THE PHYSICAL CHEMISTRY OF ASPHALTIC BITUMEN

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I. ORIGIN

Many theories have been advanced concerning the origin and methods of formation of petroleum and the naturally occurring asphaltic bitumens. The reader who is interested in the history and complete discussions of the various theories is referred to the works of Brannt (17), Peckham (75), and Redwood (82), with their numerous references to original sources. Redwood reviews very completely the inorganic, the terrestrial (plant) organic, and the marine organic theories concerning the origin of petroleum and related materials. He also summarizes very clearly the Engler–Höfer dual origin theory. Peckham expresses the opinion that asphaltic base oils are of animal origin, whereas paraffinic petroleums are derived from plant life.

One of the first papers concerning the inorganic origin of bitumen was written by the famous French chemist Berthelot in 1866. Mendeléeff in Russia was also an advocate of its inorganic origin and believed that simple hydrocarbons were formed by the action of water on metallic carbides. Later the simple gaseous hydrocarbons condensed and polymerized to form petroleum, which in turn probably was the forerunner of the naturally occurring bitumens. Both of these men argued that petroleum could not be of organic origin because carbon was not found associated with it.

Coquand advocated the theory that bitumens were formed by the condensation of marsh gas, while Hunt, Orton, and Lesley held the view that bitumen is indigenous to the strata in which it is found. Maberry (50) believed in its organic origin and thought that the decomposition had taken place *in situ*, whereas Newberry, Peckham, and others argued that bitumen is a product of distillation and secondary decomposition of organic material.

Modern knowledge (19) concerning the nature of the hydrocarbons found in petroleum and the geological conditions (e.g., low temperatures) under which they are found are decidedly in favor of the organic origin. Some investigators ascribe the large number of different hydrocarbon compounds found in petroleum and asphalt to the anaerobic degradation of organic materials, both plant and animal, buried under heavy layers of sediment. Macfarlane (51) believes that fish were the chief source of material from which these complex hydrocarbons were derived, while others (40) consider that many types of animal and plant life, such as mollusks, diatoms, algae, protozoa, etc., may have been the original source. Treibs (112) discussed the probability of the production of petroleum from materials containing chlorophyll, and the experiments of Zelinskii and Koslov (123) indicated phytosterol and abietic acid as the possible sources of the optically active constituents. Also, humus acids and associated organic compounds have been considered (80) as the intermediate products between complex plant compounds and petroleum hydrocarbons.

Certain experiments (102) point to the possible formation of asphalt by the action of microörganisms on crude petroleum, while others (64) indicate that asphalt-like materials may be obtained by heating a mixture of gelatin and casein with hydrogen under pressure in the presence of calcium carbonate and magnesium carbonate. Hackford (39) studied the conversion of algae into bitumen by acid hydrolysis, and Friedman (33) concluded that asphaltic compounds were formed by reactions between olefins and sulfur. Similar products were not obtained when paraffin hydrocarbons were used. Chernozhukov (21) decided that the high molecular weight compounds (asphaltenes) in asphaltic bitumen are formed from petroleum by sulfur compounds of unknown composition. At high temperatures the radicals CH_3, CH_2, and CH may be stable (58), but on cooling they polymerize to form the hydrocarbons found in asphalt. The conditions under which the polymerization and condensation of petroleum to asphalt may take place have been discussed by Zalogiechi and Zielenski (122).

Richardson (86, 87) proposed the theory that the bitumen in Trinidad native lake asphalt was produced from petroleum by the surface action of colloidal clay. He further believed that the petroleum was produced from gaseous hydrocarbons by the catalytic action of the mineral bodies with which they came in contact. Tycinin (113) held essentially the same theory. He believed that, as petroleum rises to the surface of the earth, certain constituents are coagulated by the sunlight and then deposited on soil particles. The more volatile portions of the oil are evaporated, and the heavier, less volatile compounds remain associated with the coagulated asphalt.

Vanadium (72, 70, 49) is frequently a constituent of the ash from asphaltic bitumens. Its occurrence leads to the belief (15) that the catalytic action of this metal may have had a prominent part in the formation of the hard asphalts from softer hydrocarbons.

II. NATURE OF THE HYDROCARBONS PRESENT

Although a large amount of work has been done to obtain data concerning the chemical constitution of petroleum hydrocarbons, very little information is available concerning the nature of the numerous complex compounds present in asphaltic bitumen. Richardson (85) mentions the series of polymethylenes which, when first found in Russian petroleum, were given the generic name of naphthenes. These compounds are not as stable as paraffinic hydrocarbons and yet are not acted upon by sulfuric acid. By substitution of various hydrocarbon radicals for hydrogen, the polymethylenes may become very complex. Comparisons of synthetic polycyclic polymethylenes from California and Louisiana petroleum and from Trinidad lake asphalt have led to the conclusion that the asphaltic compounds of low boiling point may be bicyclic or bridge compounds, while those of high boiling point are polycyclic hydrocarbons.

TABLE 1

Molecular weights of bitumens

SOURCE OF BITUMEN	MOLECULAR WEIGHT
Trinidad lake asphalt	1132
Bermudez lake asphalt	620
Gilsonite	4252

Relatively small amounts of substituted hydrocarbons of the aromatic series may be found in the more volatile fractions of asphalt-base petroleums.

Strieter (101) dissolved asphaltic bitumen in benzene and determined the molecular weight by the lowering of the freezing point. Table 1 gives the values he obtained for three naturally occurring bitumens.

Katz (45), in a study of the effect of air-blowing on the chemical composition of a series of Alberta bitumens, found molecular weights for fractions of the original bitumen which ranged from about 750 to 2200. Treatment with air, which he believed caused condensation followed by polymerization, resulted in increases in molecular weights up to almost 4700.

If the data of Strieter and Katz are taken as even approximate criteria, the compounds composing asphaltic bitumens must be very complex. The presence in asphalts of compounds containing sulfur, nitrogen, and occasionally oxygen makes even more difficult any attempt to separate and isolate individual compounds.

The saponification of mixtures of asphalt and drying oils was studied by Demarest and Rieman (25), using a potentiometric method. Previously Paillar (73) had developed titration methods for determining both the acid and saponification values for asphalts. Pöll (78) investigated the determination of the iodine number of native and oil asphalts and discussed the value of the number in determining the constitution of bitumen.

III. ACTION OF ORGANIC SOLVENTS

Fractional solution and precipitation by means of organic solvents has been used extensively in the analysis and testing of asphaltic bitumens. By this means the type and source of the asphalt frequently may be determined. Also the presence of added material, which may detract from the practical value of the original asphalt, may often be detected by the judicious use of partial solvents.

Although carbon disulfide and chloroform are two of the best solvents for asphaltic bitumens, Abraham (1) points out that caution should be exercised in using 100 per cent solubility in these liquids as a definition for bitumen.

Richardson and Forrest (84) found that bitumen, which was completely soluble in carbon disulfide, upon being treated with carbon tetrachloride frequently gave a residue or precipitate. These substances, insoluble in carbon tetrachloride but soluble in carbon disulfide, they called "carbenes." If the carbon tetrachloride solution of bitumen was permitted to stand for some time in a glass container exposed to sunlight the carbenes were increased in amount (3, 54). That the reaction producing these increased amounts of carbenes is a photochemical one is indicated by the fact that hydrogen chloride is formed and may be detected in the air above the solution. Further, light of short wave length is more effective in producing increased precipitation than is that of longer wave length. No increase in amount of precipitate will occur over a considerable length of time in the dark.

Light petroleum naphtha (86° or 88° Baumé) is another solvent commonly used to fractionate asphaltic bitumen. The usual proportions are 100 volumes of the naphtha to 1 volume of the bitumen. The soft, light-colored, low molecular weight constituents of the asphalt, which dissolve in the naphtha, are called "malthenes" or "petrolenes", whereas the hard, dark-colored precipitate made up of high molecular weight compounds possessing a high carbon to hydrogen ratio is referred to as the "asphaltenes."

Associated with the petrolenes are the asphaltic resins, which may be separated from the non-resinous portion by mixing with fuller's earth, which adsorbs the resins. The petrolenes may be washed out of the mass by means of 86° Bé. naphtha and the resins then, at least partially, recovered from the surface of the fuller's earth by treatment with carbon disulfide, chloroform, or benzene. When removed from the surface of the fuller's earth the resins again become completely soluble in naphtha.

Oliensis (71) has proposed a test for determining the degree of homogeneity of asphalts in which the asphalts are dissolved or dispersed in 5.1 times their volume of a petroleum naphtha of specified properties. A drop of the dispersion placed on an inclined clean glass plate will give a smooth, clear, glassy film if the asphalt is homogeneous and a dull, mattelike streak in the center of the stain if it is not. The name "carboids" was suggested for the substances which are precipitated or are insoluble in the solvent. Naturally the presence of mineral matter in the bitumen complicates the test.

Nellensteyn (63) found that asphaltenes which are usually in a dispersed condition go into solution if a diluent is added which is completely miscible with both the dispersing medium (the petrolenes) and the protective agent (the resins). The added liquid (diluent) should have a surface tension greater than 24 to 26 dynes per centimeter at 25°C.

A method has been proposed by Schwarz (96) for classifying bitumen. The asphalts are etched by means of benzine, carbon tetrachloride, or carbon disulfide for 5 seconds and photomicrographs are taken of the surfaces. Bitumens of various types and sources presumably give different patterns and designs under the standardized treatment.

Recently Zwergal (124) extracted asphaltic bitumens successively with methyl, ethyl, propyl, butyl, and amyl alcohols. He found that the proportion of each fraction varied with the bitumen, and that the third fraction (extracted with propyl alcohol) had a higher carbon and hydrogen content than the other fractions, owing to the small quantity of sulfur and oxygen present. This fraction also possessed the highest ductility.

The refining and fractionation of petroleum by means of solvents (46) has developed very rapidly in recent years. Although these processes are frequently concerned with the reactions of asphaltic bitumen (18), they are too involved to be discussed here.

IV. COLLOIDAL PROPERTIES

Many of the characteristics of asphaltic bitumen indicate that they are colloids; some of these properties and the theories concerning structure will be briefly discussed. Nellensteyn (59, 61) has argued that asphalts are colloids because their solutions exhibit the Tyndall effect even at dilutions of 1 to 30,000, and because ultramicroscopic examination shows perceptible Brownian movement in the solution. He reports that ultramicroscopic particles were detected (60) in solutions of both native and oil asphalts. However, in the case of the former these may have been very small mineral particles which are practically impossible to remove by even the finest filters (85). From his researches Nellensteyn has developed a theory for the colloidal structure of asphaltic bitumen which is based upon the existence of three components. They are (1) the fluid medium or dispersing phase, (2) the protective bodies which are lyophilic, and (3) a lyophobe part. The micelles of the dispersed phase are composed of the last two groups, and the stability of the system is dependent upon the interfacial forces existing between the fluid medium and the micelles. When an asphalt solution is flocculated by the addition of some organic solvent a new phase is not formed; the dispersed particles merely come together because of the change in interfacial tension which has taken place between them and the surrounding liquid. The theory assumes that elementary carbon is at the center of each micelle and, in fact, Waterman and Nellensteyn (117) claimed to have obtained carbon from artificial and natural asphalts by successive extractions with gasoline, carbon tetrachloride, and benzene. The presence of free carbon is also suggested by the dark color of the asphalt. "Most hydrocarbons are only slightly colored; the same could be expected of the colloidal solutions, even of the highly polymerized ones. The dark color of asphalt solutions therefore indicates the presence of free carbon." The micelles may be pictured as composed of successive layers of hydrocarbons in which the ratio of carbon to hydrogen becomes less as progress is made away from the center or carbon nucleus. This ratio for the outer layer of the micelles will be very nearly the same as for the dispersing phase (petrolenes).

Asphaltic bitumens are strongly adsorbed by certain types of mineral surface. By drawing asphaltic base petroleum upward through a column of dry fuller's earth, Gilpin and Schneeberger (35) obtained fractions practically free of colored material and possessing specific gravities much lower than the original petroleum. They concluded that asphaltic petroleum is an emulsoid, and that passage through a column of fuller's earth causes the adsorption and coagulation of the bitumens present, which in turn carry with them the sulfur and nitrogen compounds and the aromatic and olefinic hydrocarbons.

Guiselin and Handricourt (38) also found that the filtration of petroleum through dried earth produces a series of fractions, the first of which are water-white and possess a faint ethereal odor. Those hydrocarbons richest in carbon are the most attracted by clay.

The adsorption of asphalt from carbon disulfide solution by crushed granite, feldspar, and quartz was investigated by Dow (26). He used changes in the color of the dilute (0.5 per cent) solutions employed as a measure of the amount of adsorption. The coloring matter removed from petroleum by clay is believed by Bosshard and Wildi (16) to be colloidal in nature.

Zaharia and Lucatu (121) subjected several petroleums to ultrafiltration in an effort to determine whether the paraffins, resins, and asphalts were present in colloidal or true solution. They employed vulcanized rubber membranes (0.04 mm. thick) in the Bruckner apparatus, under a pressure of 150 atmospheres. The "resins," which are separated from the petroleum by means of 70 per cent ethyl alcohol, and the paraffins were found to be ultrafiltrable. Both hard and soft asphalts were removed quantitatively by ultrafiltration. Thus it was concluded that the asphaltic bodies present in petroleum are colloidal, but that the resins and paraffins are in true solution. The retained asphalts, dissolved in benzene and cyclohexane, were subjected to ultrafiltration, but they would not pass through the rubber membrane.

Pyridine is an excellent solvent for asphaltic bitumen. Since the author had used rubber membranes and pyridine in the study of other systems (103, 105), he applied this combination of membrane and solvent to a study of various bitumens. Cells equipped with membranes of dentist's rubber dam were filled with 5 per cent solutions of various hard asphalts in pyridine, and the under side of the membrane brought into contact with C.P. pyridine. The contents of the cells were agitated in order that a fresh layer of solution would be continuously presented to the semipermeable membrane. It should be noted that dialysis through a rubber membrane depends upon the solubility of the material in the rubber; in this respect it differs from the sieve-like action of some membranes. The pyridine outside of the cell became colored by the asphaltic materials passing the membrane. The outer liquid was changed from time to time, because as the concentration of the asphaltic materials increased therein the rate of transfer through the membrane became slower. After twenty-one days the dialysis was stopped. The pyridine was allowed to evaporate spontaneously from the combined diffusates and from the dialyzate, the latter having been washed out of the cell with pure pyridine. The residues from the diffusate and dialyzate were weighed, and their combined weight subtracted from the total bitumen used in order to obtain the amount of volatile hydrocarbons lost from the diffusate along with the pyridine.

Table 2 gives the weight per cents of the original asphalt recovered from the pyridine solutions and the loss, which probably is mainly volatile hydrocarbons lost during the evaporation (at room temperature) of the pyridine from the diffusate.

The dialyzates from all four kinds of asphalt were black, hard, and brittle. However, the characteristics of the diffusates from different bitumens may vary considerably, although the quantities obtained from a given amount of original material may be nearly the same. Examination of the results of the dialysis of solutions of various types of bitumen should be very helpful in solving the complex problems encountered in a study of the physical structure of asphaltic bitumens.

Mack (53) considers that at low temperatures asphalts are sols of asphaltenes in a mixture of resins and petrolenes. However, as the temperature is raised solution occurs; for the asphalts studied the process is complete at 120°C., and the liquids acquire the characteristics of true solutions.

TABLE 2

Fractionation of asphalts by dialysis

TYPE OF BITUMEN	WEIGHT PER CENT OF		
	Dialyzate	Diffusate	Loss
Trinidad batch steam-refined oil asphalt (10 penetration at 77°F., 100 g./5 sec.)	55	27*	18
Venezuelan batch steam-refined oil asphalt (10 penetration)	54	27†	19
Venezuelan air-blown asphalt (10 penetration)	58	22‡	20
Bitumen from Trinidad refined lake asphalt (7 penetration)	72	18*	10

* Comparatively hard. Tacky.

† Comparatively soft. Tacky but long.

‡ Comparatively very soft. Oily, slightly tacky, short. Lighter colored than the others.

The molecular weights of the asphaltenes were calculated from the concentration and viscosity of solutions in petrolenes and benzene by means of the equation,

$$\log \text{relative viscosity} = ckM \tag{1}$$

(where c = concentration in weight per cent, M = molecular weight, and k = a constant) and were found to be of the order of 1800. These determinations, together with the measurements of adsorption of asphaltic resins by asphaltenes, indicate that the high viscosities of asphalt are caused by association and not by solvation.

Bateman and his coworkers (10, 11) have studied the effect on asphalts of mixing them with sand and stone at elevated temperatures. Improvements (2) in the method of recovery of bitumen from mixtures with mineral aggregate have made investigations similar to those of Bateman much more valuable and reliable. There are many indications that different types and kinds of bitumen are affected to different extents by contact with hot sand and stone, especially in the presence of air. Recently, Sikes and Corey (99) studied experimentally the effect of continued heating on various kinds of asphalt. The fact that asphalts at atmospheric temperatures frequently possess anomalous flow properties has been taken by Traxler and Coombs (109) as evidence of the colloidal nature of bitumens.

V. OPTICAL PROPERTIES

Engler and Steinkopf (27) found the quantity of optically active material in petroleum to be so small that numerous fractionations had to be made to obtain a sufficient concentration for accurate study. They obtained evidence that the activity was due to decomposition products of cholesterol, and that overheating caused a diminution of activity either by racemization or by complete deactivation. Every petroleum studied by them showed some optical activity. Rakuzin (81) had detected cholesterol itself in petroleum, but later investigations (100), using the digitonin reaction on Java and Mendoza oils, made it appear doubtful that the free compound exists in petroleum. Marcusson (56), also, is of the opinion that the optical activity of mineral oils is due to saturated hydrocarbons formed from cholesterol or its compounds.

Solutions of untreated and sulfonated asphalts in benzene, chloroform, and hydrocarbon solvents were prepared by Rosinger (90). The solutions were poured out on glass plates and the solvent allowed to evaporate, leaving thin films of the asphalt. When these films were exposed to light, changes, probably due to oxidation, occurred in the bitumen which rendered it insoluble in the solvent used in preparing the original solution.

At about the same time Gödrich (36) found that the action of light on asphalt made it more insoluble in the usual solvents. Further, the sensitivity of the asphalt to light was increased by the presence of sulfur monochloride. Although Gödrich found that solutions of asphalt showed absorption bands in the blue and yellow, some of our own unpublished studies have shown the complete absence of absorption bands either in the visible or ultra-violet transmission or reflection spectra. In asphalts containing sulfur Gödrich found the absorption bands in the yellow to be missing. According to him, asphalt is sensitive to monochromatic light over the entire range of the visible spectrum as well as into the ultra-violet.

Bitumens exposed to air and sunlight were found by Reeve and Lewis (83) to undergo changes other than those due to loss of volatile matter.

These investigators came to the conclusion that polymerization and intermolecular reactions induced by heat and possibly by light were largely responsible for these changes.

Errera (28) has discussed the early work of Kayser (1879), who isolated three components of asphalt by dissolving successively in alcohol, ether, and chloroform. Kayser called the three fractions α-, β-, and γ-asphalt. Alpha asphalt is an oily substance, while beta asphalt is a gummy solid with a softening point of about 60°C. Gamma asphalt, the only one of the three which is really sensitive to light, is high in sulfur content and melts at about 165°C. According to Errera, Judaean and Trinidad asphalt contain 58 and 38 per cent, respectively, of gamma asphalt. This component, which roughly corresponds to the asphaltenes mentioned above, is chiefly in a colloidal state.

During an investigation of asphalts from the region of the Black Sea, Tycinin (113) found that an ether extract which was free from asphalt continued to deposit material on standing. In darkness the deposition stopped, and then started again on exposure to light. Large surfaces of nickel, glass, and other solids increased the amount of deposit. Tycinin believed the change was not a chemical reaction but only a transformation of material into another physical state. These changes are somewhat analogous to the formation of "carbenes" in carbon tetrachloride solutions of asphalt exposed to sunlight.

Macht (52) found that thin films of asphalt on glass plates gave a greenish-yellow fluorescence under ultra-violet light, and that the color of the fluorescence deepened as the asphalt became harder. Films of coal tar gave a dark brown fluorescence. Benzene and benzine solutions of asphalts from various sources showed different colors under ultra-violet light. Mixtures of tar and asphalt were tested by placing a few drops of a benzene solution of the mixture on filter paper and permitting the solvent to evaporate before irradiation. Macht claims that with practice an accuracy of 5 per cent in estimating the proportions of asphalt and tar may be attained. Bruckner and Meinhard (20) also found that petroleum pitch, coal-tar pitch, and montan wax, either in solid form or in solution in carbon tetrachloride, chloroform, benzene, or petroleum naphtha, could be identified by their fluorescence in ultra-violet light. However, they claim that one material cannot be identified when mixed with others.

Hradil (42) has examined the fluorescence of oil shales spectroscopically, and Bentz and Strobel (13) report that crude oil can be distinguished from the refined product by the fluorescence shown under ultra-violet light.

In the opinion of Schwarz (97) the refractivity of individual hydrocarbons is a source of information which has not been completely utilized in the past. He also believes that etching with benzine, carbon tetrachloride, carbon disulfide, and other solvents, followed by microscopic examination of the etched surfaces, may lead to valuable information concerning the proportions of resins, asphaltenes, carbenes, and carboids in an asphalt.

Although the Raman effect has not been studied in connection with asphaltic bitumen, Hibben (41) has discussed the applications and limitations of Raman spectra in the petroleum industry and has given data on cracked and uncracked gasolines and oils.

The colors of particular asphalts are of practical interest, especially when the bitumens are to be compounded with pigments. A Klett colorimeter has been used by the writer and his associates to estimate the color of bitumens obtained from various sources and by different methods of preparation. Although only comparative data are available at the present time, a procedure somewhat similar to the optical density method described by Ferris and McIlvain (29) for assigning numerical values to lubricating oils might be devised. Graefe (37) compared very dilute solutions of asphalt in benzene (1 to 10,000 parts) with an aqueous solution composed of 0.1 per cent iodine in a 0.2 per cent solution of potassium iodide. He found air-blown asphalts to be the darkest in color, while natural asphalts were the lightest.

VI. SURFACE TENSION

Measurement of the surface tension of asphaltic bitumens is very difficult, because at ordinary temperatures most of them are not fluid in the ordinary sense of the term. Only by making the measurements at elevated temperatures has it been possible to obtain estimates of the interfacial tension between air and asphalts of the consistencies usually employed industrially or in paving.

Surface tensions were determined for (1) Venezuelan crude oil of specific gravity 0.9509 at 60°F., (2) Trinidad petroleum of specific gravity 0.9497 at 60°F., and (3) a petroleum from the Island of Trinidad with a specific gravity of 0.9176. Table 3 gives the values obtained on these three asphaltic base petroleums at various temperatures by means of the duNoüy ring method.

The Venezuelan petroleum was saturated with water (an emulsion with water as internal phase was formed) and the surface tension measured at 28°C. by means of the duNoüy instrument. The value obtained was 33.0 dynes per centimeter, which is about the same as for the unsaturated oil. Distilled water was then agitated with about one-tenth of its volume of Venezuelan oil, allowed to stand overnight, and then separated from the petroleum. The oil-saturated water was found to have a surface tension of 58 instead of 72 dynes per centimeter. Thus, there is a difference in surface tension of 25 dynes per centimeter between Venzuelan oil saturated with water and water saturated with oil. This value represents the force which is working toward the production of an emulsion with water as internal phase in such a system. It is this force which must be overcome in producing bituminous emulsions with water as external phase from this asphalt.

When similar experiments were performed using the Trinidad petroleum, which had the same specific gravity as the Venezuelan, the difference between the surface tensions of oil saturated with water and water saturated with oil was found to be only 20.5 dynes per centimeter. Therefore, less force has to be overcome in preparing an external phase emulsion using this petroleum or bitumens derived from it by distillation than when the Venezuelan oil or its derivatives are used. Practical experience in the production of commercial bituminous emulsions has confirmed this conclusion.

TABLE 3

Surface tension of asphaltic petroleums

PETROLEUM	TEMPERATURE	SURFACE TENSION
	°C.	*dynes/cm.*
Venezuelan	26	34.5
	56	30.0
	84	27.0
Heavy Trinidad	25	34.0
	55	32.5
	85	30.5
Light Trinidad	26	28.5
	58	26.0
	83	25.0

A soft asphaltic bitumen (48 seconds float (6) at 150°F.) prepared by steam distillation of petroleum from the Island of Trinidad was agitated slowly at 85°C. with 0.01 *N* sodium hydroxide and then allowed to stand until the temperature dropped to 25°C. The asphalt was skimmed from the surface of the solution, which was dark brown in color. The original 0.01 *N* sodium hydroxide had a surface tension of 59 dynes per centimeter, whereas the above-mentioned solution gave 35 dynes per centimeter, a drop of 24 dynes per centimeter. This decrease in surface tension was due to the formation of dark-colored, soap-like substances by the interaction of the sodium hydroxide and substances present in the bitumen. These soap-like compounds, upon isolation, were found to be excellent emulsifying agents for bitumens which otherwise were rather difficult to emulsify.

Emulsions with water as external phase, prepared from the soft Trinidad residuum and 0.01 *N* sodium hydroxide, gave surface-tension values of 33 dynes per centimeter. Since this figure is almost identical with that obtained on the solution mentioned above, it may be concluded that the continuous phase of the emulsion is very similar to the soap-like solution prepared by careful extraction of the bitumen with a solution of caustic soda.

Some measurements of the surface tensions of petroleums were attempted using glass capillary tubes, but the results were unsatisfactory, probably because of adsorption at the glass wall.

Francis and Bennett (31) used the duNoüy ring apparatus to measure the surface tensions of various domestic crude petroleums, and obtained values ranging from 29.0 to 31.2 dynes per centimeter at 85°C.

Using Jaeger's (43) method, Nellensteyn and Roodenburg (62) measured the surface tensions of the following asphalts at temperatures ranging from about 100° to 225°C.

(1) Oxidized Venezuelan asphalt. (Ring and Ball softening point = 64.2°C.).

(2) Mexican asphalts. (Ring and Ball softening points = 42°, 55.7°, and 58.5°C.).

(3) Bitumen from Trinidad native lake asphalt. (Ring and Ball softening point = 65°C.).

The surface tensions of a coal-tar pitch (Ring and Ball softening point = 60.2°C.) were determined at temperatures ranging from 67° to 180°C.

They found that the surface tensions of the asphalts all fell within the limits 20.7 to 37.4 dynes per centimeter. Also, all of the temperature–surface tension curves showed a sharp break at about 150°C. Nellensteyn and Roodenburg discussed the theoretical and practical significance of this break, and attributed it to sudden changes in the internal structure of the bitumen.

They also extracted the oily medium (petrolenes) from the various bitumens by means of naphtha and acetone, and then obtained surface-tension data on the recovered, solvent-free, bituminous fractions. For these fractions the temperature range was much greater (30° to 230°C.) than for the asphalt itself, because the petrolenes are fluid at the lower temperatures. A break also occurred in the surface tension–temperature curve for the petrolenes, but at a temperature of about 50°C.

Saal (95) was unable to verify the results obtained by Nellensteyn and Roodenburg, although, using the duNoüy method, he investigated several asphalts of different origins and methods of processing. He concluded that the breaks in the temperature–surface tension curves found by the previous investigators were due to experimental errors caused by using Jaeger's bubble method to measure the surface tension of materials possessing viscosities above 15 poises. Consequently, Saal believes that Nellensteyn's conclusions concerning the internal structure of asphaltic bitumen at temperatures below the break in the curve are unjustified.

Nellensteyn and Roodenburg explain the greater miscibility of Trinidad asphalt with tar as being caused by its having a slightly higher surface tension than that possessed by most other asphaltic bitumens. When the surface tension of an asphalt is determined, it is probably the continuous phase (petrolenes) which is evaluated, since the micelles (asphaltenes) should have very little effect.

VII. INTERFACIAL TENSION BETWEEN ASPHALTIC BITUMENS AND WATER OR AQUEOUS SOLUTIONS

The formation of emulsions, in which water is the internal phase, with crude oils is of rather common occurrence, and the breaking of these oil-field emulsions is often a serious problem involving large expenditures of time and money. On the other hand, the production of bituminous emulsion, in which the asphalt is dispersed in the form of very small drops in a continuous phase usually composed of an aqueous soap solution or a very dilute clay slurry, has grown to be a business of large proportions. In both of these types of emulsion the tension which exists at the oil–water or oil–aqueous solution interface is an important property. As in determining the surface tension of bitumens, it is difficult to measure the interfacial tension between water and a hard bitumen which does not flow easily at ordinary temperatures.

Moreover, the interfacial tension must be determined at temperatures below the boiling point of the aqueous solution. Thus, a limitation is encountered immediately which does not appear in the evaluation of surface tension.

By forming drops of water in oil Johansen (44) studied the interfacial tensions developed between water and various light-colored petroleum products. The drops were counted and their total volume measured at the end of the experiment, and thus the average drop size was determined. Because of their dark color and opacity asphaltic materials could not be used as were the oils in Johansen's experiments. However, the author tried to measure the interfacial tension between soft asphaltic bitumen and water or alkaline solutions by forming drops of the bitumen in the aqueous medium. The experiments were not successful, chiefly because the water wetted the tip of the glass capillary better than did the bitumen, and because there was very little difference in density between the water or aqueous solution and the soft bitumens which were employed.

Weiss and Vellinger (119), and Vellinger (115) studied the influence of temperature, pH, and degree of refining of petroleum oils on the interfacial tensions which they develop against water.

Using the duNoüy ring tensiometer, Traxler and Pittman (104) measured, at 85°C., the interfacial tension between various concentrations of sodium hydroxide solution and two soft asphaltic bitumens. The bitumens used were prepared from Venezuelan and Trinidad petroleum by steam distillation and had specific gravities at 85°/85°C. of 0.9964 and 0.9970, and floats at 150°F. of 44 and 53 seconds, respectively. It was found that the addition of sodium chloride up to a concentration of 0.125 *M* reduced the interfacial tension, whereas greater concentrations of salt increased the tension. The presence of calcium chloride up to a concentration of 0.0025 *M* in the aqueous phase increased the interfacial tension, but beyond that figure the tension values remained constant. The influence of calcium chloride could be partially counteracted by the addition of sodium chloride; at ratios which varied from 50 to 100 parts of sodium chloride to one of calcium chloride the salts completely neutralized the effect of each other.

The same bitumens were later used (104) in experiments to determine the interfacial tension against dilute solutions of disodium hydrogen phosphate, sodium tetraborate, sodium carbonate, sodium silicate, and sodium phosphate. At 85°C. solutions of sodium silicate and sodium phosphate gave lower interfacial tensions than disodium hydrogen phosphate and sodium tetraborate. Solutions of sodium carbonate were found to give values intermediate to these two groups. Further, the nature of the anion present in the aqueous solution was found to have more influence than the pH on the interfacial tension.

Nellensteyn and Roodenburg (65), from a study of the spreading of water on asphaltic bitumens and tar, concluded that Antonov's rule applied to such systems. This rule states that the tension at an interface equals the difference in surface tensions of the two liquids. However, this relation holds only for pure liquids which are immiscible. Since water does dissolve some material from most bitumens, adherence to Antonov's rule would not be expected. Experiments conducted by the writer and his colleagues indicated that such a conclusion is correct.

VIII. ADHESION OF BITUMENS TO SOLID SURFACES

The ability of bitumens to wet and adhere to solid surfaces is of practical value in the application of asphalts to paving, waterproofing, impregnation of felts, fabrics and fibres, as binders, paints, etc. Bain (7) emphasized the necessity of proper wetting of the solid surfaces by bitumen in most of its uses, and pointed out that in the native asphalts nature has accomplished almost perfect wetting of the dispersed mineral by the bitumen.

Bartell and Miller (8) studied quantitatively the wetting of silica by various petroleums, and obtained displacement pressures which varied from about 109 to 259 g. per square centimeter. Later these same investigators (9) measured the displacement of crude oil from silica by aqueous solutions. The solutions which were most reactive toward silica displaced the petroleum most readily.

An apparatus for measuring the adhesive properties of bituminous pipe-coating compounds has been described by Christopher (22). The mechanism and theory of the wetting of solids by liquids has been presented by McLean and Kohman (55) and by Peek and McLean (74). Nellensteyn (66) reviewed the energy relations existing between bitumens and solid materials. Fricke and Meyring (32) determined the wetting power of asphalt and tar and mixtures of them for glass by measurement of the angle of contact which the materials make with a clean surface.

Recently, Lee (48) has studied the displacement of tar and bitumen films from various solid surfaces by means of water. He gives a clear, concise exposition of the use of contact angles for measuring the wetting of a solid by a liquid.

It has been proposed (120, 47), that the characteristics of bitumen-mineral mixtures are greatly influenced by the surface forces acting between the solid and liquid. Wedmore (118), during an evaluation of materials for the exclusion of water in electrical apparatus, devised a method by means of which the adhesiveness of bituminous compounds may be measured. A cylindrical steel mold filled with the material being tested rests on a very highly polished steel plate. The plate and mold are slowly pulled apart at 20°C. A satisfactory material is arbitrarily classified as one which adheres to at least 90 per cent of the exposed surface.

Saal (91) believes that the adhesion of bitumens to solids is to a great extent influenced by the surface condition of the solid. Riedel and Weber (88), also, have expressed the opinion that the properties of the stone have a greater influence on the adhesiveness in a paving mixture than do those of the bitumen. The presence of soaps and electrolytes has a definite effect on the adhesiveness between stone and bitumen, consequently the adhesiveness of hot bitumen to various stones is less variable than is that of bituminous emulsions. Dahlberg (24) objected to the work of Riedel and Weber, because it was all done at 100°C., and made the suggestion that values be obtained for adhesion at 100°, 70°, 50°, and −10°C. Nüssel and Neuman (69) test for adhesion of bitumen to stone by boiling the coated solid with solutions of sodium carbonate. Their results do not agree with those obtained by the method proposed by Riedel and Weber. Although it is rather difficult to prove, the belief is held by most investigators that the adhesion of bitumen to stone increases with time.

The presence of small amounts of paraffin wax has been shown by Riehm (89) to decrease the adhesiveness of asphaltic bitumens greatly, and he established 2.5 per cent of paraffin wax as the maximum permissible content if good adhesion is to be obtained.

The slipperiness of asphalt surfaces, a property of considerable practical importance, has been discussed by Nellensteyn (67) as a problem in the surface wetting of bitumen by water. In his opinion, an extensive knowledge of the surface and interfacial tensions of the materials involved appears to be essential to an understanding of the subject of slipperiness.

IX. FLOW PROPERTIES

Of the numerous empirical methods used for measuring the consistency of asphalts and similar materials one of the most widely used is the penetration test (4). The penetrometer measures the distance a needle of definite shape will enter the material when a standard load is applied at a standard temperature. Various methods have been developed for determining the so-called softening point, which is simply the temperature at which the material under test attains a certain consistency. The consistency of asphalts at the temperatures known as their Ring and Ball softening points (5) has been reported (30) to be about 12,000 poises. In the writer's laboratory the values for fourteen steam- and vacuum-refined asphalts have been found to vary from 14,000 to 30,000 poises. Saal (94) found that at the Ring and Ball softening points the asphalts which he investigated had viscosities from 10,000 to 20,000 poises. Although all of the tests commonly used to measure the consistency of bitumens are related in some way to the viscosity expressed in C.G.S. units, the relationship is usually very complex.

A number of instruments are available for measuring the consistency, in arbitrary units, of soft bitumens at atmospheric temperatures or of hard ones at elevated temperatures. The Saybolt-Furol and Saybolt-Universal efflux viscometers and the Stormer and MacMichael rotating machines are widely used in the United States. The Redwood is used in England, the Engler in Germany, and the Barbey viscometer to some extent in France. Each instrument has its own sphere of usefulness, and although none of them gives values in absolute units (poises) directly, conversion factors have been developed for some of the instruments which have proved to be quite satisfactory.

In recent years several methods have been devised or improved (110) for measuring the consistency of very viscous materials. Some of these instruments have been found useful in evaluating the flow properties of hard asphaltic bitumens at atmospheric temperatures. Saal (93) and Saal and Koens (92) have given excellent reviews of several of the available methods, together with the consistency ranges over which each type of instrument is applicable.

The alternating-stress method developed by Bingham and Stephens (14), and used by them to measure the viscosity of rosin, has been employed (76, 106, 107) to obtain information concerning the consistencies of asphalts possessing viscosities above 10^5 poises. When consistencies below 10^5 are to be measured, a modification (76) of the Bingham–Murray tube plastometer is a convenient and accurate method. The rotating concentric cylinder type of viscometer (23), which has been modified recently (57), is adaptable to a very wide range of consistencies, and by means of this instrument the material under test may be subjected to a considerable range of shearing stress. A number of steam- and vacuum-refined oil asphalts of the consistency used in asphalt pavements have been found to behave essentially as viscous liquids. However, hard steam-refined and air-blown asphalts were found to give a curvilinear relation between rate of shear and shearing stress. Also, these materials are frequently elastic and thixotropic.

Saal and Koens (92) also studied the flow properties of several bitumens by means of capillary and rotating concentric cylinder viscometers, and found most of them to be non-Newtonian liquids, i.e., the experimentally determined viscosities decreased with increasing shearing stress. With some of the asphalts they found evidence for the existence of thixotropy; the bitumens showed a decrease in consistency with mechanical working. The phenomenon of thixotropy is probably caused by the elimination of structure within the asphalt. Results obtained in the research laboratories of The Barber Asphalt Company indicated that the amount of structure, which appeared in the form of thixotropy, varied among different asphalts and could be increased markedly by the addition of finely ground mineral powders to the bitumen.

Viscosity was related to the penetration by Saal (93) by means of the expression:

$$\text{Viscosity (poises)} = \frac{9.1 \times 10^9}{(\text{penetration})^{1.93}} \qquad (2)$$

where the viscosity and penetration were determined at the same temperature. However, Traxler, Pittman, and Burns (106) found that such an expression did not accurately relate the penetration and viscosity of several kinds of asphaltic bitumen. No doubt the penetration of a needle into a mass of asphalt is greatly influenced by the adhesiveness of the bitumen toward the steel. This may be the chief reason why, for all kinds of bitumen, penetration cannot be expressed as a simple function of viscosity.

The change of viscosity of asphaltic bitumen with temperature is a very important property. Walther proposed a formula of the type

$$\log \log (V_k + 1) = m \log T + c \tag{3}$$

where V_k = kinematic viscosity in centistokes, T = absolute temperature (273 + °C.), and m and c are constants. It is admitted that this formula may be criticized because of the double logarithm, and over a wide range of temperatures it has been found (76) to give values which deviate from those determined experimentally by as much as 25 to 30 per cent. Duplicate experiments checked within about 5 per cent.

Using a rotating viscometer, Ůmstatter (114) investigated the influence of temperature on the viscosity of asphalts over the temperature range of 25° to 50°C., and obtained a straight line by plotting the logarithm of the viscosity against the reciprocal of the square of the absolute temperature. However, when temperature–viscosity data obtained over a wide range of temperature are tested in the manner proposed by Ůmstatter, it is found that the curve breaks in the region of the softening point of the asphalt.

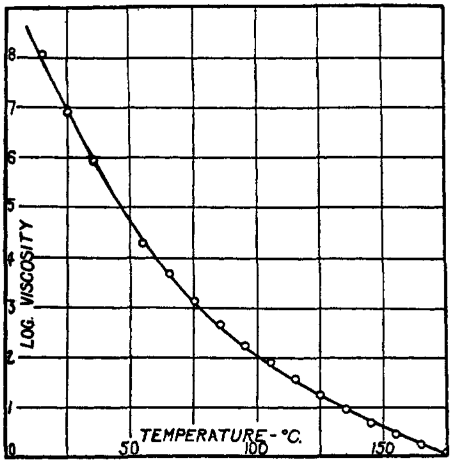

FIG. 1. Variation of viscosity with temperature for a Mexican asphalt

Although some investigators have found transition points in the viscosity–temperature relationships for asphalts, there are ample data indicating a distinct continuity throughout a wide temperature range. Figure 1 shows the log viscosity versus temperature relationship (76) of an asphalt prepared from Mexican petroleum in a batch steam still. The penetration of the asphalt at 25°C., 100 g., and 5 sec. was 62; the Ring and Ball softening point was 52.2°C. The smooth curve obtained over the wide range of viscosities is a good indication of the accuracy of the methods of measurement used. Further, the curve indicates that a gradual change occurs in the physical state of the asphalt as the temperature is raised or lowered.

Numerous empirical methods have been proposed for evaluating the susceptibility (change of consistency with temperature) of asphalts. Most of these methods have been reviewed and criticized (107), and the proposal made that the susceptibility of an asphalt be expressed as a function of the slope of some linear temperature–viscosity relation. Although the most simple expression would be the slope of an arithmetical plot of temperature against viscosity, such a plot is not linear even over a short temperature range. However, for most asphalts a plot of the logarithm of viscosity against temperature is essentially a straight line for limited temperature ranges above and below the softening point. The asphalt viscosity index proposed was expressed as

$$A.V.I. = 100\left[\left(\frac{\eta_c}{\eta_d}\right)^{\frac{1}{t_c - t_d}} - 1\right] \tag{4}$$

where η_c and η_d are the viscosities, in poises, of the asphalt at temperatures (°C.) t_c and t_d, respectively.

The *A. V. I.* evaluates the percentage change in the viscosity of an asphalt for a 1°C. rise in temperature. To obtain the index for a particular asphalt it is only necessary to determine experimentally the viscosities at two temperatures within a range where a plot of log viscosity against temperature gives a straight line. Indices may be developed for a given asphalt for temperature ranges both above and below the softening point. The former is of interest in the processing of asphaltic materials, whereas the latter is helpful in evaluating their behavior under service conditions.

Recently Nevitt and Krchma (68) developed an expression based on an equation similar to equation 3, by which they evaluated the susceptibility of a number of asphalts over a wide temperature range. Also, a new application of the penetration test to the measurement of the susceptibility of asphalts to temperature has been given by Bencowitz and Boe (12). They found that the equation

$$p = A + B \times C^t \tag{5}$$

where p = penetration in decimillimeters, t = temperature in degrees Centigrade, and A, B, and C are constants characteristic of each asphalt, held for asphalts of different sources and methods of processing.

The viscosities of bitumens were measured, years ago, by Pochettino (77), who employed a capillary viscometer and the falling coaxial cylinder viscometer proposed by Segel (98). The falling-cylinder viscometer has been used to evaluate asphalts possessing consistencies above 10^5 poises;

thus it may be used over about the same range as the alternating stress method discussed above. Further, the method has been adapted (111) to a study of the increase of consistency with time, which is a characteristic of most bitumens. After a bitumen has been melted and allowed to cool, a progressive hardening occurs, which varies markedly with the type and the source of the material used. However, the rate of hardening decreases rapidly with time. This increase in viscosity is not due to loss of volatile constituents, because careful reheating and cooling will return the bitumen to its original consistency. Mechanical working of the asphalt will have the same effect as heating, but to a lesser degree, indicating that time-hardening is a manifestation of thixotropy.

TABLE 4

Increase of viscosities of asphalts with time

ASPHALT	ELAPSED TIME AFTER COOLING	VISCOSITY AT 25°C.
	hours	*poises* × 10^{-6}
A	3	2.11
	24	2.12
	51	2.14
	96	2.14
	168	2.18
	336	2.25
	936	2.26
	2523	2.32
F	3.5	3.98
	24	4.29
	48	4.48
	75	4.62
	148	4.80
	240	5.04
	507	5.30

In the experimental study of the "time-hardening" of asphaltic bitumens a number of falling coaxial cylinder viscometers were filled simultaneously with a particular bitumen. The loaded viscometers were placed in an air bath maintained at 25° ± 1°C. Individual instruments were removed from time to time, and viscosity determinations made at 25°C. Table 4 gives the data on two asphaltic bitumens having greatly different time-hardening characteristics. Asphalt A, produced by the vacuum distillation of a Californian petroleum, had a penetration of 55 at 25°C., 100 g., 5 sec., and a Ring and Ball softening point of 47.2°C. Asphalt F, produced by batch steam distillation of a mixture of heavy gravity with some medium gravity petroleum from the Mene Grande field in Venezuela, had a penetration of 63 at 25°C., 100 g., 5 sec., and a Ring and Ball softening point of 51.7°C.

Data similar to those given in table 4 have been obtained for a number of different asphalts, and it appears that both the source and method of processing have a profound influence on the degree of hardening exhibited by the various bitumens. Since the bitumens which show the most hardening with time are the ones which also give the greatest deviations from viscous flow, it may be concluded that the degree of extent of this hardening is dependent upon the amount of "structure" potentially present in the material.

Although the elasticity of asphaltic bitumen and bituminous plastics is undoubtedly an important property, comparatively little work has been done toward its evaluation. In all measurements of the flow of bitumens of high consistency at ordinary atmospheric temperatures elastic effects are apparent. The harder the asphalt or the lower the temperature, the more evident these effects become (109), because the permanent (viscous or plastic) deformation being small obscures to a lesser extent the non-permanent (elastic) deformation of the sample.

Pochettino (77) investigated the elasticity of asphaltic bitumens and tars by means of an acoustical method. Recently Rader (79) measured the moduli of elasticity in beams of asphaltic paving mixtures at very low temperatures. The method used was similar to that employed in determining flexure in beams of the usual structural materials. Some preliminary work has been done in estimating the elasticity of compression in asphalt paving mixtures (108, 116). Efforts have been made to increase the elasticity of asphaltic bitumens by the addition of rubber and other materials. German patent 578,934 proposes to improve the elasticity of asphaltic masses by the addition of China wood oil and a condensing agent such as aluminum chloride or ferric chloride. Gemant (34) found that mineral oils possess elasticity, and he ascribes the effect to a fine lattice work of colloidal particles within which the liquid phase is held.

From the above outline it must be admitted that although rapid advancements have been made during recent years, our understanding of the physical chemistry of asphaltic bitumen is still quite elementary. The chaotic condition of the information concerning the various phases of the problem is mainly due to (1) the complex composition of asphalt, (2) the fact that asphalt from various sources and processed by different methods varies greatly, and (3) the fact that the determination of any property is frequently influenced directly or indirectly by one or more characteristics.

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