Kirk-Othmer Encyclopedia of Chemical Technology.

ASPHALT

Asphalt [8052-42-4] is defined by the American Society for Testing and Materials (ASTM) (1) as a dark brown to black cementitious material in which the predominating constituents are bitumens that occur in nature or are obtained in petroleum processing. Bitumen is a generic term defined by ASTM as a class of black or dark-colored (solid, semisolid, or viscous) cementitious substances, natural or manufactured, composed principally of high molecular weight hydrocarbons, of which asphalts, tars, pitches, and asphaltites are typical.

Canadian and European practice (2–4) and geologists and archaeologists in the United States use bitumen or asphaltic bitumen as a synonym for asphalt, and apply asphalt to the mixture of bitumen and inorganic matter that is used for paving purposes. On the other hand, pitches and tars are derived from the destructive distillation of coal, crude oils, and other organic materials.

ASTM (1) further classifies asphalts or bituminous materials as solids, semisolids, or liquids. Semisolid and liquid asphalts predominate in commercial practice today. Prior to 1907, the principal portion of asphalt used occurred naturally; since that time most asphalts have been produced from the refining of petroleum. Air-blown petroleum asphalts (5) of diverse hardness became available in the early 1900s, and as their use increased, the demand for native products diminished.

More recently, asphalts have been defined as the manufactured materials that are produced during petroleum processing whereas bitumens have been defined as the naturally occurring materials (5, 6). That is, petroleum and related materials can be divided into various class subgroups:

Natural Materials	*Manufactured Materials*	*Derived Materials*
petroleum	wax	oils
heavy oil	residuum	resins
mineral wax	asphalt	asphaltenes
bitumen (native asphalt)	tar	carbenes
asphaltite	pitch	carboids
asphaltoid	coke	
migrabitumen	synthetic crude oil	
bituminous rock		
bituminous sand		
kerogen		
natural gas		

The term tar sands is a misnomer; tar is a product of coal processing. Oil sands is also a misnomer but equivalent to usage of “oil shale.” Bituminous sands is more correct; bitumen is a naturally occurring asphalt. Asphalt is a product of a refinery operation, usually made from a residuum. Residuum is the nonvolatile portion of petroleum and often further defined as atmospheric (bp $> 350^\circ$C) or vacuum (bp $> 565^\circ$C). For convenience, the terms “asphalt” and “bitumen” will be used interchangeably in this article.

Asphalts characteristically contain very high molecular weight molecular polar species, called asphaltenes, which are soluble in carbon disulfide, pyridine, aromatic hydrocarbons, chlorinated hydrocarbons, and tetrahydrofuran.

1. Naturally Occurring Materials

1.1. Native Asphalt (Bitumen)

Construction activities in ancient times depended on native asphalts (2, 3, 7–13). The product found on the surface of the Dead Sea may have been used by the Egyptians for mummification. In fact, the word mummy is thought to have derived from mumiia or Bitumen of Judea. Standard grades of bitumens apparently were known to the Sumerians; olive oil was used as the flux and fibers were added, if necessary, to prevent flow of the mixture. Clay-stabilized mastics were used as flooring and for waterproofing aprons. The presence of asphalt seepages signals a probable crude-oil reservoir. Several centuries later, mention is made of Trinidad asphalt by Raleigh during his visit to the island in 1595.

1.2. Lake Asphalt

Trinidad Lake asphalt was first reported used for paving in the United States about 1874 (14), and the use of the asphalt from Bermudez Lake in Venezuela soon followed. Trinidad asphalt (3, 7) exists in a number of deposits on the island of Trinidad, near the northeast coast of Venezuela. The largest deposit, and the one of chief commercial importance, is an asphalt lake occupying about 0.4 km^2 and of uniform composition to a depth of 87 m. As the bitumen is mined, the openings fill in, the level appears constant and an overturning movement of the lake from center to edge keeps the composition constant. This asphalt has been used for pavement constructions and other applications throughout the world.

Trinidad asphalt has a relatively uniform composition of 29% water and gas, 39% bitumen soluble in carbon disulfide, 27% mineral matter on ignition, and 5% bitumen that remains adsorbed on the mineral matter. Refining is essentially a process of dehydration by heating the crude asphalt to ca 165°C. The refined product averages 36% mineral ash with a penetration at 25°C of about 2 (0.2 mm), a softening point (ring and ball method) of 99°C, a flash point (Cleveland open cup) of 254°C, a sulfur content of 3.3%, and a saponification value of 45 mg KOH/g. The mineral matter typically contains particle sizes from 40% finer than 10 μm to 10% from the 30–75 μm range. Because of the influence of the fine mineral particles, many of them colloidal in size, the viscosity of Trinidad Lake asphalt is higher than that of normal bitumens.

Asphalt from Bermudez Lake (7) previously was exported in bulk in cargo vessels to the United States. In the early 1900s, it was used extensively for paving and waterproofing, but has not been available since the 1940s.

1.3. Rock Asphalt

Rock asphalt (15) deposits contain from 5–25% asphalt (Table 1). When extracted the asphalt varies from a soft-flux material to hard penetration. The mineral content, usually of a sandstone or limestone nature, has many gradations. Rock asphalt mixtures, ground and sized, are placed and rolled to form pavement surfaces. Some have superior antiskid properties in wearing surfaces, particularly the sandstone type. Rock asphalts are found in Texas, Alabama, Oklahoma, Colorado, California, and Kentucky. The composition of Kentucky asphalt is suitable for paving in its natural condition if selected at bitumen contents of 7–9% (16). Some of the well-known and long-used asphalt deposits of Europe (3, 7) are located at Seyssel, France; Ragusa in Sicily; Val-de-Travers, Switzerland; and Vorwohle, Germany.

Table 1. Typical Composition and Properties of Rock Asphalts

Property	Kentucky[a]	Oklahoma[b]	Alabama[c]	Texas[d]	Sicily[e]	Germany[f]
bitumen content, wt %	7–9	12.5	4.5	10–20	8–9	4.7–9.5
softening point (ring and ball), °C		28			38	30–36
penetration of 100 g at 25°C for 5 s, mm/10	too soft	over 360	15–25	4	too soft	soft
type of mineral	sand to sandstone	sand	oolitic limestone	limestone	marly limestone	limestone

[a] Crushed to fine size, less than 6.4 mm. Spread and rolled at temperatures above 15.6°C for pavements.
[b] Product blended from various deposits or sand added.
[c] Quarried, crushed, sized from 0.95 cm to dust and fluxed with softer asphalt for use as cold-applied pavement surfacing.
[d] Mixed with trap rock and asphalt flux to obtain mix for cold rolling as pavement surfacing.
[e] Selected grades ground and used for paving purposes.
[f] Enriched by adding asphalt and marketed for use as pavements or mastic.

Asphalt (bitumen) also occurs in various oil sand (also called tar sand) deposits which occur widely scattered through the world (17) and the bitumen is available by means of various extraction technologies. A review of the properties and character of the bitumen (18) suggests that, when used as an asphaltic binder, the bitumen compares favorably with specification-grade petroleum asphalts and may have superior aging characteristics and produce more water-resistant paving mixtures than the typical petroleum asphalts.

2. Manufactured Materials

Since the early 1900s most of the asphalts produced from the refining of petroleum have been used primarily in paving and roofing applications. The advent of motorized transportation led to increased asphalt manufacture from petroleum in order to provide binders for hard-surfaced pavements.

Petroleum asphalts, compared to native asphalts, are organic with only trace amounts of inorganic materials. They derive their characteristics from the nature of their crude origins with some variation possible by choice of manufacturing process. Although there are a number of refineries or refinery units whose prime function is to produce asphalt, petroleum asphalt is primarily a product of integrated refineries (Fig. 1). Crudes may be selected for these refineries for a variety of other product requirements and the asphalt (or residuum) produced may vary somewhat in characteristics from one refinery-crude system to another and even by cut-point (Table 2) and asphalt content (Fig. 2) (5, 6). The approximate asphalt yields (%) from various crude oils are as follows:

Nigerian light	7	L. A. Basin	44
Arabian light	14	California Valley	55
North Slope	21	California Coastal	65
Arabian heavy	31	Boscan	79

2.1. Straight Run Asphalt

In crude-oil refining, the crude oil at 340–400°C is injected into a fractionating column (5, 6, 19, 20). The lighter fractions are separated as overhead products and the residuum is straight-reduced asphalt.

Crude oil containing about 30% asphalt can be refined completely in an atmospheric unit to an asphalt product. However, most crude oil cannot be distilled satisfactorily to an asphalt product at atmospheric pressure

	Louisiana	Bachaquero
Gravity, API	13.1	2.8
Sulfur, wt %	0.9	3.7
Nitrogen, wt %	0.4	0.6
Carbon, wt %	15.8	27.5
Nickel, ppm	20	100
Vanadium, ppm	8	900
Pour point, °C		55

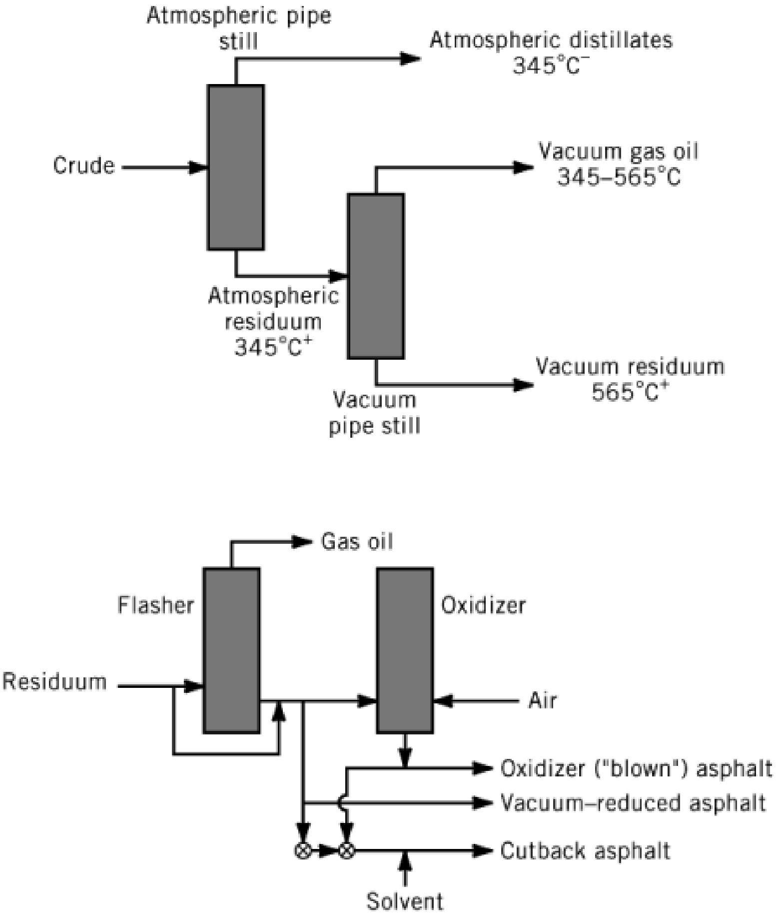

Fig. 1. Residua are obtained by removal of the volatile constituents of the feedstock at atmospheric pressure or at reduced pressure and can be converted to asphalt by various methods.

because of the presence of substantial proportions of high boiling gas oil fractions. Thus, as a supplement to the atmospheric process, a second fractionating tower (a vacuum tower) is added (Fig. 1).

This two-stage process is particularly applicable to crude oils containing 15–30% asphalt. Vacuum distillation units are continuous flow-through units and include a heating unit, the vapor–liquid flash separation zone, the fractionating zone, and the vacuum producing equipment. The heated feedstock is pumped into a flash zone where the more volatile constituents vaporize. The asphalt is the nonvolatile residual fraction which

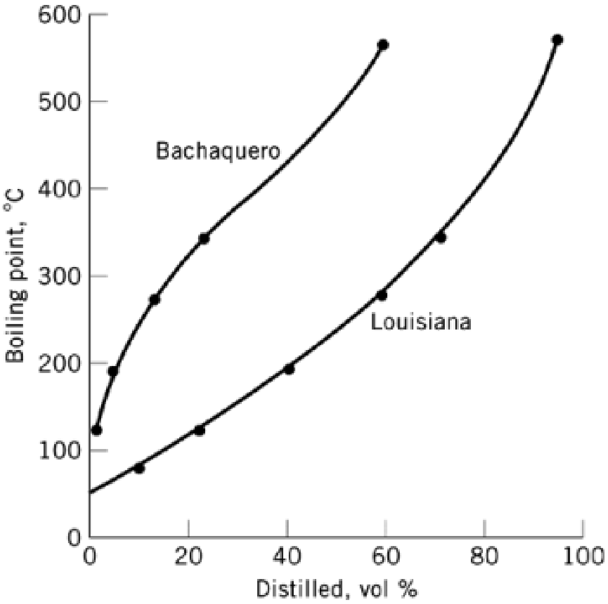

Fig. 2. Different crude oils contain different amounts of residua and the properties of specific "cut point" residua may be different, eg, for the 565°C residua:

is removed continuously. Manufacturing asphalt by straight reduction does not change the chemical nature of asphalt, other than its viscosity.

2.2. Propane Asphalt

As noted above, crude oils contain different quantities of residuum (Fig. 2) and, hence, asphalt. Asphalt is also a product of the propane deasphalting and fractionation process (5, 6, 21, 22) which involves the precipitation of asphalt from a residuum stock by treatment with propane under controlled conditions. The petroleum charge stock is usually atmospheric-reduced residue from a primary distillation tower.

Propane is usually used in this process although propane–butane mixtures and pentane have been used with some variation in process conditions and hardness of the product. Propane deasphalting is used primarily for crude oils of relatively low asphalt content, generally <15%. Asphalt produced from this process is normally blended with other asphaltic residua for making paving asphalt.

The process (Fig. 3) is a countercurrent liquid–liquid extraction. The feedstock is introduced near the top of an extraction tower and the liquid propane near the bottom, using solvent-to-oil ratios from 4:1 to 10:1. The deasphalted oil–propane solution is withdrawn overhead and the asphalt from the bottom, and each is subsequently stripped of propane.

Temperature, solvent ratio, and pressure each have an effect upon the split point or yield of the oil and asphalt components (Table 3). Contrary to straight reduction which is a high temperature and low pressure process, propane deasphalting is a low temperature and high pressure process.

There are small differences in the properties of asphalts prepared by propane deasphalting and those prepared by vacuum distillation from the same stock (Fig. 4). Propane deasphalting also has the ability to reduce a residuum even further and produce an asphalt product having a lower viscosity, higher ductility, and higher temperature susceptibility than other asphalts (23). However, such properties might be anticipated to be very much crude oil dependent. Propane deasphalting is conventionally applied to low asphalt-content

Table 2. Properties of Various Residua Produced from Tia Juana, Venezuela Light Crude Oil

Property	Values					
boiling range, °C	whole crude	>220	>295	>345	>400	>455	>505
yield on crude, vol %	100.0	70.2	57.4	48.9	39.7	31.2	17.9
gravity, API	31.6	22.5	19.4	17.3	15.1	12.6	7.1
specific gravity	0.8676	0.9188	0.9377	0.9509	0.9652	0.9820	1.0209
sulfur, wt %	1.08	1.42	1.64	1.78	1.93	2.12	2.59
carbon residue (Conradson), wt %		6.8	8.1	9.3	11.2	13.8	21.6
nitrogen, wt %				0.33	0.39	0.45	0.60
pour point, °C	−20	−9	−1	7	16	24	49
viscosity							
kinematic, mm^2/s(= cSt)							
38°C	10.2	83.0	315	890	3100		
99°C		9.6	19.6	35.0	77.0	220	7959
Furol (SFS), s							
50°C			70.6	172	528		
99°C					37.6	106	3760
Universal (SUS), s at 99°C		57.8	96.8	165	359	1025	
metals							
vanadium, ppm				185			450
nickel, ppm				25			64
iron, ppm				28			48

crudes, which are generally different in type and source from those processed by distillation of higher yield crudes.

2.3. Air-Blown Asphalt

Air-blowing is an exothermic process that is dependent upon several variable process parameters (24). In the process, an asphalt (flux) is converted to a harder product by air contact at 200–275°C. Dehydrogenation and polymerization are involved, and oxygen is not retained in the asphalt product except in a very minor amount (25). In theory, the oxygen in the air combines with the hydrogen in the asphalt to evolve water vapor. This leaves unsaturation for cross-linking. However, the chemistry may be much more complex than the simple theory predicts (24). For example, asphaltenes are produced during the air-blowing process (Table 4) and the evidence suggests that those constituent species of the asphalt which have higher proportions of heteroatoms (ie, nitrogen, oxygen, and sulfur) react preferentially with oxygen leaving less polar substances unreacted (26, 27). This also raises the specter of incompatibility of the resulting products. For example, if the more polar species, ie, the resins, are preferentially oxidized to produce more asphaltenes, then the means by which the asphaltenes are dispersed in the oily medium is removed. Incompatibility should be anticipated.

A variety of other substances can provide the same reaction: sulfur yields hydrogen sulfide; chlorine yields hydrogen chloride. In some cases, some of the bonds created are quite weak resulting in, after an induction period, a phenomenon termed "fallback." When fallback occurs, usually at a time when the hardened or oxidized asphalt is stored at or near the original processing or reaction temperature, softening of the asphalt is the result (28–31).

Air-blown asphalts, more resistant to weather and changes in temperature than the types mentioned previously are produced by batch and continuous methods. Air-blown asphalts, of diverse viscosities and

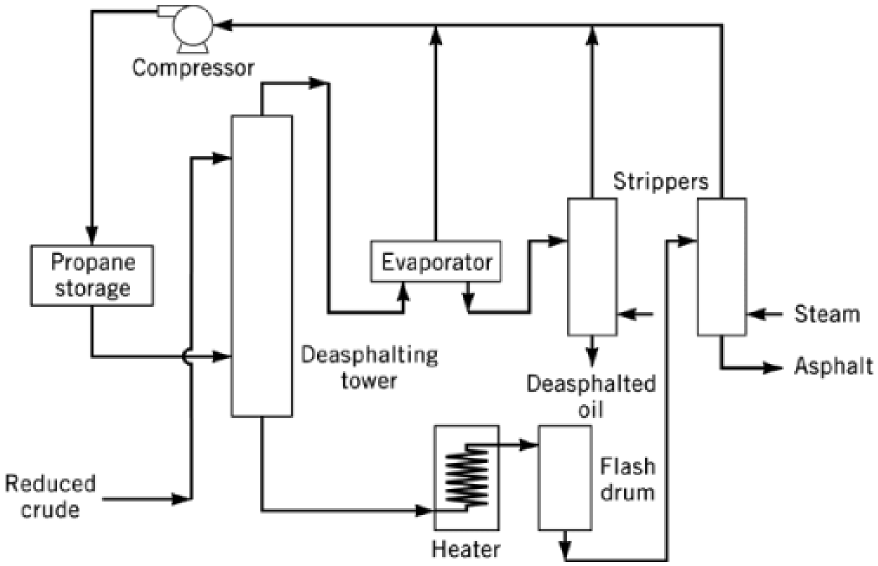

Fig. 3. Schematic representation of propane deasphalting and fractionation process.

flow properties with added fillers, polymers, solvents, and in water emulsions, provide products for many applications in the roofing industry.

2.3.1. Batch Process

In the batch process (Fig. 5), the feedstock is preheated in a tube furnace or heater placed between the feedstock storage and the blowing vessel. The air supply is provided by a variety of blowers or compressors and a vertical-tower vessel is preferable for air-blowing. Knockout drums, water scrubbers, incinerators, furnaces, and catalytic burning units have been used for fume disposal (32). Steam is used for safety and to ensure positive fume flow to the incinerator.

Temperature is the most important variable and preheating is generally necessary to 200–230°C. After air has been introduced, there is a gradual temperature rise because of the exothermic reaction, until some means is applied to hold the temperature such as a water or steam spray on the asphalt surface to maintain a temperature of approximately 260°C. The end point can be predicted by periodic testing of the softening point.

2.3.2. Continuous Process

Continuous air-blowing (Fig. 6) offers the following potential advantages: lower equipment and maintenance costs for the same production capacity; shorter blowing times with air-efficient equipment; less preheat capacity requirements; better control and operation; lower blowing losses; and lower operating labor requirement. It is particularly preferable when several principal products, such as coatings, saturants, and built-up roofing asphalts, can be processed from a single feedstock. When a comparison is made with a batch operation on the basis of the same daily capacity, the saving in blowing time is most apparent. Practical use of continuous air-blowing has been made in the manufacture of paving binders from soft vacuum residua and in the manufacture of roofing asphalts. Blends of intermediate grades from a harder air-blown asphalt product such as unfilled coating asphalt (100–115°C softening point) and a softer air-blown product such as roll saturant (40–45°C softening point) are often used.

Continuous oxidizers are usually operated at a constant temperature (260°C) and a constant liquid level with the production rate and product characteristics controlled by air rate and charging rate.

Table 3. Typical Yields and Characteristics of Products Obtained from the Propane Deasphalting Process

	Crude source				
Process	Pa.	Okla.	Ill.	Le Duc, Canada	Iraq
reduced crude					
gravity, °API[a]	25.1	19.3	13.7	12.1	7.1
kinematic viscosity at 98.9°C, mm^2/s (= cSt)	47.2	82.8	378	441	1050
Saybolt viscosity, s	220	385	1760	2050	4880
crude, vol %	24.0	26.1	11.3	15.2	16.4
deasphalted oil					
yield, vol %	83.7	75.6	50.7	47.1	34.1
gravity, °API[a]	26.6	23.6	23.4	22.7	20.2
kinematic viscosity at 98.9°C, (mm^2/s (= cSt))	30.4	29.8	40.7	42.6	38.2
Saybolt viscosity, s	144	141	190	199	179
precipitated asphalt					
yield, vol %	16.3	24.4	49.3	52.9	65.9
specific gravity at 15.6°C	0.953	1.023	1.030	1.054	1.064
softening point (ring and ball), °C		62.2	62.8	80	62.8
penetration of 100 g at 25°C for 5 s, mm/10		23	21	0	16
operating conditions					
throughput, kL/d[b]	800				
charge stock	reduced crude				
gravity charge, °API[a]	20.0				
temperature of deasphalting tower, °C	65				
solvent-to-oil ratio, by volume	6 : 1				
pressure, kPa[c]	2170(300)				

[a] API gravity at $15.6°\mathrm{C} = \frac{141.5}{\text{sp gr at } 15.6/15.6°\mathrm{C}} - 131.5$.

[b] To convert kL/d to barrels/d, multiply by 6.25.

[c] To convert kPa to psi, multiply by 0.145.

Table 4. Fractional Changes in Hardness of Asphalt[a] upon Air-Blowing

	Initial	Air-blown	Air-blown	Air-blown
Properties				
softening point (ring and ball), °C	54.4	85	96.1	173.3
penetration of 100 g at 25°C for 5 s, mm/10	36	13	9	1
Fractions, wt %				
asphaltenes (hexane insolubles)	14.8	26.9	31.4	51.3
hard resins	45.5	36.6	36.1	19.6
soft resins	25.0	22.3	20.9	16.9
oils	12.3	11.9	10.0	11.1
waxes	2.5	2.0	1.8	1.6
Total	*100.1*	*99.7*	*100.2*	*100.5*

[a] Straight-reduced Arkansas asphalt.

2.3.3. Catalytic Asphalt

The term catalytic asphalt has been accepted although this is not truly a catalytic process. The agents used are consumed in the reaction. The general effect is the reduction of blowing time as well as a change of the softening point–penetration relationship (33), which would normally be obtained from the same feedstock. Reduction of blowing time is an economic incentive, whereas the change in product properties permits manufacture to specifications not possible otherwise and the use of a wider variety of crude sources for flux.

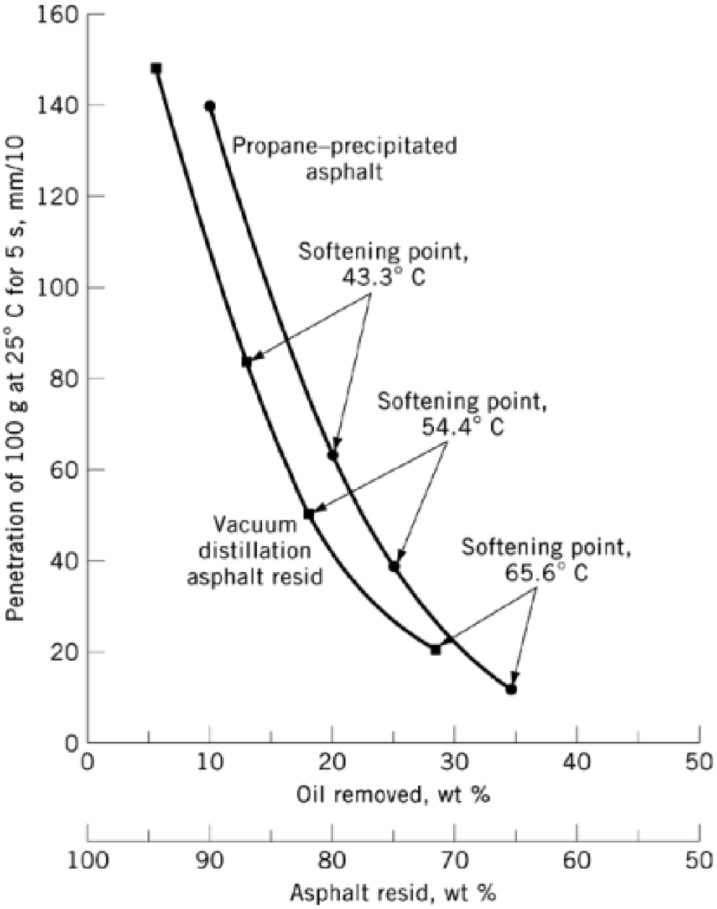

Fig. 4. Comparison of propane deasphalting with vacuum distillation of asphalt from Lagunillas, Venezuela crude.

Many agents have been proposed and patented including copper sulfate (34), zinc chloride (35), ferric chloride (36), aluminum chloride (36), and phosphorus pentoxide (37); ferric chloride, zinc chloride, and phosphorus pentoxide have been most widely used. The addition of these agents may vary from 0.1 to 3%, depending upon the feedstock and the desired characteristics of the product (Table 5) and all asphalt feedstocks do not respond to catalysts in the same way. Differences in feedstock composition are important qualifiers in determining the properties of the asphalt product. The important softening point-penetration relationship, which describes the temperature susceptibility of an asphalt, also varies with the source of the feedstock. Straight-reduced, air-blown, and air-blown catalytic asphalts from the same crude feedstock also vary considerably.

2.4. Thermal Asphalt

Thermal or cracked asphalts differ from other asphalts in that they are products of a cracking process. They have relatively high specific gravity, low viscosity, and high temperature susceptibility, and they contain cokelike bodies (carbenes) as indicated by the Oliensis test (38). Thermal asphalts have significant application as saturants for cellulosic building products such as insulation boards, brick-finish siding, and fiber soil pipes.

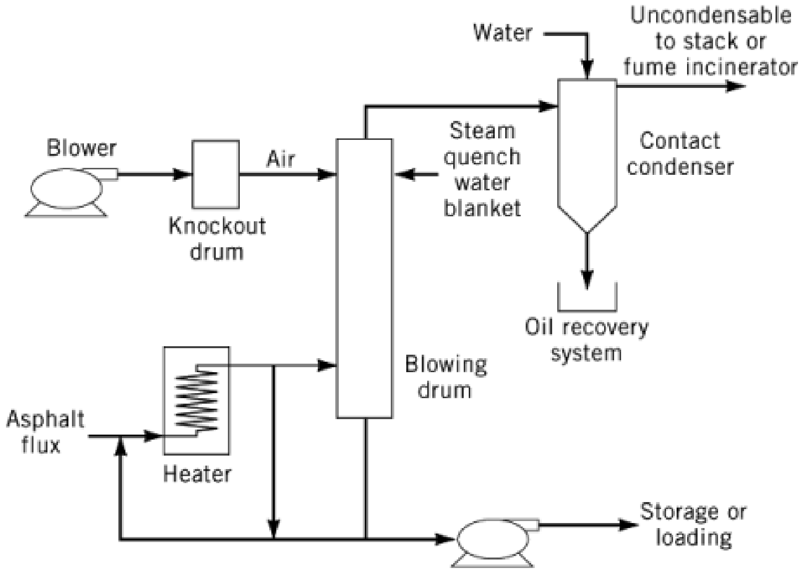

Fig. 5. Schematic representation of the batch process for air-blowing.

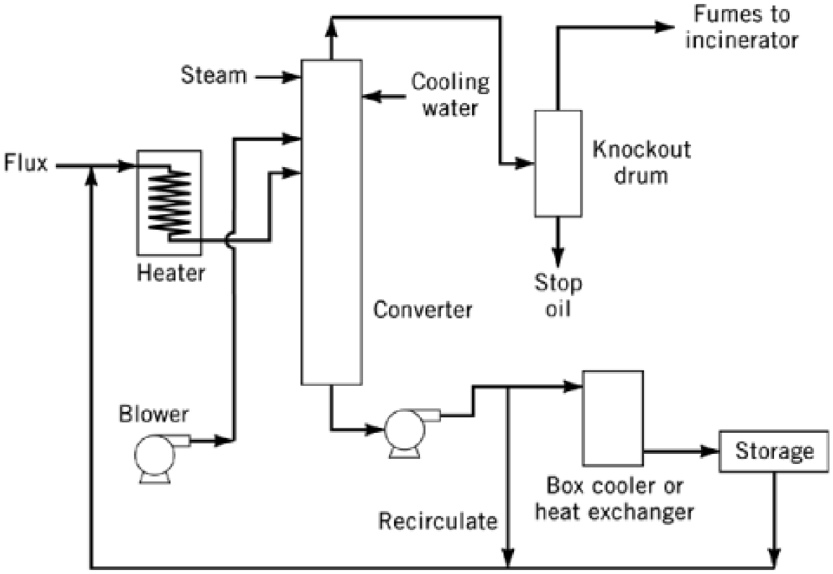

Fig. 6. Schematic representation of a continuous air-blowing process.

The thermal cracking process (Fig. 7) involves preheating of the charge to 480–600°C and then discharging into a reaction vessel or chamber under pressures up to 1480 kPa (200 psig). Cracking decomposition takes place to form both lighter and heavier products, including a certain amount of fixed carbon. Distillation is used to separate the overall products into gas, gasoline, middle distillate, and an asphaltic residuum.

Table 5. Air-Blowing of Fluxes With and Without Ferric Chloride and Phosphorus Pentoxide Catalysts

	California stock			Arkansas stock		
Property	No catalyst	0.8% $FeCl_3 \cdot 6H_2O$	0.5% P_2O_5	No catalyst	2.2% $FeCl_3 \cdot 6H_2O$	1.0% P_2O_5
blowing temperature, °C	221.1	221.1	221.1	254.4	237.8	237.8
blowing time, min	135	44	103	105	46	128
softening point[a], °C	87.8	86.1	86.1	86.7	83.3	87.8
penetration of 100 g at 25°C for 5 s, mm/10	27	51	53	27	62	59
penetration of 200 g at 0°C for 60 s, mm/10	13	30	28	15	38	38
penetration of 50 g at 46°C for 5 s, mm/10		74		48	109	110
ductility at 25°C, cm	3.5	3.4	4.8	3.3	3.9	5.3

[a] Ring and ball method.

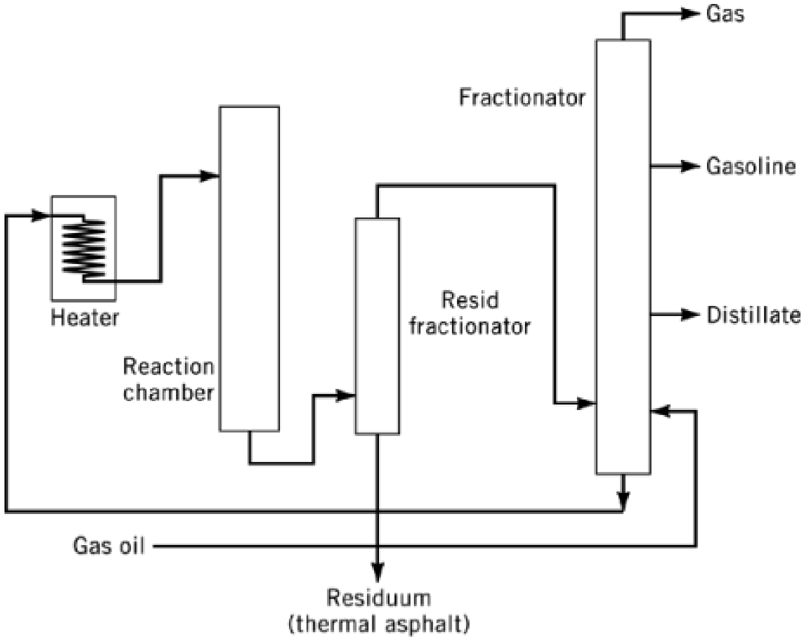

Fig. 7. Schematic representation of thermal cracking process.

2.5. Blended Asphalt

Any particular refinery may stock two grades of asphalt, one at each end of the viscosity spectrum of the entire product grade requirements. Intermediate grades are prepared by blending (proportioning) the extremes (39). The preparation of asphalts in liquid form by blending (cutting back) an asphalt with a petroleum distillate fraction is customary. There are three general types of cutback asphalt which differ mainly in the diluent used (Table 6). The slow-curing type is often called road oil, which is made by direct reduction, but most are commonly blended. The medium curing and rapid curing products usually have four grades within a given type and differ mainly in the amount of diluent used and in the kinematic viscosity of the blended product.

Table 6. Three Types of Liquid Asphalt Made by Cutting Back with Petroleum Diluents

Type asphalt	Diluent type	Diluent, %	Viscosity range[a], mm^2/s (= cSt)
slow curing (SC)	gas oil	0–50	70–6000
medium curing (MC)	kerosene	15–45	30–6000
rapid curing (RC)	naphtha	15–45	70–6000

[a] The liquid cutback asphalts are prepared in a number of viscosity grades, ranging generally from 70 to 6000. The grade number indicates the viscosity at 60°C.

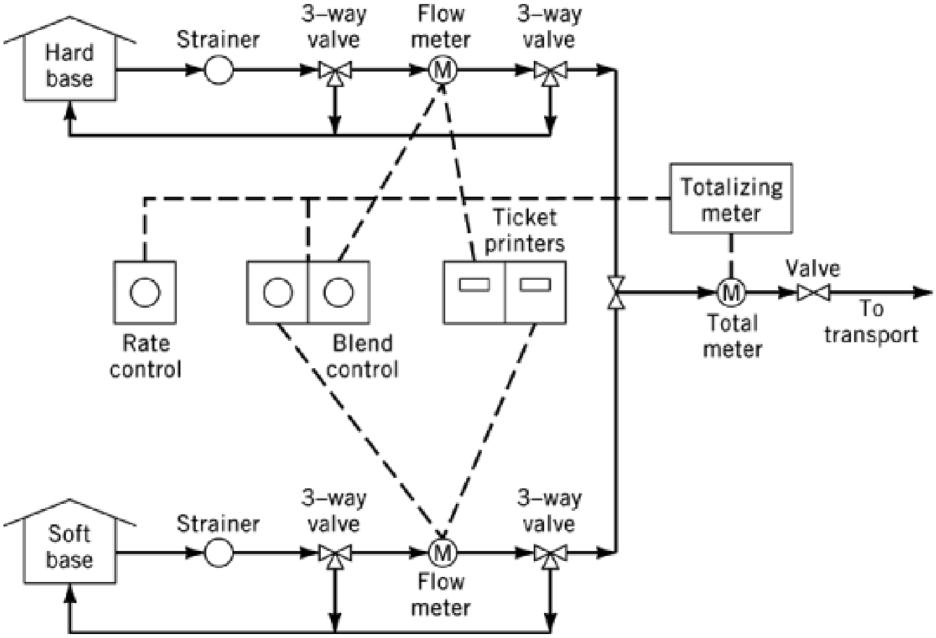

Fig. 8. Schematic representation of a continuous asphalt blender.

Preparation is accomplished by simple blending of the diluent into the hot base asphalt. This is generally accomplished in tanks equipped with coils for air agitation or with a mechanical stirrer or a vortex mixer. Line blending in a batch circulation system or in a continuous fashion (40) is used where the volume produced justifies the extra facilities. A continuous, line-blending system is applicable to the manufacture of cutback asphalts and asphalt cements (Fig. 8).

2.6. Asphalt Emulsions

An emulsion is one immiscible liquid dispersed in the other in the form of very fine droplets from about 1–25 μm and an average of 5 μm diameter. In the most common asphalt emulsion, the oil-in-water type, the asphalt is the dispersed (internal) phase, and water is the continuous (external) phase. Most of the important properties of an emulsion are dependent upon the amount and type of emulsifying agent used. The more popular cationic emulsions (41, 42) are made with cation-active agents which provide emulsion droplets with positive charges. The anionic agent is usually the sodium or potassium salt of a fatty acid (43). Nonionic cellulose derivatives are also used to increase the viscosity of the emulsion if needed. The acid number of asphalt is an indicator of its emulsifiability and reflects the presence of high molecular weight asphaltogenic or naphthenic acids. Diamines,

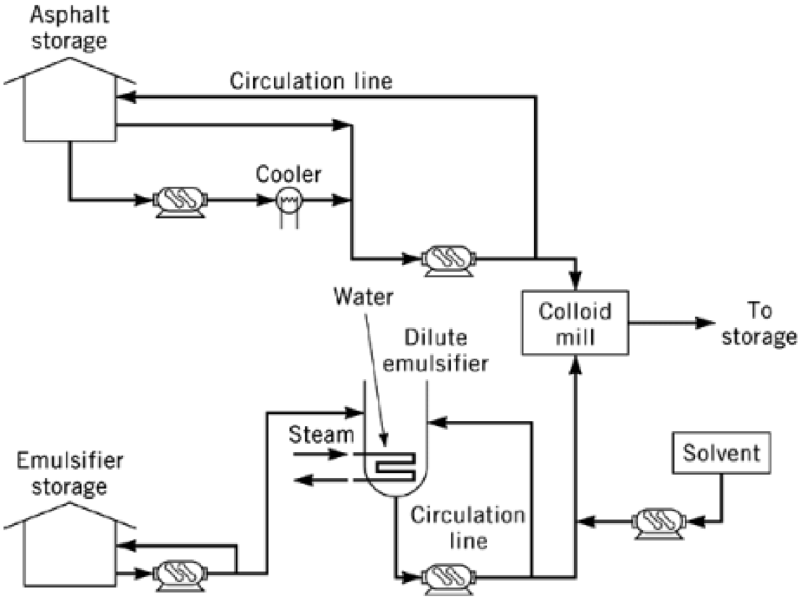

Fig. 9. Flow diagram of an asphalt emulsion plant.

frequently used as cationic agents, are made from the reaction of tallow acid amines with acrylonitrile, followed by hydrogenation.

Emulsion processes (Fig. 9) vary and the emulsions are made in rapid-, medium-, and slow-setting types for diverse application techniques in the road-building industry. Emulsions are most commonly formulated with rapid-setting properties and are designated as a spraying type, ie, for road seal-coating operations. Slow-setting emulsions are usually used for soil stabilization or in mulching applications.

Industrial emulsions have applications outside the road-building industry. They are made with harder grades of asphalt and contain clays, casein, gelatin, or blood albumin as peptizing agents. Certain clays, such as bentonite, are good emulsion dispersants and impart a buttery consistency to the emulsion. These emulsions have found a wide variety of applications, such as in surface coating of asphalt pavements, for built-up roofs, and for other weatherproof coverings.

3. Composition and Properties

Determination of the components of asphalts has always presented a challenge because of the complexity and high molecular weights of the molecular constituents (6, 44, 45). The principle behind composition studies is to evaluate asphalts in terms of composition and performance. Such studies are always suspect when this is not the overriding goal of the work.

The influence of the composition of asphalt has been recognized, for many years, as being an important factor in controlling the performance of such materials. Furthermore, rheological properties have always been associated with composition but, in order to utilize compositional data effectively, more definitive correlations between composition and properties are needed (46–48).

The methods employed can be conveniently arranged into a number of categories: (*1*) fractionation by precipitation; (*2*) fractionation by distillation; (*3*) separation by chromatographic techniques; (*4*) chemical analysis using spectrophotometric techniques (infrared, ultraviolet, nuclear magnetic resonance, x-ray fluorescence,

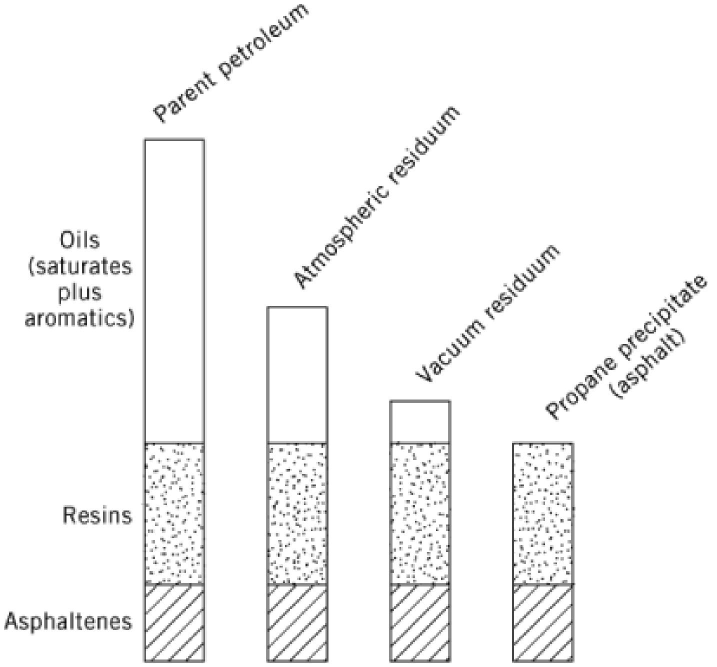

Fig. 10. The relationship between a crude oil, two residua from the crude oil, and the propane asphalt.

emission, neutron activation), titrimetric and gravimetric techniques, elemental analysis; (*5*) molecular weight analysis by mass spectrometry, vapor pressure osmometry, and size-exclusion chromatography.

However, for the past 30 years fractional separation has been the basis for most asphalt composition analysis (Fig. 10). The separation methods that have been used divide asphalt into operationally defined fractions. Four types of asphalt separation procedures are now in use: (*1*) chemical precipitation in which *n*-pentane separation of asphaltenes is followed by chemical precipitation of other fractions with sulfuric acid of increasing concentration (ASTM D2006); (*2*) solvent fractionation: separation of an “asphaltene” fraction by the use of 1-butanol followed by dissolution of the 1-butanol solubles in acetone. The acetone solution is chilled, forcing the precipitation of paraffinics from the cold acetone-soluble cyclics; (*3*) adsorption chromatography using a clay–gel procedure where, after removal of the asphaltenes, the remaining constituents are separated by selective adsorption–desorption on an adsorbent (ASTM D2007 and D4124); (*4*) size-exclusion chromatography in which gel-permeation chromatographic (gpc) separation of asphalt constituents occurs based on their associated sizes in dilute solutions (ASTM D3593).

The fractions obtained in these schemes are defined operationally or procedurally. The amount and type of asphaltenes in an asphalt are, for instance, defined by the solvent used for precipitating them. Fractional separation of asphalt does not provide well-defined chemical components. The materials separated should only be defined in terms of the particular test procedure.

The component of highest carbon content is the fraction termed carboids and consists of species that are insoluble in carbon disulfide or in pyridine (5, 6, 49). The fraction that has been called carbenes contains molecular species that are soluble in carbon disulfide and soluble in pyridine but which are insoluble in carbon tetrachloride and in benzene (Fig. 11) (5, 6, 49).

Asphaltenes seem to be relatively constant in composition in residual asphalts, despite the source, as determined by elemental analysis (6). Determination of asphaltenes is relatively standard, and the fractions

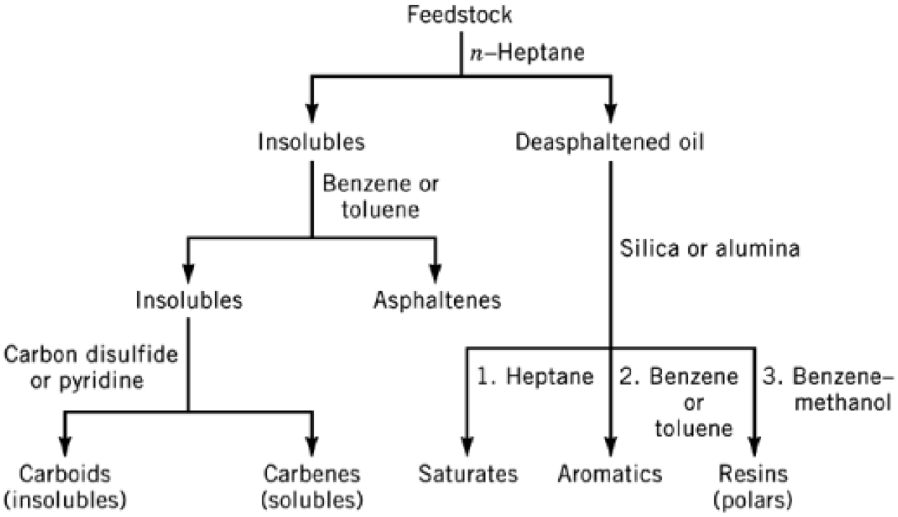

Fig. 11. Simplified representation of the separation of petroleum into six principal fractions.

are termed *n*-pentane, *n*-hexane, *n*-heptane, or naphtha-insoluble, depending upon the precipitant used (5, 6, 49). After the asphaltenes are removed, resinous fractions are removed from the maltenes-petrolenes usually by adsorption on activated gels or clays. Recovery of the resin fraction by desorbtion is usually nearly quantitative.

The forerunner of the modern methods of asphalt fractionation was first described in 1916 (50) and the procedure was later modified by use of fuller's earth (attapulgite [1337-76-4]) to remove the resinous components (51). Further modifications and preferences led to the development of a variety of fractionation methods (52–58). Thus, because of the nature and varieties of fractions possible and the large number of precipitants or adsorbents, a great number of methods can be devised to determine the composition of asphalts (5, 6, 44, 45). Fractions have also been separated by thermal diffusion (59), by dialysis (60), by electrolytic methods (61), and by repeated solvent fractionations (62, 63).

The composition data should always be applied to in-service performance (64, 65) in order to properly evaluate the behavior of the asphaltic binder under true working conditions.

3.1. Colloidal State

The principal outcome of many of the composition studies has been the delineation of the asphalt system as a colloidal system at ambient or normal service conditions. This particular concept was proposed in 1924 and described the system as an oil medium in which the asphaltene fraction was dispersed. The transition from a colloid to a Newtonian liquid is dependent on temperature, hardness, shear rate, chemical nature, etc. At normal service temperatures asphalt is viscoelastic, and viscous at higher temperatures. The disperse phase is a micelle composed of the molecular species that make up the asphaltenes and the higher molecular weight aromatic components of the petrolenes or the maltenes (ie, the nonasphaltene components). Complete peptization of the micelle seems probable if the system contains sufficient aromatic constituents, in relation to the concentration of asphaltenes, to allow the asphaltenes to remain in the dispersed phase.

Many attempts have been made to characterize the stability of the colloidal state of asphalt at ordinary temperature on the basis of chemical analysis in generic groups. For example, a colloidal instability index has been defined as the ratio of the sum of the amounts in asphaltenes and flocculants (saturated oils) to the sum of the amounts in peptizers (resins) and solvents (aromatic oils) (66):

$$I_c = \frac{(\text{asphaltenes} + \text{saturated oils})}{(\text{resins} + \text{aromatic oils})}$$

As this ratio increases so does the gel character of the asphalt cement, and its colloidal stability increases. The properties of the asphalt (softening point, ductility, embrittlement temperature, thermal susceptibility, elastic recovery, shearing susceptibility, etc) vary significantly with the colloidal instability index and hence with composition.

Many investigations of relationships between composition and properties take into account only the concentration of the asphaltenes, independently of any quality criterion. However, a distinction should be made between the asphaltenes which occur in straight run asphalts and those which occur in blown asphalts. Remembering that asphaltenes are a solubility class rather than a distinct chemical class means that vast differences occur in the make-up of this fraction when it is produced by different processes.

3.2. Elemental Analysis

Asphalt is not composed of a single chemical species, but is rather a complex mixture of organic molecules that vary widely in composition from nonpolar, saturated hydrocarbons to highly polar, highly condensed aromatic ring systems. Although asphalt molecules are composed predominantly of carbon and hydrogen, most molecules contain one or more of the heteroatoms nitrogen, sulfur, and oxygen, together with trace amounts of metals, principally vanadium and nickel. The heteroatoms, although a minor component compared to the hydrocarbon moiety, can vary in concentration over a wide range depending on the source of the asphalt. Because the heteroatoms often impart functionality and polarity to the molecules, their presence may make a disproportionately large contribution to the differences in physical properties among asphalts from different sources.

Generally, most asphalts are 79–88 wt % C, 7–13 wt % H, trace-8 wt % S, 2–8 wt % O, and trace-3 wt % N (Table 7). Trace metals such as iron, nickel, vanadium, calcium, titanium, magnesium, sodium, cobalt, copper, tin, and zinc, occur in crude oils. Vanadium and nickel are bound in organic complexes and, by virtue of the concentration (distillation) process by which asphalt is manufactured, are also found in asphalt.

Table 7. Elemental Analyses of Representative Petroleum Asphalts

Code source	B-2959 Mexican Blend	B-3036 Arkansas–Louisiana	B-3051 Boscan	B-3602 California
carbon, %	83.77	85.78	82.90	86.77
hydrogen, %	9.91	10.19	10.45	10.94
nitrogen, %	0.28	0.26	0.78	1.10
sulfur, %	5.25	3.41	5.43	0.99
oxygen, %	0.77	0.36	0.29	0.20
vandium, ppm	180	7	1380	4
nickel,ppm	22	0.4	109	6

Asphalt typically contains oxygen (<2%), nitrogen (<2%), and sulfur (<7%), as can be measured by many methods of elemental analysis. The heteroatom content tends to increase with increasing boiling point within an asphalt residue. The heteroatom content of a typical asphalt is significant, especially when considered on the molecular level. For example, if the mean molecular mass of the asphaltene fraction is 1000, then one heteroatom per molecule in the asphaltene would require the following proportions of heteroatoms: sulfur 3.2%, nitrogen 1.4%, and oxygen 1.6%. Such concentrations of heteroatoms are commonly found in whole asphalts and are typically exceeded in the asphaltene fractions. The heteroatom content seems to vary more than the hydrogen:carbon (H:C) ratio of the asphaltene fraction from different crudes (5, 6).

Techniques are available for quantitative identification of the six principal types of heteroatom compounds in asphalt: carboxylic acids, 2-quinolones, phenols, pyrroles, amides, and pyridines (67).

Many investigators have also measured the trace metal content of asphalts (68). The catalytic behavior of vanadium has prompted studies of the relation between vanadium content and an asphalt's sensitivity to oxidation (viscosity ratio). The significance of metals in the behavior of asphalts is not yet well understood or defined.

3.3. Molecular Weight

The molecular weights of the individual fractions of asphalt have received more attention, and have been considered to be of greater importance, than the molecular weight of the asphalt itself. Asphaltenes display a wide range of molecular weights, from 500 to at least 2500, depending upon the method of measurement. Asphaltenes associate in dilute solution in nonpolar solvents (69) giving higher molecular weights than is actually the case on an individual molecule basis. The molecular weights of the resins are somewhat lower than those of the asphaltenes and usually fall within the range 500 to 1000 (70). This is not only because of the absence of association but also because of a lower absolute molecular size. The molecular weights of the oil fractions (ie, the asphalt minus the asphaltenes and minus the resins) is usually less than 500, often 300 to 400.

3.4. Acid Number

Asphalt contains a small amount of organic acids and saponifiable material and the acid values of asphalt, 0.1–2.8 mg potassium hydroxide per gram of asphalt, are related to emulsification conditions and ease of dispersion. The acid content is largely determined by the percentage of naphthenic (cycloparaffinic) acids of higher molecular weight that are originally present in the crude oil. With increased hardness, asphalt from a particular crude oil normally decreases in acid number as more of the naphthenic acids are removed during the distillation process.

3.5. Rheology

Asphalt is a viscoelastic material whose rheological properties reflect crude type and, to a lesser extent, processing. The ability of the asphalt to perform under many conditions depends on flow behavior (71, 72). Asphalt films or coatings showing no appreciable change from original conditions are usually desired, ie, they should allow some structural movement without permanent deformation. Some procedures for measuring viscoelastic properties of asphalt have been described (2, 73–75). Liquid asphalts, in effect, substitute diluent (or water emulsification) for heat to allow pumping, spraying, or application of the material at lower temperature.

The viscosity of hydrocarbons and temperature are related by the Walther equation (76):

$$\log\log(100\eta_0) = a - m\log T$$

where η_0 is the limiting viscosity at low shear rates, T is the absolute temperature, a and m are constants reflecting the intercept level and slope (or measure of susceptibility of viscosity to temperature, respectively). On the other, hand, the general relationship for viscosity, temperature, and shear rate is

$$\log\log 100\eta_0\left(1 \times CD^N\right) = a - m\log T$$

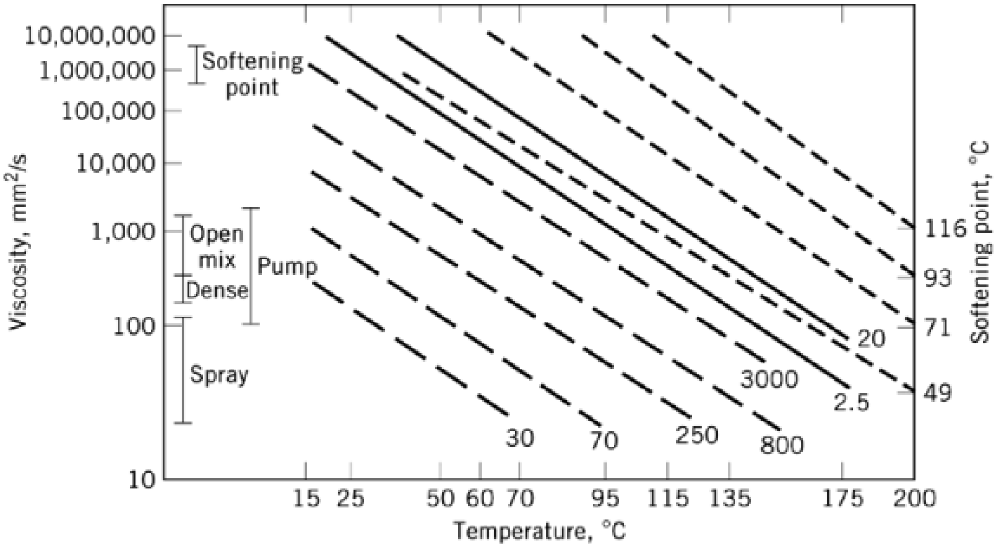

Fig. 12. A viscosity-temperature chart, $mm^2/s=cSt$; – – –, industrial asphalts;— —cutback asphalts; ___ paving asphalts.

where D is shear rate; C is a function of limiting viscosity, limiting slope, and other constants; and N is the limiting slope.

Typical profiles for the different general families of asphalts (cutbacks or liquid materials, paving asphalt cements and the harder roofing and industrial materials which are usually graded by softening point) can be generated by the use of the equation (Fig. 12). At lower temperatures (60°C and lower) and/or higher shear rates, which are typical of asphalt service conditions after incorporation in a roof or pavement, semisolid and solid asphalts display an increasing elastic component which relates viscosity with shear rate (73, 77, 78). The constant high viscosity at lower shear rates is the limiting viscosity. Viscosities in the area where viscosity changes with shear rate are generally termed apparent viscosities.

Curves for the viscosity data, when displayed as a function of shear rate with temperature, show the same general shape with limiting viscosities at low shear rates and limiting slopes at high shear rates. These curves can be combined in a single master curve (for each asphalt) employing vertical and horizontal shift factors (77–79). Such data relate reduced viscosity (from the vertical shift) and reduced shear rate (from the horizontal shift).

A number of viscometers have been developed for securing viscosity data at temperatures as low as 0°C (58, 59). The most popular instruments in current use are the cone plate (ASTM D3205), parallel plate, and capillary instruments (ASTM D2171 and ASTM D2170). The cone plate can be used for the determination of viscosities in the range of 10 to over $10^9 Pa{\cdot}s$ (10^{10} P) at temperatures of 0–70°C and at shear rates from 10^{-3} to $10^2\ s^{-1}$. Capillary viscometers are commonly used for the determination of viscosities at 60–135°C.

Tests developed for measurement of viscoelastic properties are directly usable in engineering relations. Properties can be related to the inherent structure of bituminous materials. The fraction of highest molecular weight, the asphaltenes, is dispersed within the asphalt and is dependent upon the content and nature of the resin and oil fractions. Higher aromaticity of the oil fractions or higher temperatures leads to viscous (sol) conditions. A more elastic (gel) condition results from a more paraffinic nature and is indicated by large elastic moduli or, empirically, by a relatively high penetration at a given softening point. Empirically, the penetration index PI(2)and penetration temperature susceptibility PTS3.5 have been used to measure the degree of dispersion.

$$PI = \frac{30}{1 + 90 \times PTS} - 10$$

$$PTS = \frac{\log 800 - \log \text{penetration at } 25^\circ\text{C, 100 g, 5 s}}{(\text{softening point, ring and ball,}^\circ\text{C}) - 25^\circ\text{C}}$$

This equation is based on the approximation that the penetration is 800 at the softening point, but the approximation fails appreciably when a complex flow is present (80, 81). However, the penetration index has been, and continues to be, used for the general characteristics of asphalt; for example asphalts with a PI less than -2 are considered to be the pitch type, from -2 to $+2$, the sol type, and above $+2$, the gel or blown type (2). Other empirical relations that have been used to express the rheological-temperature relation are fluidity factor; a Furol viscosity V, at 135°C and penetration P, at 25°C, relation of $(V–P)P/100$; and penetration viscosity number PVN again relating the penetration at 25°C and kinematic viscosity at 135°C (82, 83).

Asphalts develop an internal structure with age, steric hardening (3), in which viscosity can increase upon aging without any loss of volatile material (73, 83). Those with a particularly high degree of gel structure exhibit thixotropy.

3.6. Durability

The term “durable” has several meanings, but in the present context it is used to describe an asphalt that possesses the necessary chemical and physical properties required for the specified pavement performance, being resistant to change during the in-service conditions that are prevalent during the life of the pavement.

Asphalts are used as protective films, adhesives, and binders because of their waterproof and weather-resistant properties. One particularly valuable property, the ability of the asphalt to undergo movement without fracture, can occur because of the viscous (sol) nature. In addition, asphalts have long and continuous satisfactory service because of their slow rate of hardening from heat, oxidation, fatigue, and weathering (84–87). Exposed asphalt films harden partially from a loss of volatile oils and to a greater extent from the formation of additional asphaltene material, with the concurrent loss of petrolene-maltene constituents through oxidation. Such chemical change undoubtedly is catalyzed by uv irradiation (86–90). The oxidation may form water-soluble degradation products which are removed from the asphalt film (89, 90), but the conversion of the petrolene–maltene constituents to lower molecular weight asphaltene material (27) cannot be ignored.

Failure of an asphalt film is reflected in the appearance of typical crack patterns because of a decrease in the plasticity of the asphalt through insufficient lower molecular weight constituents remaining in the continuous phase. Other manifestations of failure are loosening of the bond, such as loosening of granules in roofing shingles to actual loss of the film, or the binder in pavement mixtures might become friable and crack. A stiffer asphalt, under uniform loading conditions, could reduce pavement deflection, extend fatigue life, and allow less flow deformation. A softer material would normally allow a longer weathering life before the maltene–asphaltene composition becomes critical in service. Usually the softest material allowed by initial service needs is selected.

The water resistance of asphalt films is also a manifestation of durability. Asphalts that have a low content of soluble salts show a low water absorption. The pickup of water is primarily a surface phenomenon that causes the film to soften leading to blistering. Even with a high rate of absorption, asphalt films show little loss of bond to surfaces on continued immersion in water, and continue to protect metals from corrosion for long periods of time. Bacteria and fungi can attack the very low molecular weight portion of bituminous materials. However, deterioration of the harder bituminous films as a result of such agents seems insignificant (91, 92).

Mineral fillers are often added to asphalts to influence their flow properties, reduce costs, and are commonly used as stabilizers in roofing coatings at concentrations up to 60 wt % (93). Mineral-filled films show improved resistance to flow at elevated temperatures, improved impact resistance, and better flame-spread resistance. Fillers may increase the water absorption of asphalts. Fillers commonly used are ground limestone, slate flours, finely divided silicas, trap rocks, and mica; they are often produced as by-products in rock-crushing operations. Opaque fillers offer protection from weathering. Asbestos (qv) filler has special properties because of its fibrous structure, high resistance to flow, and toughness. It has been used in asphalt paving mixes to increase the resistance to movement under traffic (94) and in roofing materials for fire-retardant purposes.

4. Specifications and Tests

In 1903 an American Society for Testing and Materials (ASTM) Committee on Road and Paving Materials was formed to develop test methods and specifications for highway materials. Test methods for volatilization, penetration, and bitumen were developed by the Office of Public Roads and were adopted by ASTM in 1911.

In the volatilization test, a 20-g sample was heated for 5 h at 163°C in a tin box 6 cm in diameter and 2 cm deep. The loss in weight was determined and the consistency of the residue was an optional requirement of that time. To provide a greater depth of sample the method was revised to use a 50-g sample and a tin box 5.5 cm in diameter and 3.5 cm deep.

For the asphalt cements produced at that time the adoption of the volatilization and penetration tests provided some degree of control of excessive changes during plant mixing that might be reflected in more durable asphalts. The adoption of the method for bitumen was intended to provide a means for identifying Trinidad asphalt by observing the amount and color of the insoluble ash.

During the 1920s the following three national specifications for asphalt cements were published: (*1*) Federal specifications, adopted in 1925; (*2*) the American Association of State Highway Transportation Officials (AASHTO) specifications, adopted in 1924, revised in 1926; and (*3*) ASTM specifications, adopted in 1922 to 1926, withdrawn in 1939, and re-issued in 1947.

The Federal specifications stipulated that only those asphalts that had been demonstrated by service tests as satisfactory for the intended use would be accepted. The specifications also indicated the type and location of construction and the relative amount of traffic for each of the grades. The AASHTO specifications indicated that the use of each grade depended on the type of road, climate, and traffic. The ASTM suggested the type of construction for which each grade would be used.

With minor exceptions the requirements for the physical and chemical properties of asphalt were essentially the same for the three national specifications and included: penetration and ductility at 25°C; flash point; % loss at 163°C; penetration of residue as a % of original; solubility in carbon disulfide; solubility in carbon tetrachloride; specific gravity at 25°C; and softening point.

Remembering that the properties of residua vary with cut-point (Table 2), ie, the vol % of the crude oil (Fig. 13) helps the refiner produce asphalt of a specific type or property. There are several properties that are usually controlled in asphalt specifications:

Asphalts are usually specified in several grades for the same industry, differing in hardness or viscosity (95). However, with the changing nature and composition of crude oil feedstocks over the past two decades, performance and supply factors are also an important consideration (95).

Specifications for paving asphalt cements usually include five grades differing in either viscosity or penetration level at 60°C (Table 8) (ASTM D496). Susceptibility of viscosity to temperature is usually controlled in asphalt cement by viscosity limits at a higher temperature such as 135°C and a penetration or viscosity limit at a lower temperature such as 25°C.

Paving cutbacks are also graded at 60°C by viscosity, with usually four to five grades of each type. For asphalt cements, the newer viscosity grade designation is the midpoint of the viscosity range. The cutback's

Property	*Test*
safety	flash point
purity	solubility, ash, water content
composition	naphtha insolubles, various separation techniques, distillation tests, homogeneity, wax content
rheology	penetration, viscosity, softening point, float, ductility, flow, impact or shock, break point, temperature susceptibility ratios
durability	thin-film oven, aging index, weathering
density or specific gravity	specific gravity
special properties	bond or adhesion, compatibility, stain, storage stability, chemical resistance, etc

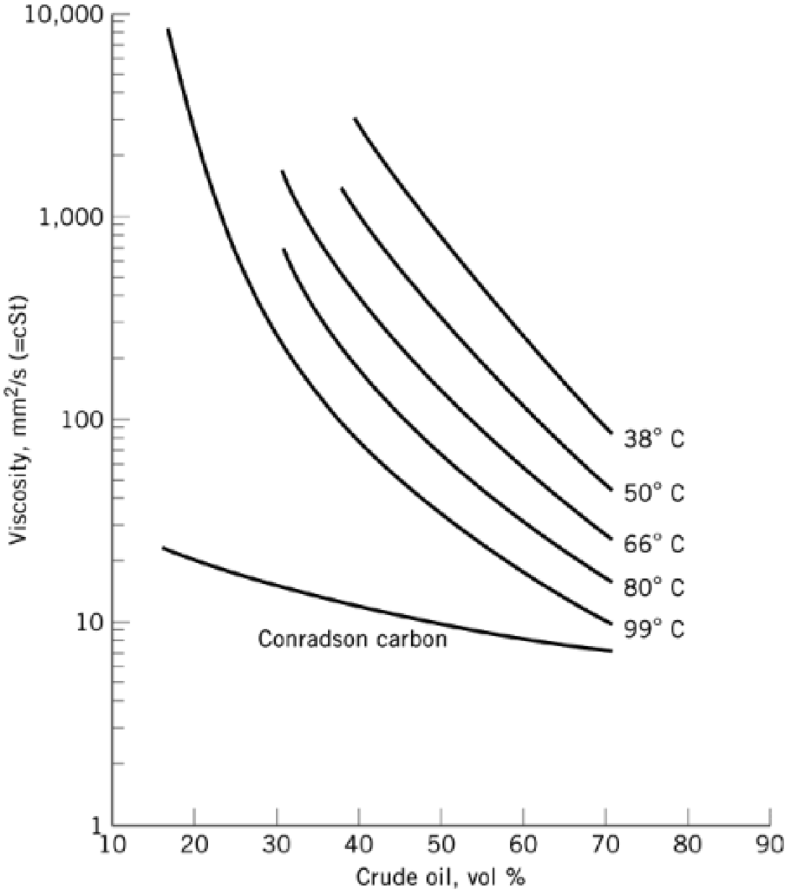

Fig. 13. Relation of physical properties to the yield of residuum from Tia Juana, Venezuela light crude oil.

grade designation is the minimum kinematic viscosity for the grade, with a maximum grade viscosity of twice the minimum.

Roofing and industrial asphalts are also generally specified in various hardnesses usually with a combination of softening point and penetration to distinguish grades. Asphalts for roof construction are specified in ASTM D312 grades and asphalts for damp-proofing and waterproofing in ASTM D449. Temperature susceptibility is usually controlled in these requirements by specifying penetration limits or ranges at 25°C and other

Table 8. ASTM Requirements for Asphalt Cement Viscosity

	Viscosity grade[b]				
Tests on residue from rolling thin-film oven test[a]	AR-1000	AR-2000	AR-4000	AR-8000	AR-16000
viscosity, 60°C, Pa·s[c]	100 ± 25	200 ± 50	400 ± 100	800 ± 200	1600 ± 400
viscosity, 135°C, min, mm^2/s (= cSt)	140	200	275	400	550
penetration of 100 g at 25°C for 5 s, min, mm/10	65	40	25	20	20
original penetration at 25°C, min %		40	45	50	52
ductility, 25°C, 5 cm/min, min, cm	100[d]	100[d]	75	75	75
tests on original asphalt: flash point, Pensky-Martens closed tester, min, °C	205	219	227	232	238
solubility in trichloroethylene, min %	99.0	99.0	99.0	99.0	99.0

[a] Thin-film oven test may be used but the rolling thin-film oven test shall be the referee method.

[b] Grading based on residue from rolling thin-film oven test.

[c] To convert Pa·s to P, multiply by 10.

[d] If ductility is less than 100, material will be accepted if ductility at 15.5°C is 100 minimum at a rate of 5 cm/min.

temperatures as well as softening point ranges at higher temperatures. The ASTM D312 asphalts for built-up roof constructions are differentiated according to application depending primarily on pitch of the roof and to some extent on whether or not mineral surfacing aggregates are specified. The damp-proofing grades reflect above or below grade construction, primarily, and whether or not a self-healing property is incorporated.

4.1. Test Procedures

Most tests applied to petroleum asphalts are empirical in nature (45). The ASTM tests are not the only ones applied to asphalt testing. Private tests of a propriety nature have been used within companies. Some of these tests are now being made public and occur from time to time in literature reports. Such tests may become a part of the ASTM standards.

The significance of a particular test is not always apparent by reading the procedure, and sometimes can only be gained through working familiarity with the test (96). The following tests are commonly used to characterize asphalts.

4.1.1. Bitumen Insoluble in Paraffin Naphtha (AASHTO T46)

This test designated by the American Association of State Highway and Transportation Officials (AASHTO) is used to indicate the content of naphtha-insoluble asphaltenes in an asphalt. Other solvents such as n-heptane (ASTM D3279), n-hexane, and n-pentane have been substituted for the naphtha solvent.

4.1.2. Bitumen Soluble in Carbon Disulfide (ASTM D4)

Asphalt is defined as a mixture of hydrocarbons that are completely soluble in carbon disulfide. Trichloroethylene or 1,1,1-trichloroethane have been used in recent years as safer solvents for this purpose. The procedure for these and other solvents for asphalt with little or no mineral matter are described in ASTM D2042.

4.1.3. Breaking Point (FRAAS, IP 80/53)

This test of the Institute of Petroleum is an approximate indication of the temperature at which an asphalt possesses no ductility and would reflect brittle fracture conditions.

4.1.4. Bond and Adhesion (ASTM D1191)

This test, designed for use on crack and joint sealers, is used primarily to determine whether a jointing material possesses an arbitrary amount of bonding strength at low temperatures where portland cement concrete is being used.

4.1.5. Compatibility (ASTM D1370)

When a coating asphalt and a saturating-grade asphalt are used together, as in prepared roofing, this test indicates whether they are likely to bleed, show strike-through, or disbond under stress at the coating felt interface.

4.1.6. Distillation (ASTM D402)

Approximate amounts of volatile constituents are determined by this test which is particularly applicable to cutback asphalt and road oils.

4.1.7. Ductility (ASTM D113)

The ductility of an asphalt is expressed as the distance in cm which a standard briquet can be elongated before breaking. Ductility is a combination of flow properties and reflects both cohesion and shear susceptibility.

4.1.8. Emulsified Asphalts (ASTM D244)

This standard covers a variety of tests for the composition, handling, nature and classification, storage, use, and specifying of asphalt emulsions used primarily for paving purposes.

4.1.9. Flash Point (ASTM D92)

The Cleveland open cup method is most commonly used although the Tag open cup (ASTM D3143) is applicable to cutbacks. Flash point is an indication of fire hazard and the test is frequently used to indicate whether a given product has been contaminated with materials of lower flash point.

4.1.10. Float Test (ASTM D139)

The consistency properties of an asphalt at a very low applied force are indicated by this test. The test is normally used for those asphalts that are too soft for the penetration test.

4.1.11. Homogeneity

Visual tests for homogeneity are generally used to judge uniformity.

4.1.12. Penetration (ASTM D5)

This is a commonly used consistency test. It involves the determination of the extent to which a standard needle penetrates a properly prepared sample of asphalt under definitely specified conditions of temperature, load, and time. The distance that the needle penetrates in units of mm/10 measured from 0 to 300, is the penetration value. Soft asphalts have high penetration values.

4.1.13. Sampling (ASTM D140)

This standard provides guidance for the sampling of asphalts, liquid and semisolid, at point of manufacture, storage, or delivery.

4.1.14. Softening Point (Ring and Ball Method, ASTM D36)

The softening point of an asphalt may be defined as that temperature at which an asphalt attains a particular degree of softness under specified conditions of test. It is commonly used to classify industrial and roofing asphalt grades. A method (ASTM D2398) has been developed to provide a single bath medium for the full range covered by the two media in ASTM D36.

4.1.15. Specific Gravity (ASTM D70)

For solid and semisolid asphalts a pycnometer is generally used and a hydrometer is applicable to liquid asphalts (ASTM D3142).

4.1.16. Spot Test (AASHTO T102)

The test distinguishes asphalts that contain bodies poorly tolerated by the asphalt system.

4.1.17. Stain (ASTM D1328)

This test measures the amount of stain on paper or other cellulosic materials by asphalt. Variations of the cigarette paper stain procedure include the Barber stain, usually conducted at 54.4°C and 3.9 MN (400 g-force). Talc stain tests are also used.

4.1.18. Temperature Susceptibility

This is the term used to designate the change in consistency of an asphalt with changes in temperature. The Walther equation slope constant m can be used as a fundamental measure.

4.1.19. Temperature–Volume Correction (ASTM D1250)

Tables are provided to allow the conversion of volumes of asphaltic materials from one temperature to another or, as generally used, to adjust volumes to a temperature of 15.6°C, the standard basis of measurement in the United States. The value commonly taken for mean coefficient of expansion is 0.00036 in the range 15.6–121.1°C.

4.1.20. Viscosity

This is a measure of resistance to flow. A number of instruments are in common use with asphalt for this purpose. The vacuum capillary (ASTM D2171) is usually used to classify paving asphalt cements at 60°C, although it is applicable to materials in the range $4.2 - 20,000 \text{Pa·s}$ (42–200,000 P). Kinematic capillary instruments (ASTM D2170) are used in the 60–135°C temperature range for both liquid and semisolid asphalts in the range of $30 - 100,000$ mm^2/s (= cSt). Saybolt tests (D88) are also used in this temperature range and at higher temperature (ASTM E102). At lower temperatures the cone and plate instrument (ASTM D3205) has been used extensively in the viscosity range $10^2 - 10^9$ Pa·s (10^3–10^9 P). Other techniques include use of the sliding plate microviscometer and the rheogoniometer (see RHEOLOGY).

4.1.21. Thin-Film Oven Test (ASTM D1754)

This test has the purpose of determining the hardening effect of heat and air on a static film of asphalt when exposed in a thin film. An analogous procedure is the Rolling Thin-Film Test (ASTM D2872) which has the same purpose but utilizes a moving film exposed for 75 min at 163°C.

4.1.22. Water Content (ASTM D95)

This test covers the water content of asphalt by distillation using a Dean-Stark receiver.

4.1.23. Wax Content

The Deutsche Industrie Normen (DIN) method utilizes destructive distillation of the asphalt, followed by freezing out of the wax in the distillate fractions.

4.1.24. Weathering (ASTM D529)

This test evaluates the relative weather resistance of asphalts used for protective-coating applications, especially for roofing. No direct measure of outdoor life or service can be obtained from this test. Methods for preparing test panels (ASTM D1669) and failure end-point testing (D1670) are available.

Finally, these are not the only tests used for determining the property and behavior of an asphaltic binder. As in the petroleum industry (5, 6), a variety of tests are employed that evolved through local, or company, usage (97–99) without having passed through the ASTM system of approval. Tests are also necessary to determine the most practical design of asphalt-aggregate mixtures (100).

5. Uses

Properties, and therefore uses, depend upon the method of manufacture (Table 9). The Asphalt Institute lists a multitude of uses for asphalt (101), including hydraulics (dam facings, canal linings, pond linings) (102), recreation (substrate for artificial surfaces, tennis courts, running tracks) (103), agriculture (mulches, underground water barriers, stockyard paving) (104–107), transportation (railroad ballast treatment and roadbeds) (108), and metals (ore leaching pads, ore and coal briquetting, etc).

Table 9. Properties of Asphalts

Property	Straight-run, residual	Thermal	Air-blown residual
softening point (ring and ball), °C	46	113	93
penetration of 100 g at 25°C for 5 s, mm/10	90	0	20
ductility at 25°C, 5 cm/min, cm[a]	150+	too hard	3.2
specific gravity, 15.6/15.6°C	1.03	1.12	1.05
mean coefficient of cubical expansion/°C			
15.6–65.6°C	0.00063	0.00058	0.00063
15.6–232°C	0.00068	0.00063	0.00068
specific heat, J/(kg·K)[b]			
4.4°C	1675	1549	1633
93.3°C	1968	1842	1926
204.4°C	2345	2177	2303
thermal conductivity at 26.7°C, W/(m·K)	0.16	0.16	0.16
permeability constant at 25°C, $kg{\cdot}m/(m^2{\cdot}s{\cdot}N/m^2)$			
water vapor	$0.62 - 1.93 \times 10^{-15}$	1.1×10^{-15}	$1.25 - 2.4 \times 10^{-15}$
oxygen			0.08×10^{-15}
water absorption of 10-mil[c] films on aluminum panels, wt %			
50 wks			1.5–10
100 wks			2.5–16.5
surface tension, mN/m (= dyn/cm)			
25°C	34		32
100°C	27		28
dielectric strength, spherical electrodes, V/m	$11 - 45 \times 10^6$	36×10^6	$30 - 35 \times 10^6$
dielectric constant, 50 Hz at 20°C	2.7	3.0	2.7

[a] A + sign after a number indicates a minimum value.

[b] To convert J to cal, divide by 4.184.

[c] 10 mil = 6.254 mm·

5.1. Straight-Run Asphalt

The largest use of straight-run asphalts is in the paving industry (101) where they serve primarily as binders in paving mixes and as bases in liquid asphalts used as seal coatings, surface treatments, road mixes, and soil stabilizers. The most important technical innovation in asphalt paving has been to utilize asphalt throughout the entire pavement structure (termed total asphalt) to provide more efficient distribution of traffic stresses to the subgrade and provide better protection of the base from intrusion of outside materials such as water and soil. It has been established that 2.5 cm of asphaltic concrete can replace at least 5 cm of aggregate base for this purpose. In these mixes the binder contents usually vary from 4.0–10% depending on the aggregate gradation and nature and the construction.

The hot mixes are designed by using a standard laboratory compaction procedure to develop a composition reflecting established criteria for volume percent air voids, total volume percent voids between aggregate particles, flow and stability, or compressive strength. Tests such as the Marshall, Unconfined Compression, Hubbard-Field, Triaxial Procedure, or the Hveem stabilometer method are used (109).

If straight-run asphalts are reduced to a hardness below 300 penetration (30 mm), they are termed asphalt cements. For hot-mix paving, either the AC-10 viscosity grade or the next harder AC-20 grade is commonly specified.

Propane-precipitated asphalts have properties similar to the straight-run asphalts, assuming the same crude source, but are also obtainable in harder grades with higher softening points. The possible degree of reduction is much greater than with the distillation process. A practical limitation is the ability to remove and handle the precipitated asphalt fraction. These materials are often employed in fesco board manufacture and as a component in self-sealing roofing shingle adhesive.

5.2. Air-Blown Asphalts

Air-blown asphalts can be used in prepared roofings (110, 111) as well as for saturating the felts used in asphalt shingles and mineral-surfaced roll roofing. The shingle saturant is commonly a flux air-blown to the 50–60°C softening point level with a 50–90 penetration (5–9 mm) at 25°C, and the coating is the same flux air-blown to the 100–115°C softening point level with a penetration of 16–25 (1.6–2.5 mm). The coating asphalt is commonly filled with 50–60% mineral stabilizer, most of which passes a 74 μm (200 mesh) screen, and then is applied at approximately 35% of the finished weight of roofing shingles. This coating is also lightly applied to the back of the felt for protection. In addition to providing the waterproof surfacing, the coating also bonds the colored granules to the saturated felt. The opacity of the granule protects the coating from the hardening influence of light catalyzed reactions. The combination provides economical but highly durable mineral-surface shingles or roll roofing.

Built-up roofing constitutes several plies of a saturated roofing felt (low melt, flexible asphalt saturant) with each ply mopped in place and the structure covered by air-blown asphalts of from 60° to 105°C softening point, with the hardness selected depending primarily on roof slope. These roofs are usually surfaced with mineral aggregates.

A wide variety of industrial products are made from air-blown asphalts, such as laminants, pipeline coatings, waterproofings, potting compounds, and joint fillers. Additionally, the oxidized asphalts can be cut back with various solvents to produce a variety of protective coatings and paints. These coatings are often reinforced with mineral fillers to produce cold-applied roof coatings, adhesives, sound deadeners, railroad protective coatings, and undercoatings for automobiles.

5.3. Thermal Asphalt

Thermal asphalt products are in low supply because the thermal process has been virtually replaced by catalytic cracking processes. Thermal pitches, because of their high viscosity temperature susceptibility, are very hard at ordinary temperatures (Table 9), but become quite fluid when heated. They are especially useful as binders and as saturants for fiberboards, and as sizings for fiberboard when ground or dispersed and introduced directly into the wet furnish. Their weatherability on exposure in thin films is such that they are usually not satisfactory for use as protective coatings.

5.4. Liquid Asphalt

Liquid asphalt products comprise cutback asphalts and emulsions. A number of grades of different viscosities are available, which permit application from ambient temperatures to 150°C. The lower viscosity products are used for dust-laying purposes and as tack coats, prior to laying asphalt surface courses. The heavier grades are used for mix-in-place road mixes.

The properties of asphalt emulsions (ASTM D977 and D2397) allow a variety of uses. The rapid-setting grades are used for surface treatment and seal coat or surface treatments requiring cover aggregate. The medium-setting grade has higher stability to break on contact with surfaces and is used for mix-in-place macadam aggregates. It may also be used in plant mixes to produce a cold-laid macadam aggregate. Both of these types are less stable than the slow-setting type which has sufficient stability so that a finely divided material such as cement may be mixed without breaking the emulsion. The slow-setting grade is suitable for mixing with very finely divided dense-graded aggregates, or for the so-called slurry seal. The slow-setting grade is also used as a tack coat, and as a prime for dust laying and for soil treatment mixtures (Table 10).

In addition to the paving grades of emulsions, a variety of products are available that are suitable for industrial uses, for paper sizings, and for use in the roofing application field. Asphalts emulsified with colloidal clays are especially suitable for outdoor applications because of their excellent weathering properties. Some of these products have been adapted for use with roofing systems, either with brush or spray application.

6. Modified Asphalts

The deterioration of asphalt pavements under heavy traffic loads and/or under hostile weather conditions, coupled with the inability of many modern crude oil feedstocks to meet the challenge of producing specification-grade asphalts, has resulted in the search for asphalt modifiers. These are materials that can be added to the asphaltic binder to improve service life through enhancement of a particular property or providing a stronger bond between the binder and the aggregate thereby reducing the susceptibility of the mix to, for example, water damage (112, 113).

A variety of materials has been proposed to modify the properties of asphaltic binders to enhance the properties of the mix (112), including fillers and fibers to reinforce the asphalt–aggregate mixture (114), sulfur to strengthen or harden the binder (115, 116), polymers (98, 117–121), rubber (122), epoxy–resin composites (123), antistripping agents (124), metal complexes (125, 126), and lime (127, 128). All of these additives serve to improve the properties of the binder and, ultimately, the properties of the asphalt–aggregate mix.

The addition of fossil fuel derived materials has also been investigated. Of particular interest are the materials which contain functional groups that are capable of enhancing the asphalt–aggregate bond. Modifiers such as those isolated from the products of coal liquefaction (129) and the components of shale oil and even shale oil residua (130) have been used. The latter is especially interesting since the concept focuses on the use

Table 10. General Uses of Emulsified Asphalt[a]

	D977[b]					
Type of construction	RS-1, CRS-1[c]	RS-2, CRS-2[c]	MS-1, HFMS-1	MS-2h, HFMS-2h	SS-1, CSS-1[c]	SS-1h, CSS-1h[c]
Bituminous-aggregate mixtures						
for pavement bases and surfaces						
plant mix (hot) D2629				X[d]		
plant mix (cold)						
open-graded aggregate				X		
dense-graded aggregate					X	X
travel plant (mixed-in-place)						
open-graded aggregate			X	X		
dense-graded aggregate					X	X
sand					X	X
sandy soil					X	X
slurry seal					X	X
Bituminous-aggregate applications						
treatments and seals						
single-surface treatment (chip seal)	X	X				
multiple-surface treatment	X	X				
sand seal	X	X	X			
penetration macadam						
large voids		X				
small voids	X					
Bituminous applications						
fog seal			X[e]		X[f]	X[f]
prime coat-penetrable surface					X[f]	X[f]
tack coat			X[e]		X[f]	X[f]
dust binder					X[f]	X[f]
mulch treatment					X[f]	X[f]
crack filler				X	X	X
Maintenance mix						
immediate use			X	X		

[a] Only those grades of emulsified asphalt in general use have been indicated herein. It is possible that under certain variation of aggregates and/or climatic conditions, additional selections might be appropriate. Where the use of emulsified asphalt for applications other than those listed in the table are contemplated, the emulsion supplier should be consulted.

[b] Unless otherwise noted.

[c] Cationic D2397.

[d] ASTM D2629 permits use of other emulsion grades by note; grades of emulsion other than MS-2h may be used where experience has shown that they give satisfactory performance.

[e] Diluted with water by manufacturer.

[f] Diluted with water.

of basic nitrogen functions in the shale oil which enhance the adhesion of the asphalt to the aggregate. Test strips of shale oil modified asphalt have been laid on highways in various parts of the United States.

7. Aggregates

Although much of the focus tends to be on the composition and behavioral characteristics of the asphalt (ie, the binder or cement), the properties of the aggregate also play a significant role in determining the ultimate properties of the asphalt–aggregate mix. There are many factors to consider and they include: the functionalities in the asphalt (131), absorption of the asphalt into the pores of the aggregate (132), the aging properties of the asphalt when it is on the aggregate (133), as well as methods for coating the asphalt on to the aggregate (134).

Attempts have also been made to carry out surface modifications of the aggregate to enhance interactions with the asphalt (135) and other workers have made attempts to measure or predict the strength and type of asphalt–aggregate bonds (136, 137). However, it must also be remembered that mix design parameters play an important role in determining the performance of asphalt–aggregate mixes (138–142).

8. Health and Safety

The word asphalt has been carelessly used in that it is not adequately differentiated from thermally degraded materials, especially coal tar and derivatives. It is essential to differentiate asphalt from these materials which contain known carcinogens and health hazards. For this reason, the use of cracked asphalts must be treated with caution.

There are a variety of tests for asphalt emissions (Table 11). No significant air pollution problems are associated with emissions from hot paving operations using several asphalt cements (143). In fact, the concentrations of gaseous substances and emissions from paving asphalt cement have been found to be in very low concentration and within existing EPA and OSHA standards, even when the ambient air sampling was done under confined conditions (144–146). In addition, the high molecular weight polynuclear aromatic constituents that occur in asphalt have been studied as health hazards (147–151). The general conclusion from these studies is that surveillance should be continued although asphalt has not been shown to be a material of significant hazard.

Table 11. Analysis Techniques for Asphalt Emissions

Sample	Analytical technique
air	mass spectrometry
volatile hydrocarbons (C1–C6)	gas chromatography
carbon monoxide	infrared spectroscopy
volatile sulfur compounds	gas chromatography
nitrogen dioxide	uv-vis spectroscopy at 550 nm
aldehydes	uv spectroscopy
phenols	uv spectroscopy
particulates	optical microscopy
polynuclear aromatics (PNA)	gas chromatography

Steps to minimize potential safety hazards in the handling of asphalt are set forth by the American Petroleum Institute (152). These include: (*1*) sudden pressure increases from hot asphalt in contact with moisture in enclosed tanks or transports; (*2*) exposure to air at 150°C or above; (*3*) local overheating above heating coils; flashing of asphalt volatiles in the presence of an ignition source or possible autoignition; and (*4*) hydrogen sulfide from high temperature operations.

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