the air/water balance have been stabilised.

They are used for sowing seeds or striking cuttings, and for bringing young plants to the potting-on or plant out stage.

11.8 Agglomeration and briquetting

11.8.1 Introduction

Many industrial processes produce fine particles, either dry or as a suspension in water which cannot be easily handled or re-used. Often these materials are disposed of as waste representing an economic loss to the industry and frequently a cause of pollution. Dry fines are agglomerated to allow safe handling for re-use or disposal and muds are treated to recover the solids, see photograph 11.14.

For example:

Ores are very often crushed for beneficiation by a flotation process or by magnetic enrichment and generate fine particles.

By-products from industrial treatments can be mostly composed of fine particles such as rolling mill scales.

Fume scrubbing plants lead to muds while electrofilters lead to ultra-fines production.

Photograph 11.14 — Recovery of industrial waste by briquetting allows materials to be easily handled and re-used in a process

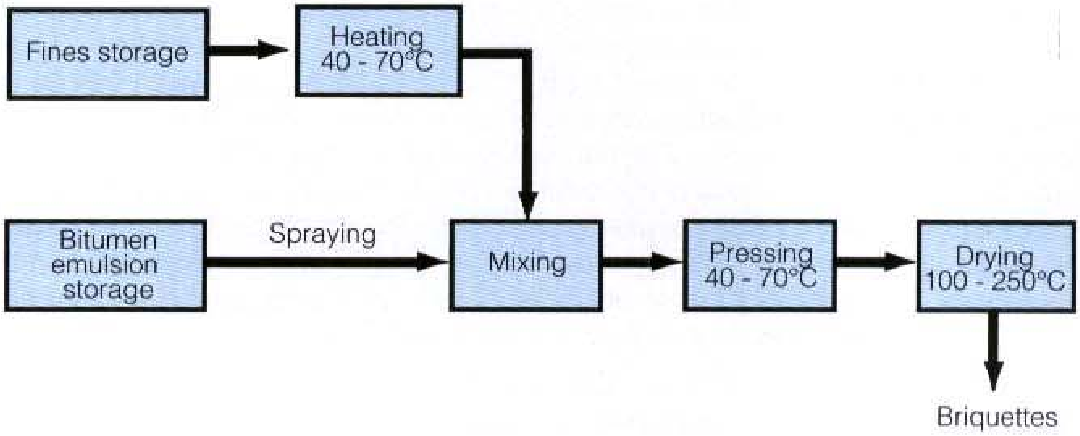


Figure 11.14 — Briquetting with a bitumen emulsion

To allow easier handling, use or reuse of these fines, agglomeration techniques using special bitumen as a binder have proved to be very suitable because they are easy to put into practice and economical compared to other techniques.

Bitumen may be used as a water emulsion which is liquid at ambient temperature. The solid particles within a mud then stick to the bitumen particles and the emulsion breaks leaving clear liquid about a 'mastic'. The mastic requires 'kneading' to form a cohesive agglomerate and to release all free water. Because of the ambient temperature used, a soft bitumen is required, normally 200 to 300 pen, to fully coat the mineral particles. Mastic produced can be pressed to form briquettes or extruded and left as 'worms'.

A scheme illustrating the essential parts of an agglomeration process is shown in figure 11.14.

The more widely used method is to mix bitumen liquid at 150-200°C with the fine particles. The particles are dried and pre-heated sufficiently to ensure good wetting and adhesion to the binder. On cooling the mix is plastic at about the softening point of the binder and can be easily moulded into the required shapes in a briquette press. These 'green' briquettes can be used as they are but for some applications such as smokeless fuel or blast furnace coke the briquettes have to undergo further thermal treatment. During pyrolysis at 350-500°C bitumens produce volatile matter and coke residue. In a briquette this coke forms a skeleton which holds the particles together and gives the briquette physical strength. The most common application of this technique is the manufacture of smokeless fuel which started in the 1920s. More recently barbecue briquettes have been made this way.

11.8.2 Required properties of the binder

Products made by briquetting must be strong and not sticky at ambient temperature in order to be handled and stored easily. Bitumens used as binders must therefore be hard at ambient temperature. In the process the bitumen has to change rapidly from a liquid to a hard solid. To satisfy this requirement the bitumen requires a high temperature susceptibility, that is, a low PI. Oxidised grades therefore are not suited to this application. To ensure sufficient strength during heat treatment up to sintering temperatures, which can be around 1,200°C for iron ore, the bitumen needs a coke residue higher than 35 per cent (measured by Conradson carbon content). For briquettes used in steel production it is generally desirable for the bitumen to have a low sulphur content, at least as low as the fines being agglomerated. For green briquettes which are burned directly the binder should have a high calorific value. In practice H80/90 is the grade most commonly used although on mainland Europe binders with softening points of 95-110°C and penetrations of 1-4 dmm are also used. Typical properties of H80/90 are given in table 11.17.

Compare the properties on a bitumen test data chart of a normal 40/50 pen bitumen with that of a special agglomeration bitumen R95/1, see figure 11.15.

The chemical constitution of the binder and its consequent changes in properties during heat treatment are also important. In practice, agglomerates may have to be hardened by heating to maintain sufficient mechanical strength when charged to an industrial furnace. Figure 11.16 shows the loss of weight of 40/50 pen bitumen and that of one of the special agglomeration binders when heated in an inert atmosphere.

It is important that a high coke residue is obtained if the agglomerates have to undergo thermal treatment since the coke skeleton, if present in sufficient quantity, can impart strength to a briquette up to the sintering temperature of the ore. From figure 11.16 it can be seen that the residual weight of the special bitumen is 43 per cent compared with 20 per cent for a normal bitumen.

			15 Pen	H80/90	B101
Penetration at 25°C, IP 49		dmm	10-20	6-12	1-4
Softening point IP 58		°C	63-76	80-90	90-95
PI (typical)			0.2	1.4	0.4
Conradson Carbon Residue, IP 13,		% mass	24	18	>39
Calorific value,		MJ/kg	41	41	
C		% mass	84	84	
H		% mass	10	10	
S		% mass	3.5	3.7	<6.0
N		% mass		1.2	
Flash point, COC, IP 36		°C	300	338	
Ash, IP 4		% mass	0.08	0.07	
Volatility					
RTFOT, ASTM 2872, loss		% mass	0.5 max	—	
TBP/GLC		Recovery @ 450°C	2	1.5	
		Recovery @ 500°C	4	3.5	
Viscosity	Temperature at 20 Pa.s,	°C	111	134	126
	Temperature at 2 Pa.s,	°C	143	167	158
	Temperature at 0.2 Pa.s,	°C	190	217	205

Table 11.17 — Typical properties of briquetting binders

Photograph 11.15 — Industrial briquetting press. Note bitumen-bound briquettes at the base of equipment

11.8.3 Binder content

The process can be applied to any material which has a particle size in the range of 0 - 8 mm although even in this size range crushing may be required. The briquettes are manufactured in a roll press, the shape and volume being largely dictated by the end use, see photograph 11.15. The amount of binder required depends on the characteristics of the feed material and the final product:

- particle size
- particle shape and porosity
- fines content below 75 µm
- required abrasion resistance of briquette
- required crushing strength of briquette.

For coal briquettes binder content of a green briquette would be approximately 4 to 8 per cent on weight of coal.

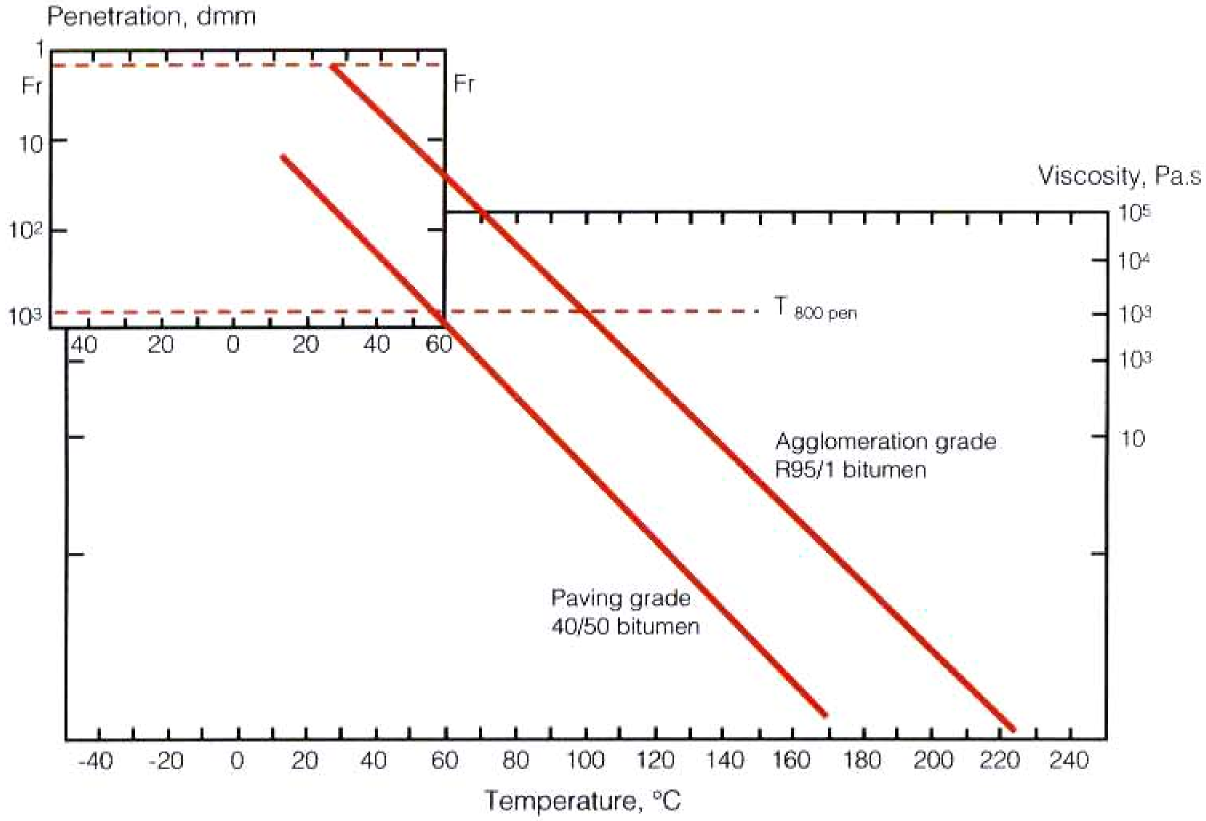


Figure 11.15 — Properties of a conventional bitumen and a special bitumen binder

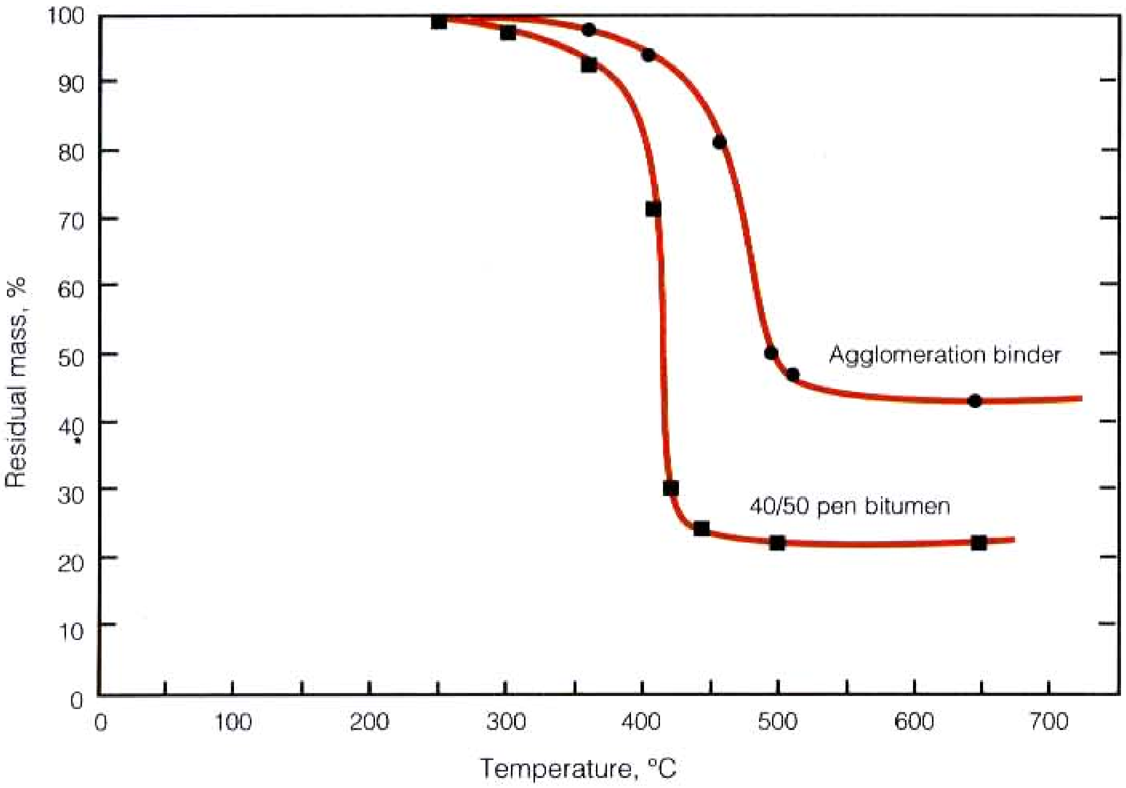


Figure 11.16 — Residual weight of bitumens after pyrolysis

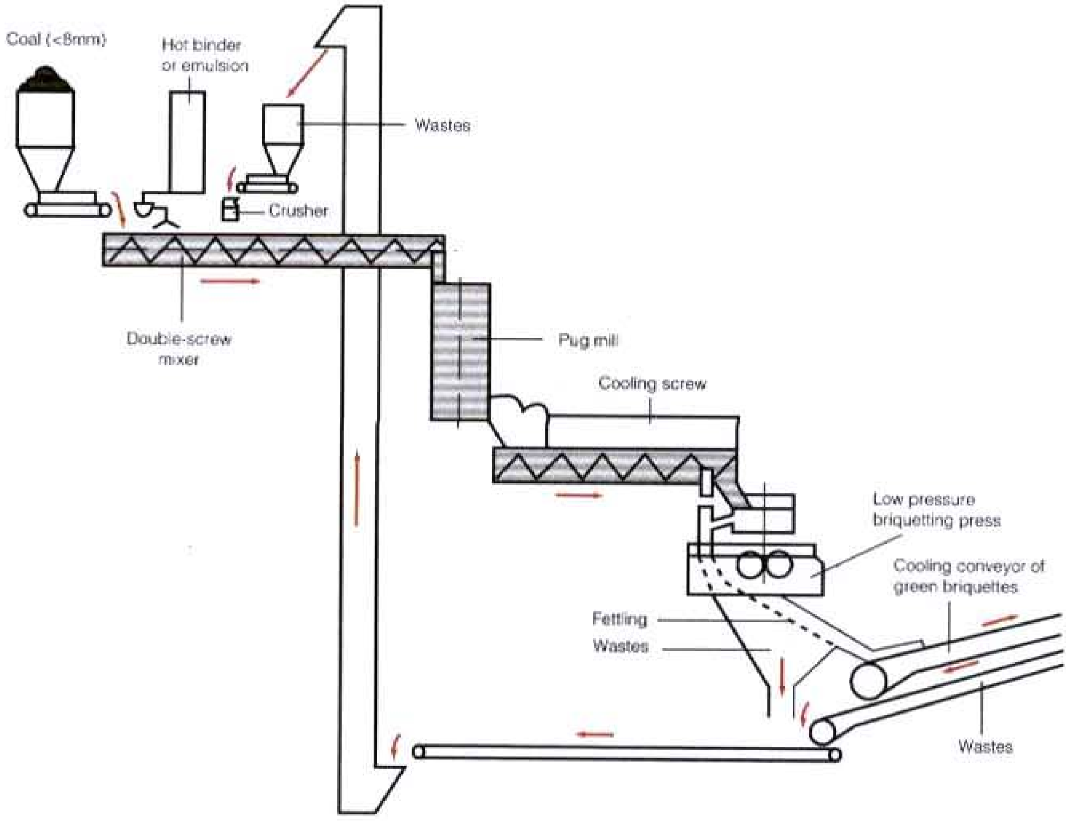


Figure 11.17 — Briquetting of coal

11.8.4 Briquetting with hot bitumen

This process can be applied to any material with a particle size in the range 0 to 8 mm. Coal briquetting is well established and is a typical application of low pressure briquetting. Different types of binder are used depending upon the coal quality and the end use of the briquette. Conventional hard bitumens and special binders are amongst the products in commercial use. Agglomeration grades R95/1 and R85/3 are particularly suitable binders for this process and have been widely used in France for many years for briquetting coal fines. To comply with increasing controls on pollution, a process was developed by Shell for the manufacture of smokeless briquetted fuel which involves the heat treatment of green coal briquettes in a specially designed oven. A typical scheme is given in figure 11.17.

11.8.4.1 Application in a steel converter

The scrubbing of steel converter fumes produces a mud of iron oxides whose handling and re-use is troublesome. Consequently, the mud is stockpiled or dumped. If they are recycled, the muds are usually added to the sinter strand mixture although they cannot be said to improve sinter strand operation. A blend of iron oxide muds and mill scale (a coarse iron-rich waste) bound with 3 per cent by mass of agglomeration bitumen produces a mixture suitable for low pressure briquetting with sufficient mechanical strength to be used directly in the steel converter.

11.8.4.2 Application in a Cupola furnace

Industrial trials made with a charge consisting of coke and zinc ore fines briquetted with bitumen have shown that the behaviour of the furnace was satisfactory with the bitumen bound briquettes.

The briquetting process with bitumen utilises a well established briquetting press working at low temperature and low pressure and with a high throughput. For this system, process control is not at all critical.

11.8.5 Briquetting with bitumen emulsions

It is possible to apply this process to any material with a particle size in the range of 0 to 8 mm. However, for the emulsion technique it is unnecessary to dry out the fines even at a moisture content of 10 per cent by mass. Part of the water in the mix can be pressed out during processing depending upon the operating conditions. After pressing, the briquettes formed have a low mechanical strength which needs to be improved during the drying stage. Heat treatment at 250°C provides briquettes with a mechanical strength unaffected by temperature. By increasing the residence time in the drying oven the bitumen binder 'polymerises' and imparts a very much improved strength to the cured briquettes. Briquetting using emulsified bitumen for waste treatment has been extensively studied by Shell in France, two examples of which are given here:

11.8.5.1 Flotation ores

When a barytes flotation ore is reduced in a rotary kiln, considerable amounts of fines are blown into the flue gases. This pollution problem is typical of furnace processes which use flotation fines. However, if the furnace is fed with briquetted fines, the loss to the flue gas is small. The emulsified binder technique is particularly well suited to the agglomeration ores because the water content of the filter coke need not be reduced prior to treatment. Barytes filter coke can be briquetted by incorporating 3 to 5 per cent by mass of special bitumen emulsion, which can be fed directly into the refinery furnace.

11.8.5.2 Industrial muds

As an alternative to the briquetting of steel converter muds together with mill scale these muds can be briquetted on their own. A pretreatment is required to evaporate some of the water from the filter coke/binder emulsion mix, after which briquetting of the mix is straight forward. The briquettes, dried and oxidised, may be used as a cooling charge additive for the steel converter. With this process the apparent density of the briquettes is in the range 2.2. to 2.4.

11.8.6 Refuse

Environmental protection is now a major issue for everybody. With increased attention being given to recycling, many industries are already examining the end-use and disposal routes for their products. Several companies have looked at recycling paper, which accounts for a very high proportion of household waste, as a fuel. It must be dried and chopped and is simply mixed with bitumen and either briquetted or extruded. As well as agglomerating the paper, the bitumen increases calorific value and waterproofs the product.

11.8.7 Agglomeration market

It is estimated that over 0.5 million tonnes of bitumen are utilised for agglomeration purposes throughout the world. The major part of the bitumen is absorbed by a few major uses in the coal and steel industries.

11.9 Paints

11.9.1 General

Bitumen is a widely used anti-corrosion and waterproofing medium which is both cheap and effective. However, before considering bitumen as a coating medium it is important to recognise the following:

1 Bitumen does not have any intrinsic anti-corrosion properties; it works simply by excluding water because it is virtually impermeable.

2 Like most paints it is not totally impermeable to water but any desired degree of impermeability can be obtained by applying a sufficiently thick coating.

3 Bitumen exposed to the atmosphere weathers noticeably, particularly in the case of thin films.

Hence it follows that the life of a bitumen film as an effective anti-corrosion coating is dependent upon its thickness. No figures are available but an approximate guide is:

- thin films	< 0.1 mm	weeks - months,
- moderate films	0.1 - 1 mm	months - year,
- thick films	1 - 4 mm	many years.

Paint solutions consist of a hard bitumen in a volatile solvent such as kerosene.

Bitumen paints have a high gloss initially but quickly turn matt and dull especially in sunlight. Their dark colour makes bitumen unsuitable for colouring with pigment.

Bitumen paint is utilised for such purposes as:

- Anti-corrosion coatings for:
  - wheelbarrows;
  - manhole lids;
  - train chassis;
  - sign post bases;
  - agricultural implements (barrows etc);
  - military ordnance shell cases, missile interiors.

- Anti-vandal paint:
  - a non-drying paint for use on down pipes etc. to deter unauthorised entry; typically a soft grade such as Mexphalte 70 pen would be used.

Bitumens selected for solutions or paints are usually the hard (H) grades which are generally preferred to oxidised (R) grades because they are less permeable to water. Also they require less solvent than blown bitumen to give the same viscosity solution. Oxidised grades usually require a more aromatic solvent.

Bitumens with a low wax content give solutions which keep their gloss longer than bitumens which contain more wax; the wax content depends on the bitumen origin.

11.9.2 Aluminium paints

Aluminium powder is mixed with bitumen paints to give a solar reflective paint which can reduce roof temperature on sunny days by up to 30°C. The aluminium is used at 25 - 30 per cent by mass of the finished paint formulation. For use on roofing felt 100 pen could be the base bitumen but for use on metal H80/90 or a similar hard grade should be used. The aluminium may be added as a powder, in which case a small quantity of stearic acid is required to give the leafing properties which characterise the paint. Alternatively it is possible to buy a ready made paste of aluminium which already contains the required quantity of stearic acid.

11.9.3 Stoving paints

Stoving paints consist of a hard bitumen, a drying oil and a solvent; the painted surface is baked in an oven to harden the paint which gives better adhesion, hardness and durability than air drying.

A typical formulation is shown in table 11.18.

Component	Concentration % by mass
Linseed oil	30
Mexphalte H80/90	19
Manganese dioxide	1
White spirit	50

Table 11.18 — Typical formulation for a stoving paint

11.9.4 Car body underseal

Bitumen has been used as a protective for car bodies for many years although its use has declined recently with the introduction of polymer coatings. In order to be effective against moisture and damage by small stones the bitumen must be present as a thick coat, typically 1 to 2 mm, and must be well bonded to the substrate. This in effect means the bitumen has to be applied as a thickened paint. Asbestos fibres were originally used but these have now been largely replaced by cellulose. As well as allowing a thick coat to be applied in a single application the fibres help resist cracking of a coating subject to continual stress and vibration. The solvent used is of a high volatility such as xylene to allow rapid cure after spray application. The bitumens most commonly used are soft oxidised grades such as R75/30 or hard penetration grades such as 35 or 25 pen.

Bitumen emulsions can also be used, although careful formulation is needed to ensure that blistering does not occur under the rapid drying conditions used on car production lines. Use of emulsions avoids the problems of flammability, toxicity and pollution associated with fast-evaporating solvents.

11.9.5 Problems encountered with bitumen solutions

- Gelling of solutions may be prevented by the use of a solvent with a higher aromatic content.
- Bitumen solvents will not bond to newly galvanised surfaces, but will bond to weathered surfaces.
- The dried solution is not resistant to petroleum products or solvents.
- It is almost impossible to avoid pin-holes. Two or three coats are recommended, even for temporary protection.

11.10 References

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Chapter 12 - General properties of bitumen

12.1 Thermal properties

12.1.1 Specific heat

The specific heat of bitumen(1) varies slightly with temperature as shown in table 12.1.

12.1.2 Thermal conductivity

Bitumen is a moderately good thermal insulating material. Thermal conductivity(1) is approximately 0.16 W/m°C (0.14 kcal/m hour°C).

12.1.3 Coefficient of cubical expansion

The coefficient of cubical expansion(1) (ie volume expansion) is approximately 0.00061/°C.

Thermal properties do not vary significantly with bitumen grade.

°C	kJ/kg/°C	cal/g/°C
0	1.67	0.4
100	1.89	0.45
200	2.10	0.5

Table 12.1 — Variation of specific heat with temperature

Application	Viscosity required (cSt)
Spraying (in general, the higher the viscosity, the coarser the spray)	20-100
Filling in joint boxes, etc, to ensure that all cavities are filled and that bubbles escape	100-200
Mixing with filler, etc	200
Impregnating paper, felt, etc	20-200
Coating paper, felt, etc	200-1000
Painting/brushing	600
Coating by dipping	1000
Pumping	1500-2000
Trowelling	200,000

Table 12.2 — Typical application viscosity of bitumen compositions

	To obtain unknown viscosity multiply by:						
Known viscosity	Kinematic, mm^2/s	Redwood I sec	Redwood II sec	Saybolt Universal, sec	Saybolt Furol, sec	Engler, ^{0}E	Standard Tar Viscometer, sec
Kinematic, mm^2/s	—	4.05	0.405	4.58	0.458	0.132	0.0025
Redwood I, sec	0.247	—	0.1	1.13	0.113	0.0326	—
Redwood II, sec	2.47	10	—	11.3	1.13	0.326	0.0062
Saybolt Universal, sec	0.218	0.885	0.0885	—	0.1	0.0287	—
Saybolt Furol, sec	2.18	8.85	0.885	10	—	0.287	0.0054
Engler ^{0}E	7.58	30.7	3.07	34.81	3.48	—	—
Standard Tar Viscometer (10mm cup), sec	400	—	162	—	183	52.8	—

Table 12.3 — Conversion factors for viscosities

12.2 Viscosity

Table 12.2 shows typical application viscosities for a variety of uses. The table assumes that application will be carried out at the maximum viscosity, ie the minimum temperature possible. Lower viscosities may be used in some cases provided that the temperature is not excessive and that material being treated is not damaged.

In most applications, bitumen is heated until it becomes sufficiently fluid for each particular application. If the optimum application viscosity is known, the temperature to which any grade of bitumen must be heated can easily be read from figure 5.11.

Conversion factors for viscosities measured by a number of different methods are shown in table 12.3. These are applicable only to liquids having Newtonian flow characteristics.

12.3 Density

The densities of some bitumens are given in table 5.9. Specific gravity varies with temperature by approximately 0.00054/°C as shown in table 12.4. Volumes of bitumen at various temperatures are shown in table 12.5.

12.4 Resistance of bitumen to chemical and biological attack

12.4.1 Chemical resistance

Bitumen is generally considered to have good resistance to attack by chemicals although quantitive information is scarce. General information on the properties affecting resistance is as follows:

- resistance to attack increases with increasing hardness of the bitumen;
- oxidised bitumens are more resistant than penetration grade;
- attack becomes more severe with increasing time, temperature and chemical concentration;
- fillers have little effect provided that they themselves are resistant to attack, eg slate dust or silica for acid conditions. The use of fillers which are not resistant has a very adverse effect and must be avoided;
- resistance to acid attack can be improved by adding five per cent of hard paraffin wax to bitumen.

Temperature, °C	Specific gravity at 25°C					
	1.00	1.01	1.02	1.03	1.04	1.05
15.5	1.006	1.016	1.026	1.036	1.046	1.056
25	1.000	1.010	1.020	1.030	1.040	1.050
45	0.988	0.998	1.008	1.018	1.028	1.038
60	0.979	0.989	0.999	1.009	1.019	1.029
90	0.961	0.971	0.981	0.991	1.001	1.011
100	0.955	0.965	0.975	0.985	0.995	1.005
110	0.949	0.959	0.969	0.979	0.989	0.999
120	0.943	0.953	0.963	0.973	0.983	0.993
130	0.937	0.947	0.957	0.967	0.977	0.987
140	0.931	0.941	0.951	0.961	0.971	0.981
150	0.925	0.935	0.945	0.955	0.965	0.975
160	0.919	0.929	0.939	0.949	0.959	0.969
170	0.913	0.923	0.933	0.943	0.953	0.963
180	0.907	0.917	0.927	0.937	0.947	0.957
190	0.901	0.911	0.921	0.931	0.941	0.951
200	0.895	0.905	0.915	0.925	0.935	0.945

Table 12.4 — The specific gravity of bitumen at various temperatures

Temperature, °C	Specific gravity at 25°C					
	1.00	1.01	1.02	1.03	1.04	1.05
25	995	984	973	963	953	943
45	1010	999	988	978	968	958
60	1020	1009	998	988	978	968
90	1041	1030	1019	1009	999	989
100	1047	1036	1026	1015	1005	995
110	1054	1043	1032	1022	1011	1001
120	1060	1049	1038	1028	1017	1007
130	1067	1056	1045	1034	1024	1013
140	1074	1063	1052	1041	1030	1019
150	1081	1070	1058	1047	1036	1026
160	1088	1076	1065	1054	1043	1032
170	1095	1083	1072	1060	1049	1038
180	1103	1091	1079	1067	1056	1045
190	1110	1098	1086	1074	1063	1052
200	1117	1105	1093	1082	1070	1058

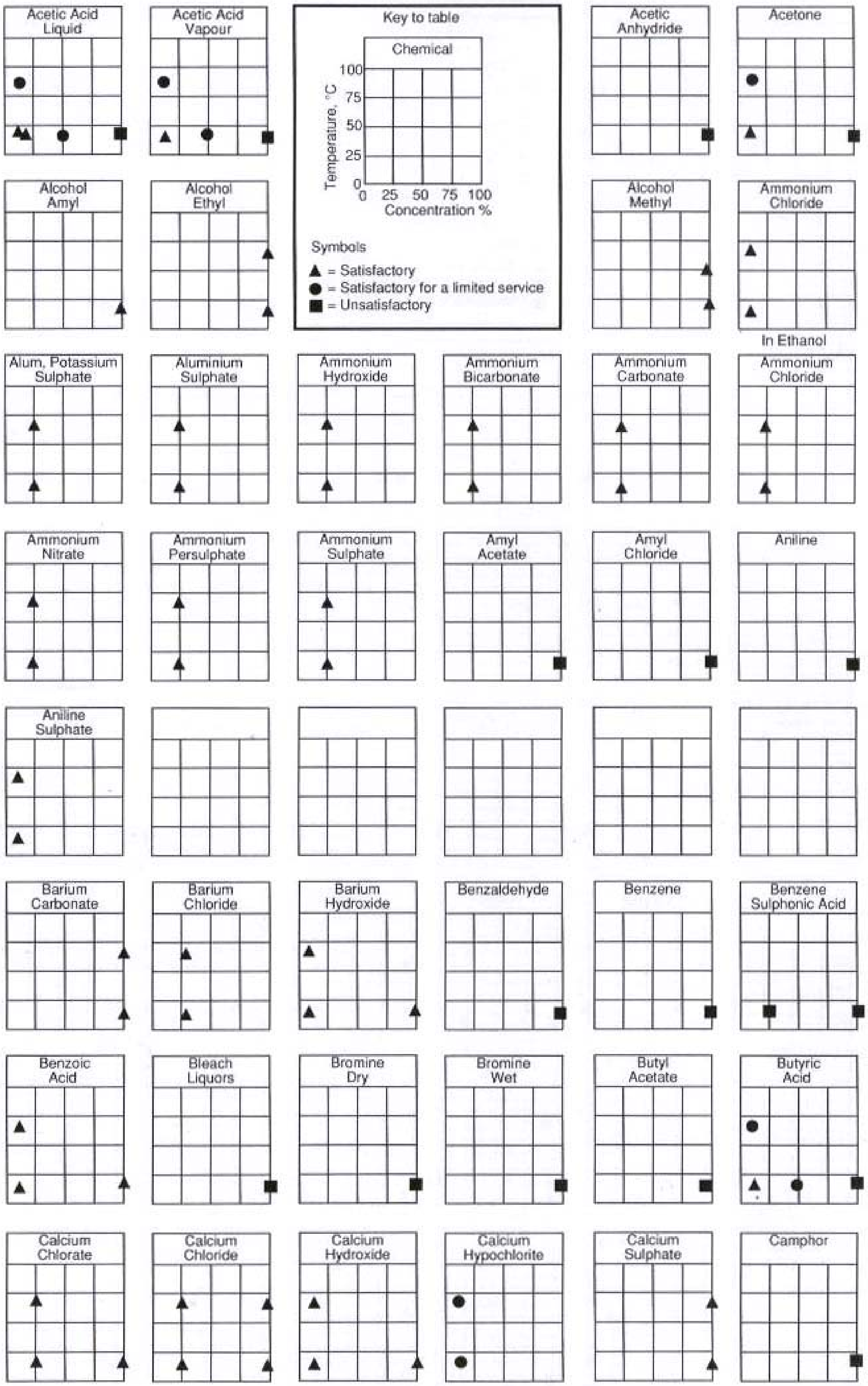
Table 12.5 — The number of litres per tonne of bitumen at various temperatures and specific gravities

Information is given for some specific substances in table 12.6 and figures 12.1 - 12.5. The information is a compilation of data from literature sources and from Shell's Amsterdam laboratory and does not represent any systematic investigation.

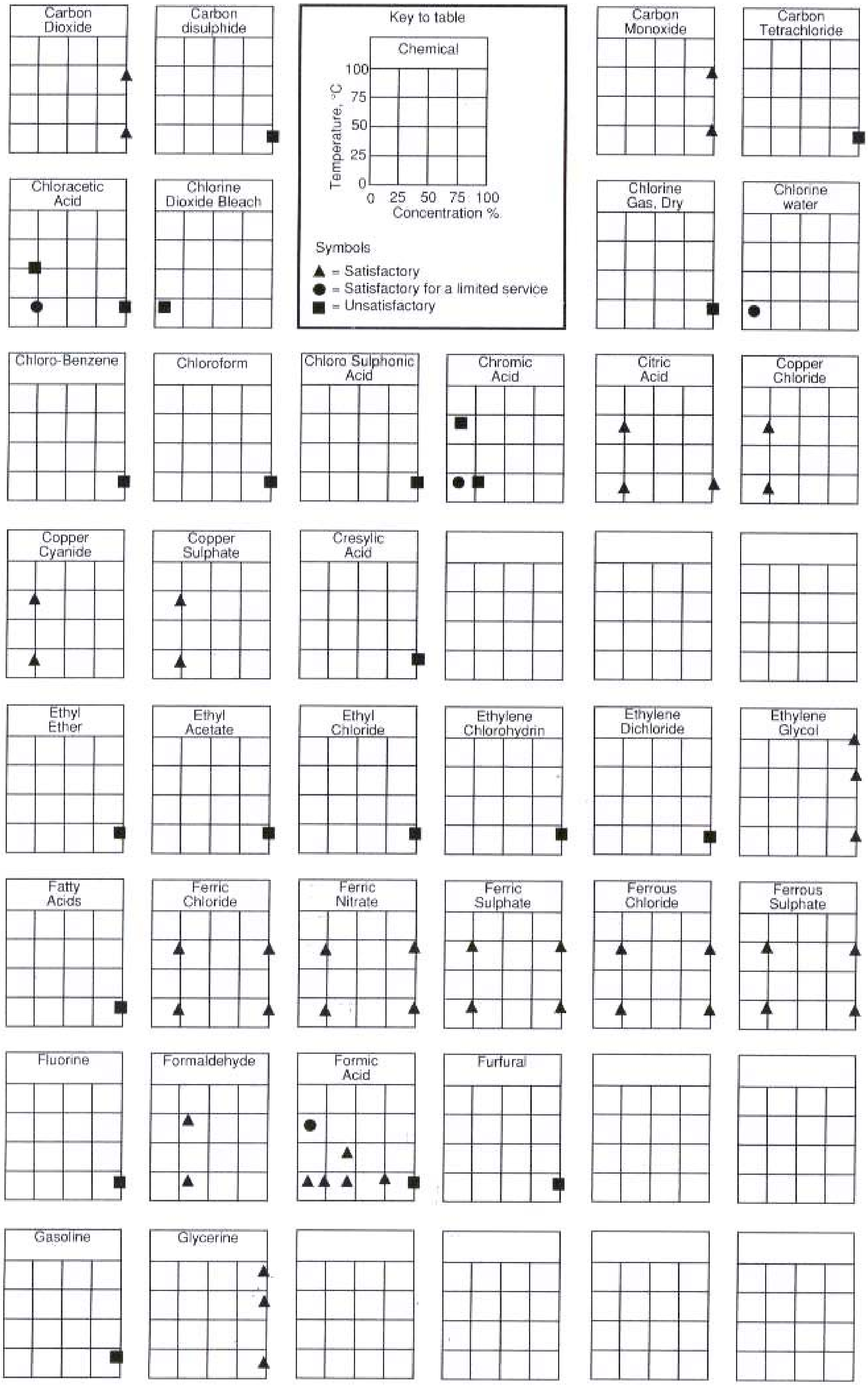
Chemicals		Penetration bitumens (50 or harder)				Oxidised bitumens			
Exposure time, months		6	12	18	24	9	12	42	60
Inorganic acids									
Hydrochloric acid up to	10%	0	†		●				0
Hydrochloric acid from	10-30%	†	†		●				0
Sulphuric acid up to	50%	0		†	●				0
Nitric acid up to	10%	†	●						0
Nitric acid up to	25%	●							†
Nitric acid up to	50%	●							●
Phosphoric acid	5%					0			
Hydrofluoric acid	40%						0		
Organic acids									
Lactic acid	10%			●					0
Butyric acid	10%			●					0
Formic acid	85%					0			
Acetic acid	20%					0			
Benzoic acid	1%						0		
Picric acid	1%						0		
Salicylic acid	0.1%						0		
Phenol solution	1%						0		
Inorganic alkalis									
Caustic soda up to	30%							0	
Ammonia	25%						0		
Soda solution	10%							0	
Soda solution (saturated)						0			
Salts									
Common salt solution (sat)								0	
Chlorine-containing brine								0	
Sea water									0
Magnesium chloride	14%					0			
Sodium hyposulphite soln (sat)						0			
Sodium sulphate soln (sat)						0			
Sodium hypochlorite	5 g/l					0			
Waterglass						0			
'Teepol'								0	0
Formaldehyde solution	30%					0			

0 not affected
† little to moderate
● strongly attacked

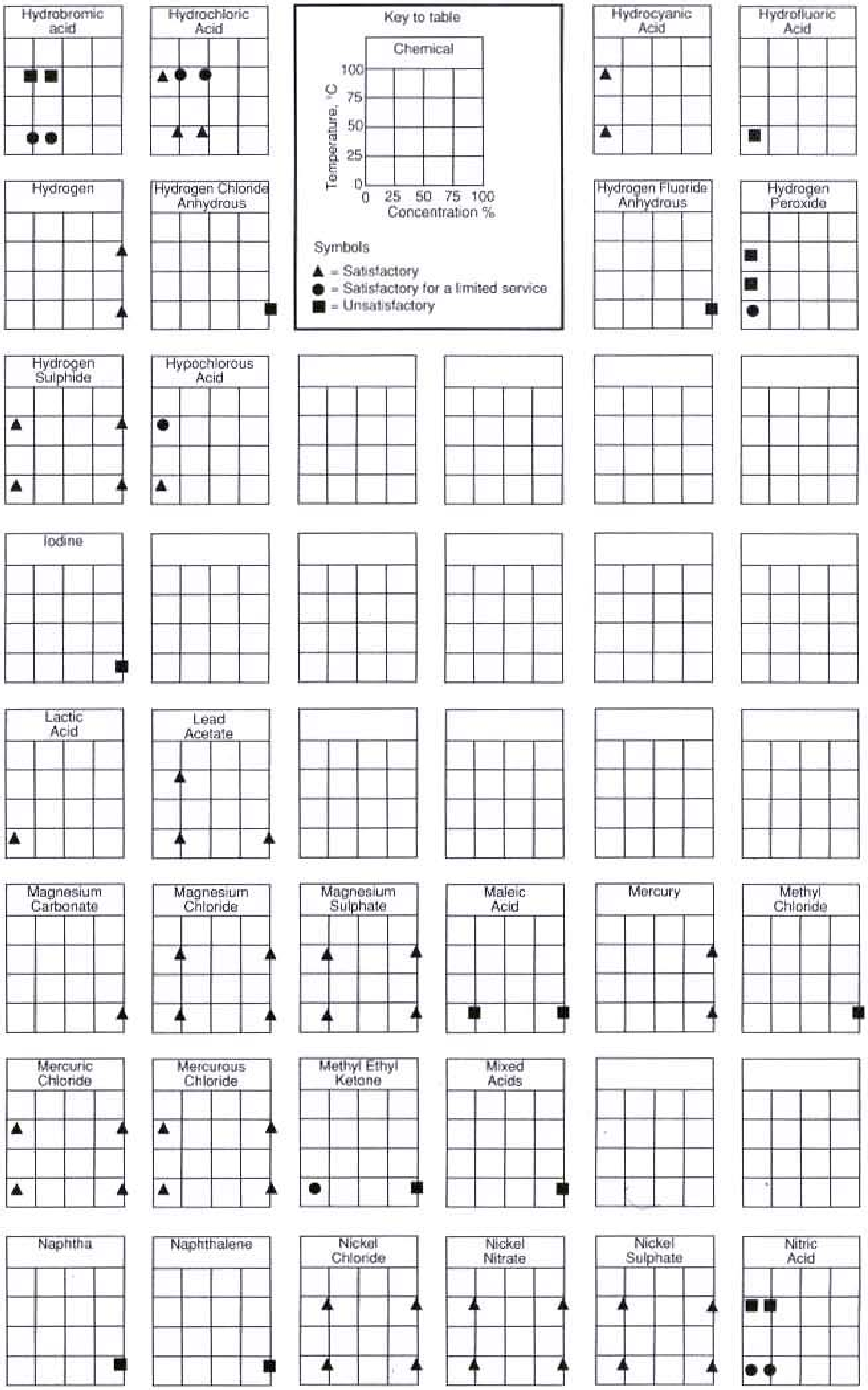
Table 12.6 — Resistance of bitumen to the effects of chemicals at room temperature



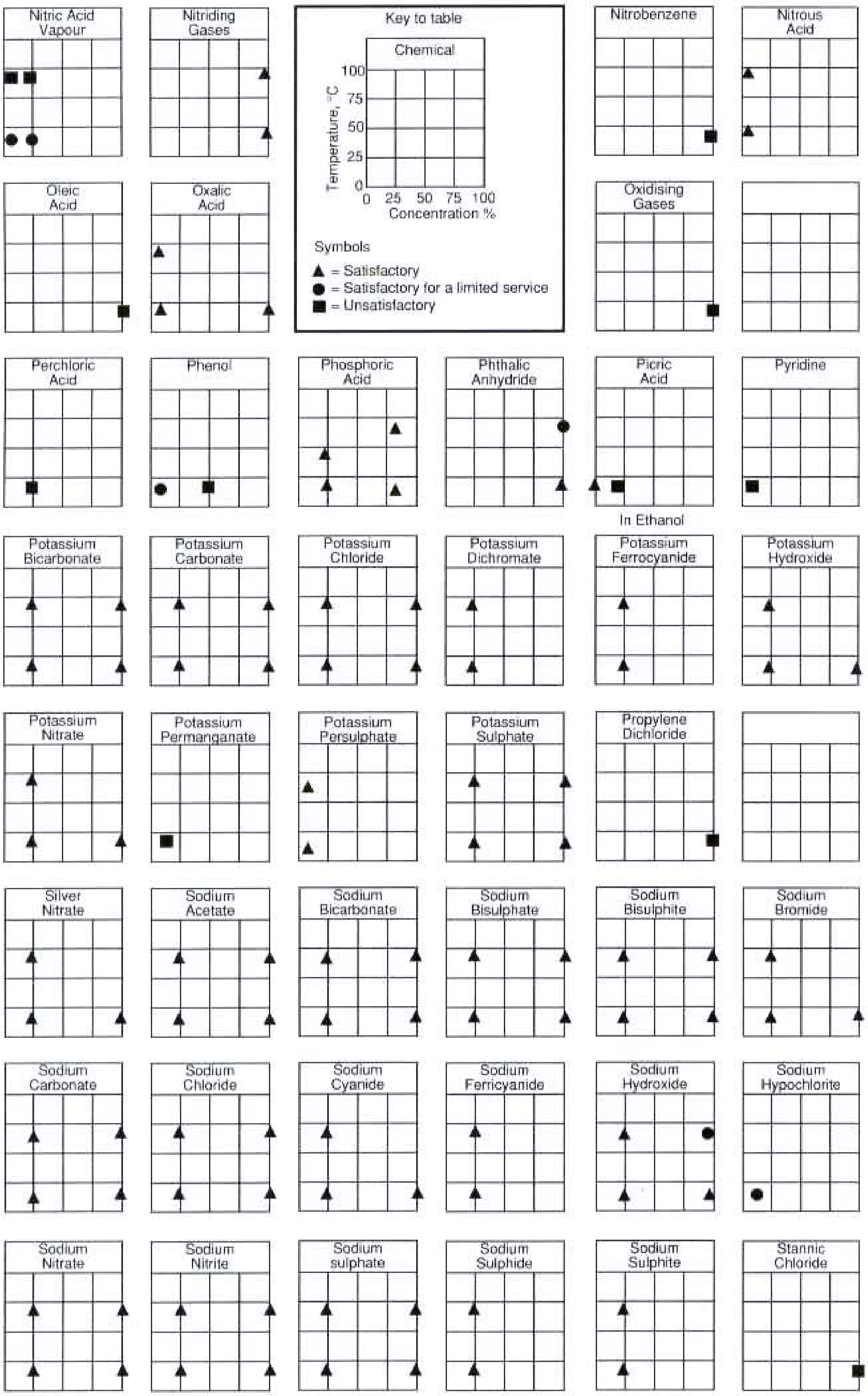
Figures 12.1 — Chemical resistance of bitumen



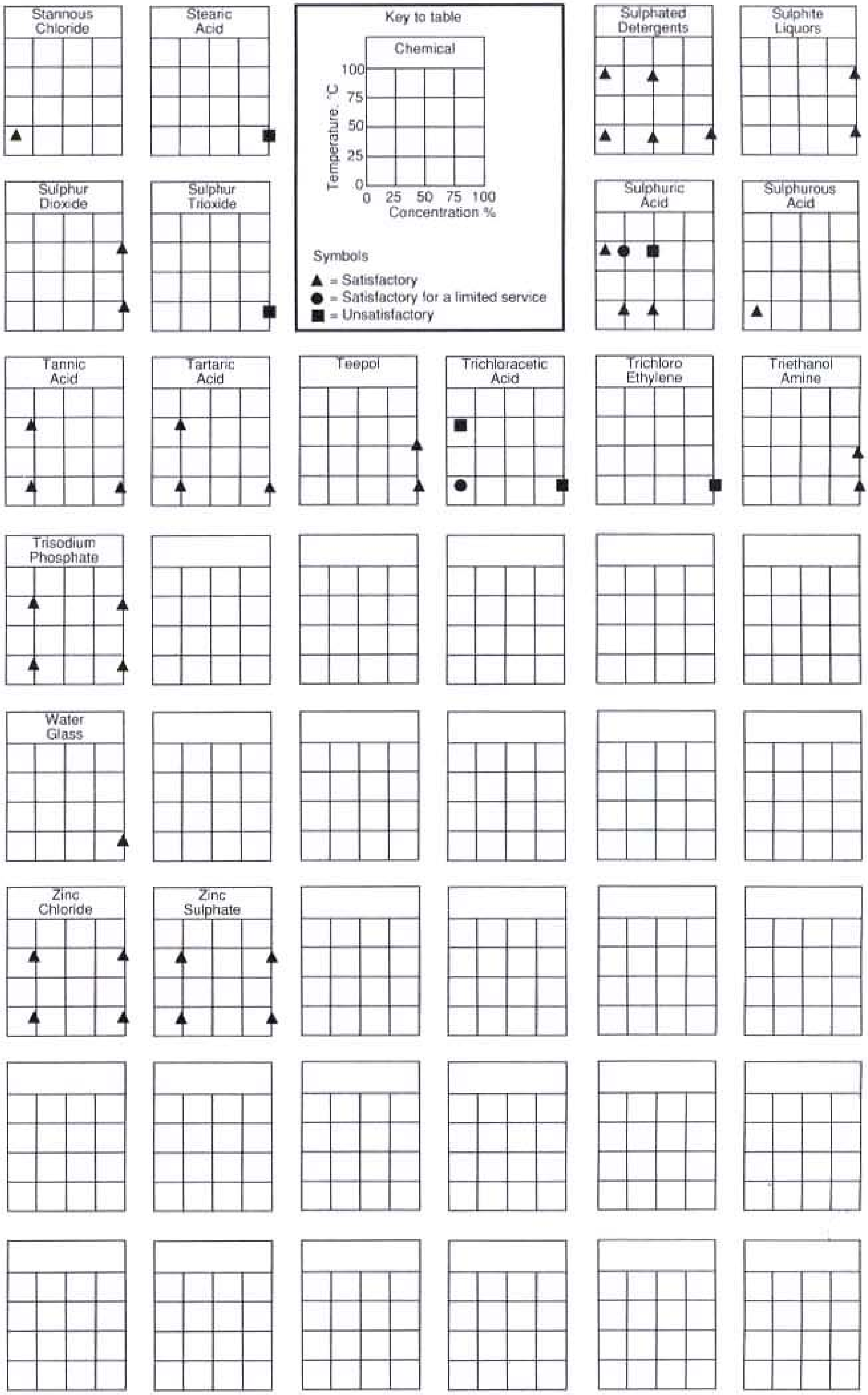
Figures 12.2 — Chemical resistance of bitumen



Figures 12.3 — Chemical resistance of bitumen



Figures 12.4 — Chemical resistance of bitumen



Figures 12.5 — Chemical resistance of bitumen

12.4.2 Biological resistance

There is much published information on the effect of biological agents on bitumen. Two principal studies have looked at the resistance of bituminous products to attack by biological agents. Jones(2) has reviewed the effects of bacteria, moulds and fungi on bitumen, while the biological deterioration of bitumen and coal tar by microbes, insects, rodents and plants has been investigated by Nicolle and Pankhurst(3). The findings of these two surveys are summarised below.

12.4.2.1.1 Bacterial action on bitumen

The durability and longevity of bituminous constructions, as demonstrated by the survival of structures from pre-biblical times, has led to the general belief that bitumen is immune to biological deterioration. Many ancient artefacts have used bitumen as either an adhesive or preservative and many have been recovered in excellent condition(4), see chapter 1. However, it has been shown(5) that bacteria can attack and degrade bitumen.

Despite the fact that the micro-organisms, fungi and moulds capable of degrading bitumen are widely distributed in nature, there is no reported evidence to show that bacterial action on bitumen had led to any catastrophic failure of a bituminous material or structure. Many reported examples of the effects of bacteria on bitumen have been conducted under ideal conditions for bacterial propagation which would, generally speaking, never be present on a well designed roof, road or other construction. Bacterial and fungal attack is, therefore, not a major factor in the deterioration of any well designed, well constructed bitumen structure.

Many organic materials containing bitumen such as asphalt, coal tar, fatty acid pitch(6-13) and pine tar pitch are attacked by micro-organisms which are present in the air, water and soil. The rate of attack is dependent on a number of factors including(6,13,14).

- the nature of the material
- temperature
- moisture content of the culture
- the availability of salts for growth,
- the adaptability of the micro-organisms.

Oxygen in one form or another is also a necessity to sustain microbial action. Whether the oxygen is required in molecular form is debated and it has been reported(15) that attack of bitumen under anaerobic conditions can occur.

One bacterial group, *Pseudomonadae,* contains members that can attack bitumen either aerobically or anaerobically. One known strain is more vigorous under anaerobic conditions than in air,(15,16) attacking oxygenated molecules in the bitumen. In general, *Pseudomonadae* bacteria of various strains show attack on bitumen under acid, alkaline and neutral conditions both aerobically and anaerobically.

Desulphovibrio desulphuricans, an anaerobe that reduces sulphate to metal sulphides or hydrogen sulphide by utilising the sulphate ion as a source of oxygen, can cause severe pitting and corrosion on exposed steel, particularly on pipelines(33). Cyclic wet and dry soil conditions surrounding a pipe can be troublesome. Under these conditions the metallic sulphides or hydrogen sulphide generated by the biological activity will attack steel during the wet anaerobic cycle(17). During the following dry season, sulphur oxidising bacteria such as *Thiobacillus thiooxidans* convert metallic sulphides back to sulphate ions. In acidic soils, sulphuric acid is formed which rapidly corrodes bare steel. *Thiobacillus thiooxidans* has shown pH levels of one or less in cultures(18).

12.4.2.1.2 Fungi, moulds and yeasts

Fungi, moulds and yeast have been found to be capable of attacking bitumens, bitumen constituents and bitumen degradation products(19,20,21). Such growth has occasionally been found on roofs in warm humid climates. Limestone dust, a common filler in bituminous products, combines with bitumen degradation products to buffer an aqueous system to a pH of about four which is very favourable for fungal growth. Bacteria generally prefer a pH range of six to eight(20,22,24).

12.4.2.2 Micro-organisms

It is apparent from published literature that microbial attack on bitumen and asphalt is far more commonly reported than for materials containing coal tar. This is undoubtedly due to the higher content of polynuclear aromatic hydrocarbons found in coal tar which are toxic or inhibitory to many micro-organisms(23), see table 12.7.

Microbial attack on large scale bituminous constructions, however, tends to be so slow that for all practical purposes they may be considered immune to attack from bacteria and fungi(25). It has been shown(21) that the susceptibility of bitumens manufactured by different processes to microbial attack is highest for penetration grades of bitumen and lowest for blown bitumen.

Within the bitumen, attack tends to be on the lower molecular weight, more paraffinic constituents of the maltenes(14,26) with slower attack on the resins, and very much slower attack on the asphaltenes. The rate of attack tends to be fastest for paraffins, then isoparaffins, naphthenes and finally aromatics(12,13,14,20).

Most bacterial and fungal attack of bitumen and hydrocarbons is by oxidative reaction(6,12,14,20) and acids, aldehydes, esters, ketones, olefins, and alcohols have been found as microbial action intermediates. The hardening action of this attack has been attributed to the following:

- loss of lower molecular weight oils which are effective solvents and plasticisers,
- conversion of lower molecular weight hydrocarbons to high molecular weight oxygenated compounds,
- polymerisation of unsaturated compounds that result from microbial attack.

It is assumed that microbial attack would be slowest for bitumens with:

- high flash point, high molecular weight,
- naphthenic rather than paraffinic characteristics,
- high viscosity.

12.4.2.2.1 Penetration and oxidised grades of bitumen

Both roofing and paving grades of bitumen have been shown to be susceptible to microbial degradation, with thin films of penetration grade bitumen losing 3 to 25 per cent in weight within one week(15,16).

Penetration grades of bitumen are often used in circumstances where the bitumen is in close proximity to soil, which can supply micro-organisms, moisture and nutrient salts. In these circumstances, cases of rapid asphalt deterioration might occasionally be expected. However, no failures of asphalt pavements have been attributed to microbial attack.

For properly designed and constructed roads, conditions are such that microbial attack on the bitumen in the asphalt is highly unlikely. The temperature range between high and low tends to be too great. There is no continuous supply of moisture needed for continual growth and attack. Without prolonged growth there cannot be a sustained attack on the bitumen necessary to cause major deterioration.

Air blown bitumens have been established as being more resistant to microbial degradation than penetration grades of bitumen(21). This may be due to the higher concentration of asphaltenes and resins in the blown bitumen as compared with the penetration grades. It has been established that microbial attack on bitumens is concentrated on the maltenes phase of the bitumen(14) with attack being less rapid on the resins and slowest on the asphaltenes.

12.4.2.2.2 Bitumen emulsions

Bitumen emulsions are suspensions of bitumen droplets, typically five microns or less in diameter, suspended in an aqueous medium. After application, the emulsions rapidly lose water and agglomerate to form a solid bitumen film, see chapter 6. This process is typically used in road surface dressing applications and in roofing applications for fixing loose chippings.

The types of application for bitumen emulsions, including tile setting, surface dressings, damp proof course, etc, are so different that the conditions necessary for sustained microbial growth and attack would only very rarely be simultaneously present. Furthermore, bitumen emulsions are manufactured and stored under conditions that would exclude the growth of micro-organisms. Emulsion manufacturing temperatures are typically 70 to 100°C which effectively sterilises both the aqueous and the bitumen phases of the emulsion, excluding the presence of live organisms.

12.4.2.2.3 Cutback bitumen

Cutback bitumen contains a hydrocarbon solvent diluent to reduce its viscosity and simplify its application, see chapter 6. Owing to the presence of relatively large amounts of low molecular weight hydrocarbon solvent, such as kerosene, cutback bitumen could be expected to be more vulnerable to microbial attack than other forms of bitumen. However, microbiological deterioration of cutback bitumen appears to be a relatively minor factor contributing to failure(14). The solvent cutter used in the bitumen is very volatile, is rapidly lost through evaporation and thus not available to micro-organisms for very long following application.

12.4.2.3 Effect of microbiological activity on some bituminous materials

12.4.2.3.1 Bituminous roofing

Air blown bitumens have been established as being more resistant to microbial degradation than penetration grades of bitumen(21). However, it is also well known that bacteria and fungi are found on roof surfaces in warm humid climates. It has not been established with any certainty that these biological agents contribute in any way to the deterioration of the bitumen in roofing felt or shingles.

Deterioration of built-up roofs has sometimes been attributed to fungal attack. This is to some degree unlikely as fungi ideally require a substrate at about pH 4 to sustain growth. It has been suggested that microbial attack of the roofing in combination with normal weathering might produce degradation products which could react with limestone filler, etc, to produce a substrate buffered to an ideal pH for fungal growth. In combination with a warm, wet, shady location, fungal attack could possibly occur. However, the most likely point for fungal attack of built-up roofing is on the organic fibre carrier of the felt or shingles, although it is believed that UV degradation of the fibre would normally be faster than microbiological attack.

Mastic asphalts used for roofing have generally performed satisfactorily for many years.

Material		Replicate tests				
		1	2	3	4	5
1	Pipeline grade bitumen 120/20 (unfilled)	++	+	++	+++	+++
2	Pipeline grade bitumen 115/15 (filled)	+	+++	+	++	+
3	Bitumen 85/40	++	++	+++	++	++
4	Cut back spraying bitumen	-	-	-	-	+
5	Petrolatum 1	+	+	+	+	+
6	Petrolatum 2	+	+	++	++	+++
7	Petrolatum with additive	+	++	+	++	+
8	Bitumen 1	++	++	+++	+++	+++
9	Bitumen 2	+	+++	+	+++	++
10	Asphalt grade enamel 8.15 pen	+	+	++	++	+
11	As 1, but with 3% proprietary herbicide	-	-	-	-	-
12	Coal tar enamel	-	-	-	-	-
13	Unfilled modulate 115/15	-	-	-	-	-

- = no growth
+ = a little growth
++ = more growth
+++ = pronounced growth

Table 12.7 — Ability of soil micro-organisms to grow on the surface of coal tars or bitumens used in coatings or wrappings(3)

12.4.2.3.2 Bituminous pipe coatings

Due to the conflicting nature of the evidence it is very difficult to ascertain the degree of attack by micro-organisms on pipe coating enamels. Many of the studies of microbial action have been conducted under highly accelerated conditions in the laboratory as well as from actual observations of pipelines(17,19,22,27).

Nicolle and Pankhurst(3) conducted microbiological growth tests on bitumen and coal tar enamels exposed to a mixture of soil and distilled water over a two-month period. These tests demonstrated that the bitumen enamel would support microbiological growth except where a three per cent concentration of a herbicide based on a proprietary amine and pentachlorophenol derivative were added to the enamel, see tables 12.7 and 12.8.

Product	Species								
	Bacteria			*Yeasts*		*Actinomycetes*		*Fungi*	
	1	2	3	1	2	1	2	1	2
PVC tape with petrolatum	++	+++	++	0	0	+	+	+	+++
Polypropylene wrapping with bitumen	++	++	+	0	0	0	0	++	+
Polyethylene with bitumen	++	++	+++	0	0	0	+	++	++
Nylon/coal tar tape	-	-	+	-	0	---	-	0	0
Nylon/coal tar wrapping	--	--	---	-	-	---	-	0	0
Rubber/bitumen mastic	++	++	0	0	0	0	0	+	++

0 = no growth or inhibition of growth of test organism
- = a little inhibition
-- = more inhibition
--- = pronouncd inhibition
+ = a little growth
++ = more growth
+++ = pronounced growth

Table 12.8 — Results of growth tests with wrapping tapes containing coal tar or bitumen(3)

From the results of their work they conclude that:

> *"although (bituminous) pipeline coatings are more likely to support growth of micro-organisms than their coal tar counterparts, the properties of the reinforced bitumen enamel based on 115/15 bitumen of the minimum thickness (4 mm) . . . are unlikely to be seriously affected by superficial microbial growth."*

The exception to this would probably be pipe coating enamel situated downstream of a compressor station where soil temperatures may reach 50°C in close proximity to the pipe.

Nicolle and Pankhurst(3) also make the point that the ability to support surface growth is not necessarily related to the ease with which a particular coating or wrapping undergoes microbiological attack.

One example of this thesis concerns the use of bituminous linings for potable water pipes which have been used for more than 60 years and have proved to be effective, reliable and environmentally acceptable. For a number of years now the water industry in the UK has required that all materials and fittings used in conjunction with potable water should be subjected to tests which determine their suitability by measuring(27):

(a) toxicological properties (to ascertain the extent to which substances are extracted by the water passing through or contained in the fitting or component of a fitting);

(b) organoleptic and physical properties (to ascertain whether the fitting or components of a fitting give rise to taste, odour, colour or turbidity of the water passing through or contained in it);

(c) microbiological growth properties (to ascertain the extent to which the fitting or component supports the growth of micro-organisms).

Bituminous enamel coatings generally pass test (a) and (b) and may also pass test (c). However, it is not uncommon for some enamels to fail the microbiological growth test which then classifies them as unsuitable for lining potable water pipes. That bitumen will support the growth of micro-organisms is not surprising as bitumen is a non toxic, hydrocarbon, petroleum derivative. Where the bitumen has passed these tests it has proved to be highly satisfactory as a corrosion protection medium and extensive experience of the use of bituminous linings for potable water pipes has not highlighted any problems associated with its use.

Somastic, and other types of mastic asphalt used for the external coating of pipes and fittings, have given good service for many years. In common with other types of pipe coating, when in service under severe operating conditions, cathodic protection is often provided as additional insurance against corrosion(28). Cathodic protection polarises the steel pipe surface to prevent localised galvanic cell reaction. It also appears to minimise certain types of microbial growth close to the outer surface of the coating.

12.4.2.3.3 Hydraulic applications

Asphalts for lining canals are generally laid in thick layers (about six centimetres). Investigations conducted on the microbial degradation of canal linings(25) have shown that even under the most severe conditions, such as burial under moist, active compost for up to three years, degradation is limited to a depth of about one millimetre on the asphalt surface. These conditions were considered to be atypical of the real life situation of canal linings.

12.4.2.4 Damage to bituminous materials by small animals

Nicolle and Pankhurst(3) have reviewed the potential for damage to bituminous coatings by insects, rodents and small animals and their investigation, summarised below, has revealed some interesting facts.

In Australia 10,000 pipeline coating failures have been attributed to action by tropical white ants(29). Whilst it is difficult to estimate the risk of similar damage to bituminous coatings in temperate climates, it is known that termites are a nuisance to cables in Germany and the old territory of Czechoslovakia and beetles and cockroaches have also been implicated in damage to cable coatings, especially in warm climates.

Rodents and other small animals are known to sharpen their teeth by gnawing at hard materials. Other sharp toothed mammals are able to gnaw inedible materials without ingesting them(30) and to cause serious damage to lead and copper pipes. Some rodents are believed to have teeth sharp enough even to damage iron.

Rodents commonly bite through domestic cables and polythene and PVC piping. Field mice and voles cause considerable nuisance in European rural areas in damaging cables and in parallel the pocket gopher is implicated in the USA. However, such small mammals are considered to be unlikely to damage pipes and cables greater than two to five centimetres in diameter, as they would be unable to sink their teeth into them properly(31).

Whilst there is no record of small animals damaging bituminous pipe coatings in Europe, the American gopher is reputed to be able to rapidly penetrate bitumen/asbestos cable coverings. The risk of damage to buried bituminous coatings by small burrowing mammals cannot be discounted as the bitumen coating offers no discouragement to animals either in the form of smell or taste. Even if the animals do not gnaw on the materials themselves, by burrowing under and around buried pipelines they may well cause soil subsidence and thus increase the risk and incidence of mechanical damage to the pipe coating.

12.4.2.5 The effect of plant growth on bituminous coatings

It is well known that grasses, trees, bushes and other plants readily grow on, in and through bitumen and asphalt surfaces. Growing vegetation often causes extensive damage to these types of surfaces. Plants are known to grow on and through damp-proof membranes, roofing and insulating felts containing bitumen. Often proprietary herbicides are added to these materials to control rooting.

The low toxicity of bitumen combined with the ability of roots to penetrate bitumen coated surfaces has led to the introduction of plant pots made from bitumen coated peat and bitumen impregnated paper, see chapter 11. This type of pot is sufficiently strong to hold soil and young plants but does not hinder root growth and is biodegradable in soil.

The impact of plant growth on bituminous coatings is of most concern to the pipe line industry where the protection of a multi-million pound investment from premature failure and the avoidance of ecological catastrophe caused by corrosion due to failure of the pipe coating has resulted in much investigation of the effects of plant growth.

Pipe lines are commonly buried in trenches which cross fields and agricultural areas. Whilst the pipe line way-leave areas are normally cleared of trees and shrubs, and the pipes are usually buried at a minimum soil cover of 1.1 metres, it is generally assumed that crops or other vegetation normally found in these areas are insufficiently deep rooted to interfere with the pipe coating. However, in the USA(3) grasses, cereals and forage crops have been identified with roots which can penetrate to depths of one to two metres and include springwheat, winterwheat, rye, maize, sorghum, and barley. Vegetation in Europe, however, tends to be less deeply rooted.

A number of factors influence the depth to which plant roots will penetrate soil and threaten buried assets including:

- plant species,
- soil conditions,
- climate.

Plant	Grade of bitumen	Results after 3 months	Rating
Lupin	R85/40	Roots penetrating deeply through disc in all 3 pots	Fail
Lupin	R85/40 + 10% coal tar	No roots penetrating as far as 5 mm, none through disc or between disc and pot	Pass
Lupin	R85/40 + 3% herbicide 1	No roots penetrating, none through disc or between disc and pot	Pass
Lupin	R85/40 + 0.5% herbicide 2	No roots penetrating as far as 5 mm, none through disc or between disc and pot	Pass
Lupin	R115/15	Roots penetrating through disc or between disc and pot in 2 of 3 pots	Fail
Lupin	R115/15 + 10% coal tar	No roots penetrating as far as 5 mm, none through disc or between disc and pot	Pass
Lupin	R115/15 + 3% herbicide 1	No roots penetrating, none through disc or between disc and pot	Pass
Lupin	R115/15 + 0.5% herbicide 2	No roots penetrating as far as 5 mm, none through disc or between disc and pot	Pass
Maize	R85/40	Roots penetrating disc completely in both pots	Fail
Maize	R115/15	Roots between disc and pot in both pots and completely through disc in one	Fail
Maize	R115/15 + 10% coal tar	Roots penetrating disc completely in both pots	Fail
Maize	R115/15 + 3% herbicide 1	Roots between disc and pot and penetrating further than 5 mm in both pots	Fail
Maize	R115/15 + 0.5% herbicide 2	No roots penetrating, none through disc or between disc and pot	Pass

Table 12.9 — Penetration of bitumen by roots of lupins and maize(3)

Plant roots have considerable tensile strength and are capable of penetrating and lifting pipeline coatings. Some types of plants, such as couch grass *(Agropyron repens),* have roots which are particularly tough and are often strengthened. Couch grass is an example whose cuticle contains a high silica content making it particularly tough. Fine roots are often stronger and more aggressive than thick ones.

The susceptibility of bituminous systems to penetration by roots has led to the adoption of test methods to measure the damage produced. One commonly used method is described in the German Standard DIN 4038(32). Three dry, unglazed, earthenware pots about 22 cm high and 19 cm in diameter are required for each test. A circular strip of bituminous material, typically 4 cm thick is fixed onto the inside of the pot. The pot is half filled with a suitable compost such as John Innes Number 1. A disc of the bitumen is placed firmly on the top of the compost and sealed into position with the bitumen under test. The pot is then filled with a further amount of compost and the appropriate seeds are sown. In DIN 4038, *Lupinus* *albus* (lupin) is specified as the test plant. However, the test is often conducted using other plants representative of the type of forage crops likely to be encountered in agricultural land, such as maize (*Zea mays*). The plants are allowed to grow under standardised conditions and the pots are examined for root growth after a period of three months.

Tests conducted by Nicolle and Pankhurst(3) on R115/15 and R85/40 bitumens in comparison with coal tar showed that bitumen was susceptible to root penetration and the coal tar coating resisted root penetration, see table 12.9. The incorporation of suitable root dissuading additives, however, was successful in preventing root penetration of the bituminous coatings.

12.4.3 Surface discolouration of bitumen coatings

Atmospheric oxidation of bitumen surfaces is a common phenomenon for all grades of bitumen. Fresh bitumen loses its gloss within days to weeks depending on atmospheric conditions and takes on a matt dark-grey appearance. Normally such weathering goes no further and does not affect the integrity of the coating. Occasionally bitumens can take on a brown or even yellow colour. The reasons for this are not clear, but may be a combination of atmospheric and biological attack. Investigations have shown that water and filler are important. For example, a bitumen painted roof produced yellow patches where rain water puddled and a macadam surface turned brown following rainfall. This latter case returned to its black colour when the surface dried in the sun. In all cases of discolouration the integrity of the bitumen coating is not affected.

12.5 Resistance of bitumen to burning

Bitumen is not a very flammable material as indicated by its flashpoint which is usually higher than 200°C (open cup method). Under severe conditions it will, however, burn, and in some applications attempts have been made to reduce the flammability and burning rate by the use of fire retardant additives. The following compounds have been suggested for use in bitumen but no data regarding relative effectiveness is available:

- chlorinated hydrocarbons in conjunction with antimony oxide,
- triphenyl phosphate,
- zinc chloride,
- borax,
- ammonium sulphate,
- antimony or bismuth chloride,
- chlorinated polyphenols or chlorinated wax.

Fire retardants generally work in one of two ways:

- a component is volatilised and the energy required draws heat from the flame causing it to go out;
- a chemical reagent combines with the reactive gases within the flame causing the reaction to stop and hence the flame to go out.

The concentrations to be used and their effectiveness must be assessed in the particular product and the fire test to be passed. In general, they have to be used at concentrations of several percent to be effective and as they are very expensive in comparison with bitumen their use is not widespread. Also, since many of these compounds are toxic and/or volatile, their incorporation into many products requires considerable plant modifications. However, in Scandinavia legislation is already in force which restricts the presence of naked flames on roof constructions, effectively limiting fixing of roofing felts to those processes which do not require the use of hot torches or gas burners. It is probable that future legislation will require roofing materials, carpet tiles, etc, to be self extinguishing. Only then will the use of fire retardant additives become widespread.

It should be noted that bitumen will only burn at temperatures above around 300°C. To reach this temperature there must already be a substantial fire burning on other structures.

12.6 Grinding of bitumen

Low penetration bitumens can be ground to produce a powder with a particle size below 500µm. The limit depends on the ambient temperature, but for temperate climates, the following generally applies:

Penetration at 25°C, dmm

greater than 10	not grindable
5 - 10	difficult
2 - 5	grindable
less than 2	easy

Penetration at 60°C, dmm

less than 15	no problems
greater than 15	may cause problems.

Caution

Dust explosions can occur during grinding of any combustible material, and appropriate precautions must be taken.

12.7 Permeability to water

Bitumen is not impermeable to water although any level of impermeability can be achieved by the application of a sufficiently thick coat. The water permeability coefficient of bitumen(1) is approximately 1.4×10^{-8} g/h/cm/mmHg. Softer grades are more permeable because of their lower viscosity.

12.8 Chemical composition

The chemical composition of bitumen is not exact and will vary according to crude source, method of manufacture and grade (see also chapter 4). Inorganic elements found in bitumens include 0, N, S, Na, K, Ca, V, and Ni.

12.9 Calorific value

The calorific value of bitumen will vary slightly according to grade but is approximately 41 MJ/kg.

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