

Constitution and Characterization of Paving Asphalts

JAMES H. HAVENS, Research Chemist, and
W. F. DANIELS, Assistant Research Chemist, Kentucky Department of Highways

This paper contains results of analyses with asphalts of various composition and derivation. The objective of the study is to define and correlate constitution and fundamental character of asphalts in a manner significant to their use in highway pavements.

Further confirmation of the existence of three discrete solubility fractions in asphalts was obtained by extraction methods and by paper-partition chromatography. Paraffin bodies were revealed by microscopic examination of thin films. Asphaltene fractions showed the presence of particulate material by electron microscopy and also revealed indications of peptized asphaltene bodies. Oils dialyzed from asphalt exhibited fluorescence, when exposed to ultra violet radiation, similar to components of the oil fractions obtained by extraction. Oven tests revealed increases in asphaltenes and resin fractions and attendant hardening of the asphalt.

It is suggested that proper interpretation of asphalt composition is contingent upon adequate means for measuring the fundamental shearing characteristics and other rheological properties of the composite asphalt.

●IN 1908, Clifford Richardson, in a treatise which he chose to entitle "The Modern Asphalt Pavement" (1), documented the current status of asphalt technology and quality criteria. Many of the basic concepts which he promulgated are still worthy of some reflection and review. He seems to have been one of only a few at that time who entertained a profound interest in the composition and characterization of paving asphalts. At that time native asphalts, such as Bermudez and Trinidad, comprised the primary sources of paving material, while petroleum residues and distillates were used largely as fluxes and solvents. It was known then that solubility in light naphthas varied with different asphalts; that portions of the naphtha-insoluble materials were soluble in carbon tetrachloride; and that the remaining fractions, except for inert minerals and elemental carbon, were usually soluble in carbon disulfide.

The naphtha-soluble fractions were first called "petrolene" and the insoluble fraction called "asphaltene." Richardson elected to use these terms in the plural in order to gain the inference of mixtures of compounds belonging to a solubility class. He also suggested that the term "malthene" might preferably be used to designate the naphtha-soluble portions because they resembled oily materials to which the term "maltha" had been applied elsewhere, and that the term "petrolenes" be reserved for those portions volatile at 325 F.

He proposed the term "carbenes" for those materials insoluble in cold carbon tetrachloride but soluble in carbon disulphide. He rejected the existence of a "resin" fraction on the basis that alcohol-soluble portions of oils did not resemble resins in their behavior toward reagents. Although he published analytical data intended to characterize asphalts on this basis, he did not apply the terms directly. He regarded the oil constituents as being comprised of paraffinic, olefinic, and naphthenic hydrocarbons and the asphaltenes as being comprised of polycyclic aromatics. He differentiated petroleum crudes by their yield of asphaltic residues or paraffin residues and wax contents.

In 1916, Marcusson (2), in Germany, criticized Richardson's scheme for fractionation, because it did not take into account the saponifiable portions and did not reflect the chemical character of the separated constituents. He surmised that, besides the oily constituents, asphalts contained products formed by oxidation, condensation, polymerization and sulfuration.

He divided the transformed products into: (1) neutral petroleum resins, (2) asphaltene, and (3) asphaltous acids and their anhydrides. Acids and anhydrides were isolated as water-soluble salts. Asphaltenes were precipitated from a benzene solution of the asphalt by adding a large volume of naphtha. Resins were isolated by pouring

the naphtha solution through absorbant fuller's earth from which they were extracted by refluxing with chloroform. The naphtha effluent, on subsequent evaporation, yielded the oil fraction, and the chloroform solution yielded the resin fraction.

He characterized the recovered oils as resembling viscous, fluorescent mineral oils consisting of saturated and unsaturated hydrocarbons. On the basis of the formalite reactions, he concluded that the oil constituents were, at least in part, unsaturated and cyclic compounds. He found, in characterizing the resins, that they softened at the temperature of boiling water and that on heating in a naphtha solution they darkened, became insoluble, and assumed the character of asphaltenes.

Marcusson's work has served as a pattern for further development and refinement of analytical study of asphalts. Strieter (3) substituted pentane for naphtha in the precipitation of asphaltenes and ethyl ether for benzene and chloroform (or carbon disulfide) in extracting the resins from the fuller's earth. He assumed that the determination of asphaltous acid would usually be omitted from ordinary fractionation procedures and considered the essential fractions to be simply asphaltenes, resins, and oils.

Holberg, et. al. (4, 5), have extended and refined fractionation procedures to include differentiations of hard and soft resins and waxes; and observed further that asphalts deficient in resins are characteristically associated with poor serviceability, poor adhesion, and a "cheesy" appearance; while high asphaltene and high resin contents (favorable to dispersion of the asphaltenes) impart low-temperature ductility and good serviceability to the asphalt.

As early as 1924, Nellensteyn (6) attempted to explain the rheological behavior of asphalts on the basis of colloidal theory. Richardson had suggested that asphaltenes imparted body to the asphalt. The oil fraction, of course, is expected to exhibit pure Newtonian or purely viscous flow; and if the asphalt does exhibit non-Newtonian properties, these characteristics are attributed in some way to the presence of asphaltenes and resins. Mixtures of asphaltenes and oils differ greatly from mixtures of asphaltenes, resins, and oils. Without resins, the asphaltenes tend to be somewhat insoluble in the oil and to flocculate. The presence of resins seems to enhance their dispersion or mutual solubility, and the degree of interassociation is thought to be the controlling influence in non-Newtonian properties. The resins are intermediate between oils and asphaltenes, both in structure and molecular weight, and may be considered either as a necessary link in a progression of dependent solubilities or as protective colloids.

The present study emanates from a desire to further characterize and correlate the fundamental properties of asphalts in a way that would be significant to their use in highway pavements. The study has been largely exploratory, guided by three general theses: (1) the composition of an asphalt is outwardly manifest in its physical properties, and the two can be correlated if expressed in fundamental terms; (2) the fundamental rheological properties of an asphalt provide the only rational criteria from which to judge its usefulness as an aggregate binder for paving; and (3) criteria for paving-mixture design must be developed on an equally fundamental basis before these properties can have significant meaning. Changes in asphalts with time and ambient temperatures are naturally of particular interest, because permanence is inferred as a quality sought in a pavement and because hardening of the binder is thought to contribute detrimental influences to the pavement, causing it to crack and unravel.

ANALYSES OF ASPHALTS BY SOLUBILITY FRACTIONS

Conservative estimates suggest that the number of specific compounds that might exist in an asphalt would be so overwhelming as to preclude any possibility of ever isolating or cataloging them in this manner. Fractionation into solubility classes or groups (such as oils, resins, and asphaltenes) conveys considerable significance as to the molecular structure of the compounds and their relative proportions within the asphalts. Any further differentiation of types of compounds within these general solubility classes would serve to further characterize the fraction as to its relative susceptibility to reactions such as those causing hardening. In this respect, the ultimate objective would be to ascertain the relative proportions of paraffinic, olefinic, or naphthenic types of compounds comprising the oil fraction and, possibly, to characterize the resins more

specifically as to their compound structure and derivation.

The feasibility of fractionating asphalts, although guided by numerous published procedures, was approached with some skepticism. The procedure described by Strieter and patterned after Marcusson was selected for its simplicity but was appropriately modified to fit the convenience of the situation. N-heptane and n-hexane, instead of pentane, were used as solvents for the oils and resins.

A 5-gram sample was used. The hexane- or heptane-soluble asphaltenes were filtered out, washed and dried to constant weight, and the percentage was calculated directly. The filtrate containing oils and resins was washed through fuller's earth contained in a Soxhlet filter thimble. This filtrate, slightly amber in color, was evaporated to constant weight to obtain the oil fraction. The fuller's earth was then refluxed with ether in the Soxhlet apparatus for a period of several days to extract the resins. Resins were recovered from the ether solution by evaporating to constant weight.

The results of these analyses for seven asphalts used in the study are presented in Table 1. The table also shows the analysis of the same asphalts after "weathering" for 7 days in a forced-draft oven at 100 C. ($\frac{1}{8}$ inch film thickness).

TABLE 1
ANALYSIS FOR CONSTITUENTS OF ASPHALTS
(Unweathered and after 1 week of oven weathering at 100C., $\frac{1}{8}$ -inch film)

Sample	Source of Crude and Method of Refining	77 F. Pen.	77 F. Duct.	Soft. Pt.	Asphal- tenes	Resins	Oils	Totals	Loss on Heating	Diel Const.
				F.	%	%	%	%	%	
Unweathered										
S-0 ^a	(Unknown)	75	150+	122	16.93	14.01	68.42	99.36		
A-1 ^a	Mid. Cont., St. Run	90	150+	113	15.02	14.59	66.42	96.03		2.89
F-1 ^a	Unknown, St. Run	88	150+	115	13.93	13.82	68.99	96.74		
F-1	Unknown, St. Run	88	150+	115	11.92	18.10	67.00	97.02		
D-1	Cal. St. Run	81	150+	115	12.30	23.90	57.80	94.00		3.39
B-1	Venez., St. Run	89	150+	118	17.80	22.90	53.70	94.40		2.99
C-2	Rocky Mt., Cracked	77	150+	119	24.40	18.50	52.10	95.00		2.69
E-2	Mid. Cont., Cracked	70	150+	112	19.40	14.30	70.80	104.50		2.99
Weathered										
S-0		26	39 & 65	140	18.53	21.17	58.63	98.33	1.39	
A-1		21	26 & 30	139	19.26	22.02	59.69	100.97	1.25	
F-1		24	12 & 15	141	17.25	20.27	63.10	100.62	0.19	
D-1		12		153	21.70	25.50	49.60	96.80	1.08	
B-1		23		154	25.90	23.90	47.50	97.30	0.81	
C-2		11		198	31.20	15.50	52.90	99.60	1.05	
E-2		10		181	27.40	14.10	60.30	101.80	0.81	

^a Asphaltenes determined as n-heptane insolubles, other samples, determined as n-hexane insolubles

The mere accomplishment of the fractionations was not particularly satisfying but was a necessary expedient to further study. The precision achieved was somewhat disappointing and may be adjudged from the summations of separated fractions. The accuracy of the separations, of course, can only be appraised from the standpoint of fraction purity. An attempt was made to evaluate fraction purity, as well as fraction character, by the use of paper-partition chromatography, the results of which are discussed elsewhere in the report.

The oven exposure was deliberately made severe in order to produce extreme hardening. It was suspected, or feared, that the accuracy of the fractionations would not reveal slight changes in composition, but the analyses after hardening showed increases in asphaltenes and reductions in oils in every case and little change in resins. Insofar as the asphaltenes and oils are concerned, the results conform with and confirm the concepts of composition that have appeared in the literature during the past several years. Susceptibility to hardening has been considered by Pauls and Welborn (7), on the basis of accelerated oven tests, to be variable with respect to source of crude and method of refining.

With respect to resins, it is possible that the rate of conversion of oils to resins was naturally balanced by the rate of conversion of resins to asphaltenes. This possibility of dynamic balance or equilibrium has been suggested by earlier theorists. For example,

it has been noted that the formation of asphaltic substances in lubricating oils is attended or even preceded by the formation of resin-like compounds and that their concentration may remain fairly constant while the asphaltene-like substances increase in concentration.

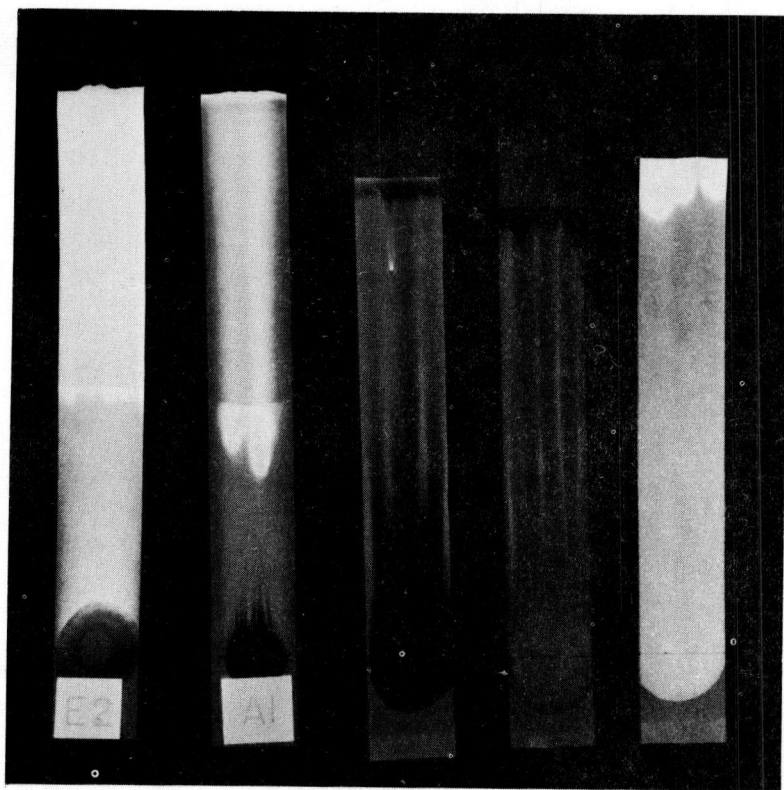


Figure 1. Typical chromatographs of composite asphalts and fractions. The two asphalts, E-2 and A-1 were developed about half way with hexane and butanol and then full length with acetone and methanol. The asphaltenes remained at the bottom, and resins developed half way up, and the oils developed to the top. The three unlabeled strips at the right are asphaltenes, resins, and oils separated from A-1, developed with benzene.

It is of interest to note, too, that the hardening process involved only a slight net loss in weight; this implies that either there was no appreciable evaporation of lighter constituents or else that the evaporation loss was compensated by oxygen absorption from the air.

STUDY OF CONSTITUENTS BY PAPER CHROMATOGRAPHY

As mentioned previously, the purity of the fractions and the discreteness of the boundary between the fractions was of some concern. It was felt that greater significance could be attributed to the fractionation if it could be demonstrated, at least qualitatively, that a recognizable boundary did exist or, if such did not exist, to characterize the boundary condition by some recognizable qualities. Paper-partition chromatography seemed to offer some interesting possibilities.

Basically, partitioning of complex mixtures by paper chromatography results from the combined influences of capillary migration of the solvent, the adsorptive attractions between the solutes and the paper, and the solubility of the solutes. Adsorption and degree of insolubility are assumed to exert restraint upon the movement of the solutes. By shifting the dynamic balance among these principal forces by a judicious selection of sol-

vents, the rate of migration of some components may be increased or retarded or may be caused to succumb to absorption and remain in situ.

Partitioning of complex mixtures by this method has been used rather extensively in studying certain biochemical processes, but its application to asphalt analysis originated within the past 2 years (8). During the course of the present study, Mariani (9), Herd (10), and Csanyi (11) have made independent chromatographic studies of this nature.

The value of partitioning is, of course, contingent upon a suitable method of identifying or characterizing the material after partitioning has been effected. In this case, fluorescence to ultra-violet light served as a natural distinguishing characteristic.

It was found that chromatographs of the oil fractions fluoresced a bluish white to a deep yellow and contained slight traces of orange; resin fractions, although predominately orange to brown, contained slight traces of yellow on the most advanced extremity and traces of black on the opposite extremity. Asphaltenes were predominately black but contained slight traces of orange and brown on the most advanced extremity. These observations suggest that discrete color boundaries do exist and, also, that the fractionation is not as discriminating as paper partitioning.

When benzene alone was used as a developing solvent for the composite asphalts, a continuous color spectrum from bluish white to black resulted. Differences among samples were easily recognized. The most-advanced oils of Sample No. B-1, a Venezuelan asphalt, fluoresced a bluish white, which is thought to be indicative of naphthenic character. Pure paraffins are thought to be water clear and nonfluorescent. Complexity in molecular structure, therefore, is thought to be related to the progression in coloration from the blue side of the spectrum to black on the red side.

Using n-hexane as the developing solvent for the composite asphalts, it was found that the asphaltenes tended to migrate. Since they were assumed to be insoluble in this solvent in the fractionation procedure, there seemed to be a disparity in solvent selectivity in the two methods. Additions of n-butanol to the hexane imparted greater selectivity to the solvent and permitted the resins and oils to migrate without interference from the asphaltenes.

It was possible, too, to develop the oils and resins to some length with hexane and butanol and then to remove that solvent and to develop the oils further in a 1-to-1 mixture of acetone and methanol, leaving the asphaltenes and resins in situ. Without the methanol, acetone permitted resins and oils to migrate together. If acetone and methanol were used as the original developer, the oils migrated with the same selectivity.

In general, discrete partitioning of color boundaries could be achieved by controlling solvent selectivity. Just where these color boundaries should be established for fractional analyses is still somewhat a matter of conjecture. The fact that traces of orange appeared in the separated oil fractions, while an abundance of orange appeared in the resin fractions, leads to the conclusion that some interfractional contamination does result from the method used and that double precipitations and extractions may be necessary in order to obtain purity in the fractions.

It further suggests that the oil fraction should in all probability be considered to consist of three discrete subfractions: (1) the yellow-fluorescing portion; (2) the blue-fluorescing portion; (2) which are thought to be naphthenic; and (3) nonfluorescing oils, which would be largely paraffinic in character. It also suggests that the resins consist of at least two subfractions, since they seem to consist in part of an orange-fluorescing material contrasted against a material somewhat brownish in color.

Typical chromatographs of developed composite asphalts and fractions are illustrated in Figure 1. The strips here were $1\frac{1}{2}$ inches wide and 12 inches long. Although the photograph was made with ultra-violet light, the separation of components is inadequately portrayed, unless viewed in true color. The sample to be developed consisted of 0.2 cc. of solution (0.2 gm. of asphalt in 50 cc. of benzene) placed dropwise about an inch from one extremity of the strip. Development was carried out by suspending the strips, sample end down, in a closed jar containing just enough of the desired solvent to touch the lower ends of the papers. Full development was usually accomplished in about 4 hours. The chromatographs were then dried of solvent and viewed under light of 3600 Å. It was not possible, however, to preserve them for any length of time without

incurring significant losses in fluorescent brilliance of the lighter constituents.

The selectivity of solvents, although differing somewhat when used as a chromatographic developer as compared with use as an extractant, was guided in a general way by accepted rules of solubility as applied to organic analysis (12): (1) A substance is most soluble in a solvent to which it is most closely related structurally. (2) As one goes higher in any homologous series derivatives exhibit properties more and more like the parent hydrocarbon. (3) Compounds of very high molecular weight exhibit decreased solubility in the inert solvents even though the solvent and solute may be of the same homologous series.

Predictions of solubility must, however, be considered from the standpoint of dielectric properties of solute and solvent. A solvent of high dielectric strength, for example, would tend to be a poor solvent for a low-dielectric solute. On the other hand, a solvent differing radically in structure but having similar dielectric strength may prove to be an effective solvent. Benzene, for instance, is usually an effective solvent for asphalt and paraffinic hydrocarbons, although differing greatly in structure. Solubility predictions have also been extended to include a consideration of similarity in surface tension.

Insofar as asphalt solubilities are concerned, it may be summarized that the greater the departure in structure from the paraffinic type of compound the more deficient in hydrogen the compounds become, and in the higher molecular weights, increasing hydrogen deficiency is indicative of more-highly condensed cyclic or aromatic structures attended by reduced solubility (13, 14).

DIALYSIS STUDIES

Sample A-1 was dialyzed with benzene in a combined osmoticdialysis cell, shown in Figure 2, for a period of 6 months. After about 2 weeks, the benzene began to exhibit some bluish-white fluorescence, which increased steadily throughout the remainder of the period. Under white light the benzene first assumed a slight yellow coloration, which progressed steadily to a deep amber. At first, the bluish-white fluorescence was taken as an indication that only naphthenic and paraffinic types of oils were being permitted to diffuse through the membrane; however, subsequent chromatographic studies of the benzene solution revealed the presence of the yellow-fluorescing component typical of the oil fraction. Since the possibility of transformations occurring within the dialyzed oils during this length of time can not be completely discounted, the yellow component cannot be attributed exclusively to diffusion. Actually there was a slight indication of asphaltenes registered on the chromatograph, which would be even less likely to occur as a result of diffusion. Considering these factors, it is not quite possible from this experiment to assign a specific selectivity or permeability limit to the membrane.

If there were any osmotic pressures occurring during the period, they were so small in magnitude that they could not be observed or measured in the cell used. Osmotic pressures, however, are sometimes considered to be a measure of the forces that attend diffusion. Since the observed rate of diffusion was extremely slow, it may not be so surprising that the osmotic pressure could also be extremely low.

This interest in osmotic pressures is based on their compliance with the fundamental gas law, $PV = nRT$, in which n is the mole concentration of solute or, in the case of colloids, the equivalent concentration of particles having the same kinetic energy as a molecule. Solutions normally exhibit higher osmotic pressures than colloids because of inherent differences in particle weight. As a hypothetical case, consider a liter of asphalt containing 200 gm. of asphaltenes and exhibiting osmotic pressure in the order of 1mm. of Hg., then the mean theoretical particle weight would be in the order of 75 million. In contrast, consider that only 20 gm. of sucrose in a liter of water is sufficient to exhibit over 100 cm. of Hg. pressure while the mean theoretical particle weight, on the same basis as in the case above, is in order of 350, which is in close agreement with its accepted molecular weight.

MICROSCOPIC STUDY OF THIN PREPARATIONS

Although no attempt was made to isolate solid paraffins in the fractionation proced-

ure, microscopic examination of thin preparations by dark-field and oblique illumination revealed a structural quality which might be attributed to the presence of solid paraffins. All seven of the asphalts studied exhibited these bodies to some extent.

Figures 3 and 4 are bright-field photomicrographs of thin preparations, approximately 1000X magnification, showing highly refractile bodies which appear much lighter than the matrix material. Under direct examination through the microscope, they appear prismatic or crystalline.

In the early days of petroleum asphalts, according to Richardson, some crudes yielded asphaltic residues so high in waxes or solid paraffins that they tended to scale, due to crystallization, and to concentrate on the surface. These effects were considered to be a detriment to both adhesion to aggregate and to internal cohesion. Now, by the use of dewaxing processes, similar crudes are probably used indiscriminately; but the amount of wax tolerated in the asphalt is usually in the order of 3 to 5 percent or less. The presence of fairly large percentages of waxes is usually apparent from specific volume-temperature curves, because they may exhibit a volume change of as much as 10 percent over their melting-point range.

According to Pfeiffer (15) paraffin-wax content is still considered by some particularly in Europe, to be closely related to quality of the asphalt; however, this view is probably taken in regard to adhesion and the effect that the paraffins may have on temperature susceptibilities.

ELECTRON MICROSCOPY

The rheological behavior of asphalts, particularly with respect to their degree of departure from strict Newtonian flow, suggests that at least some of them are not true solutions and that their behavior can only be explained on the basis of internal structure. In general, it is now assumed that the oils constitute the continuous phase and the asphaltene the disperse phase, while the resins serve as peptizing agents (the degree of peptization of the asphaltene bodies being the principal factor imparting elasticity and thixotropy to non-Newtonian asphalts).

Katx and Beu (16) failed to find indications of the existence of a distinguishable asphaltene micelle by electron microscopy but concluded that asphaltene may be "potential colloids." In other words, they could be visualized as undergoing molecular aggregation or dispersion, depending upon their degree of solubility or insolubility in the oils with which they are associated.

Figure 5 shows a typical view of Sample S-O, at a magnification of 6,900X, in which the oily phase is quite apparent and separate from the black, presumably solid, asphaltene and resin bodies. In the more-concentrated areas, the large flakes may possibly be platy wax, and there is a somewhat vague, but very real, impression of fibrous structure. Figure 6, shows an area selected from the center of Figure 5 magnified to 41,400X. Unfortunately, however, resolution was not improved due to the thickness of the sample; but the fibrous quality of the structure has been made more apparent. The darker fringes surrounding the black bodies may be indicative of a more-highly concen-

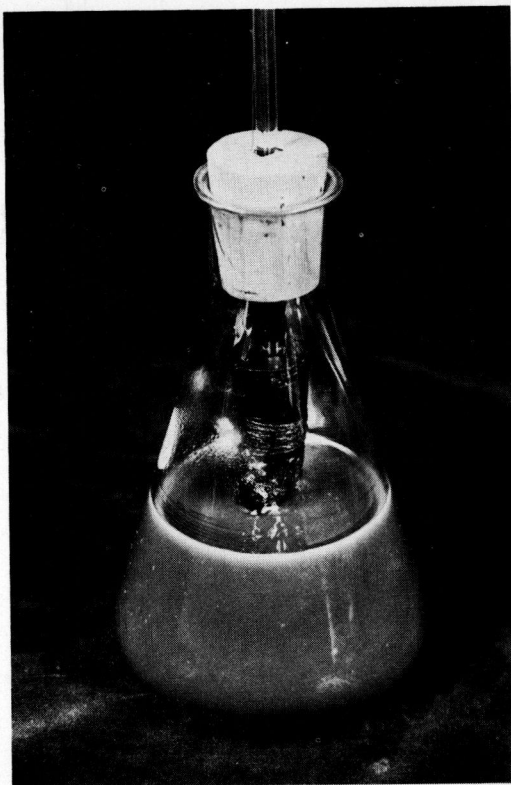


Figure 2. Combined dialysis-osmotic-pressure cell.

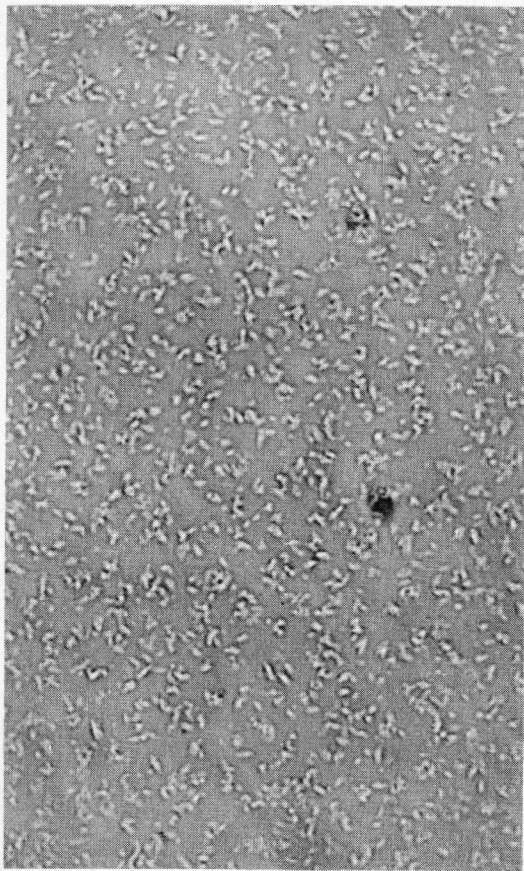


Figure 3. - Photomicrograph of sample C-2, brightfield, magnification approx. 1000X.

trated fibrous aggregation, the dark bodies themselves being the flocculated or precipitated asphaltenes and resins. Since the films here were prepared from a benzene solution, they may not represent an equilibrium condition of dispersion.

In Figure 7 a similar preparation was shadow-cast with vaporized chromium and is shown at a magnification of 17,500X. The black bodies convey the impression of a completely flocculated system, and the oily phase seems to have migrated out into the chromium film.

In a generally way, at least, these studies seem to confirm the existence of structure in asphalts.

RHEOLOGICAL STUDIES

If composition of an asphalt is to be correlated with its rheological properties, the tests must describe a fundamental physical property of the material and

should be expressed in equally fundamental terms. For the sake of clarity, it may be of interest to consider the following generalized version of some classic, though perhaps elementary, concepts applied to the flow properties of matter. They are best illustrated graphically as in Figure 8.

If a material possesses elastic properties as portrayed above, its elastic deformation is proportional to the stress applied ($\text{stress/strain} = \text{a constant}$, called modulus of elasticity). If $\Delta \text{stress} / \Delta \text{strain}$ departs from a constant with increasing stress, the deformation is not elastic but permanent and is called shear (re-arrangement of molecular units) or plastic flow.

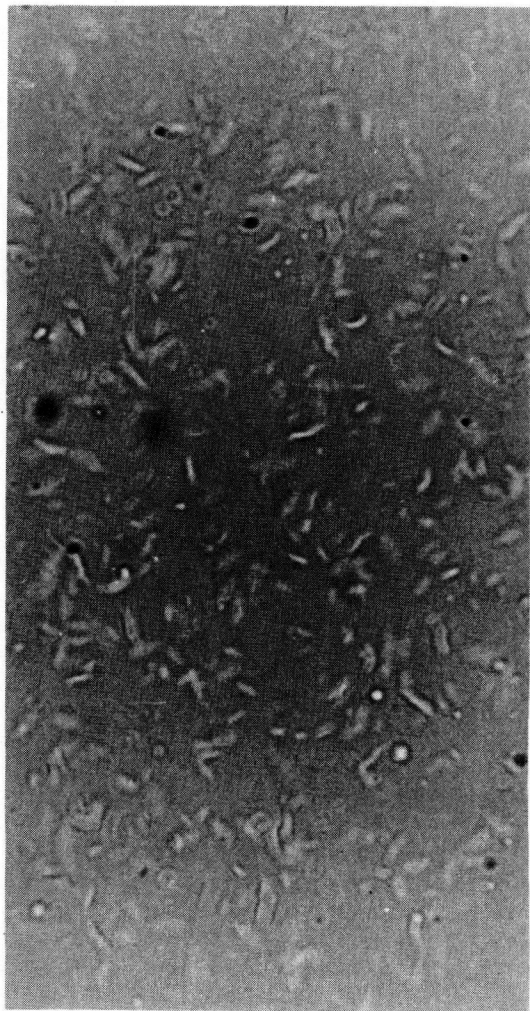


Figure 4. - Photomicrograph of Sample S-O, brightfield, magnification approx. 1000X.

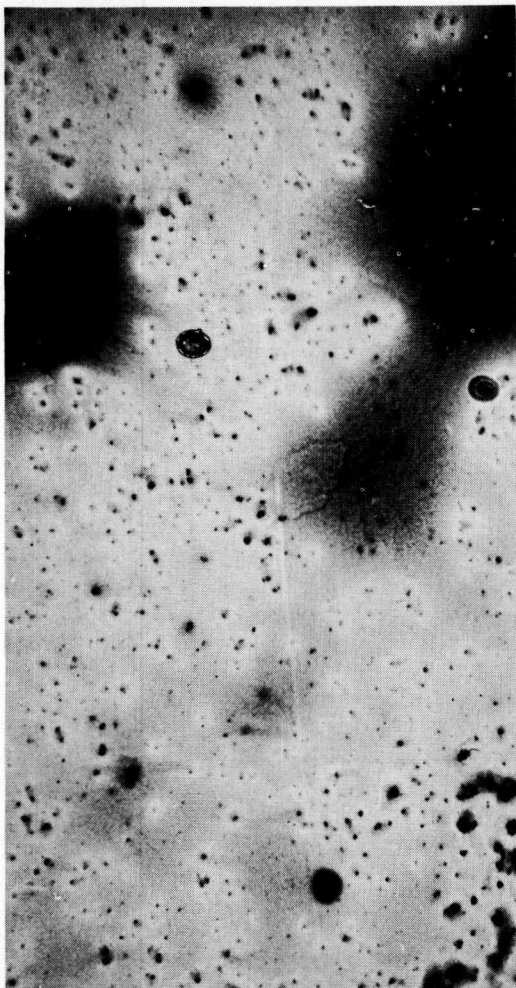


Figure 5. Electron micrograph, asphalt film Sample S-O, magnification 6,900X.

Eventually a point is reached where $\Delta \text{ stress} / \Delta \text{ strain}$ is zero, and the ratio ceases to describe one as a function of the other. Then the material is presumed to be within a region of pure plastic flow and undergoing equilibrium shearing. The summation of deformations first involves an elastic component and then a shear component. This is then an idealized plastic, sometimes referred to as the Bingham solid (17).

A viscous material, or pure Newtonian liquid, is by definition one in which rate of shear is proportional to stress; and $\Delta \text{ stress} / \Delta \text{ rate of shear} = F/R = \text{a constant } (n)$ called the coefficient of viscosity. Thus, if stress and rate of shear are the quantities measured, they should yield a linear relationship when plotted to arithmetic scale; and on extrapolation

to zero rate of shear, should yield zero stress.

If a similar plot of stress versus rate of shear should yield a linear relationship which failed to intercept the origin when extrapolated to zero rate, then the material is considered to be plastic and to have an elastic threshold to shear and complies with the equation $n' = \frac{(F-f)}{R}$. The point of intersection on the stress axis would then indicate the magnitude of the elastic component of the stress. Here, where $\Delta \text{ stress} / \Delta \text{ rate of shear} = n'$, n' has the same dimensions as the viscosity coefficient (n) above. Both express fundamental physical constants of materials and are variable only with respect to temperature. The threshold stress (f) is also a fundamental material constant describing a discrete physical property.

Experimental conformity to either of these idealized concepts would serve to characterize an asphalt as purely viscous or purely plastic. Disconformity would mean that the material possesses visco-elastic properties of somewhat greater

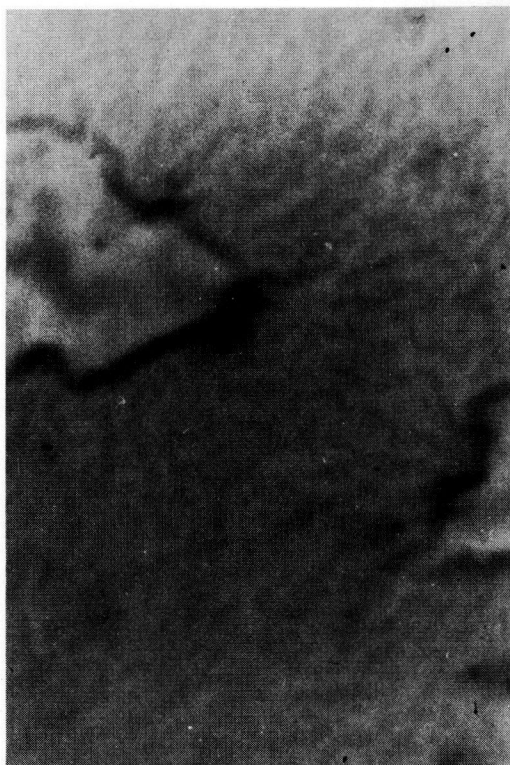


Figure 6. Electron micrograph, Sample S-O, magnification 41,400X.

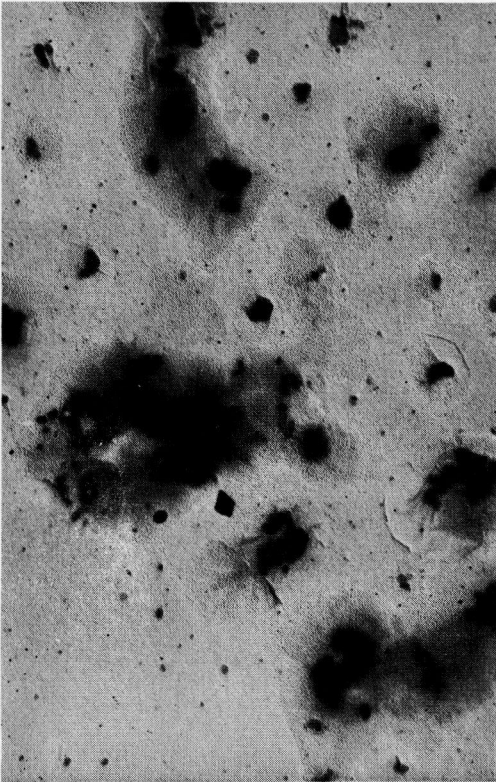


Figure 7. Electron micrograph, Sample S-O, magnification 17,500X, shadow-cast.

Although this treatment may be an oversimplification of concepts, it should be pointed out that the real difficulties involved in an experimental study or evaluation of the rheological behavior of asphalts arise from deficiencies in measuring instruments. In

complexity, which may or maynot be definable (18). Other anomolous flow characteristics have been recognized. In some cases, it has been found necessary to include an abstract exponent in the Bingham equation in order to correct for nonlinearity. An apparently viscous material, for instance, may have internal elastic elements visualized as discontinuous springs acting in a viscous medium or as Maxwell's mechanical model, consisting of a spring and dash-pot connected in tandem (19).

Plastic materials may be considered to have a permanent but deformable internal structure, while thixotropic materials have internal structures variable states of development and decay with respect to time and environmental conditions. Thixotropy would not be revealed as a discrete property of a material from the relationship as discussed above and would have to be evaluated on the basis of time versus rate-of-deformation relationships under constant stress in order to describe such decay and development of structure. In the case of the Bingham solid and the pure Newtonian liquid above, deformation rate (R) necessarily represents equilibrium rates of shear or constant rates of shear with respect to time.

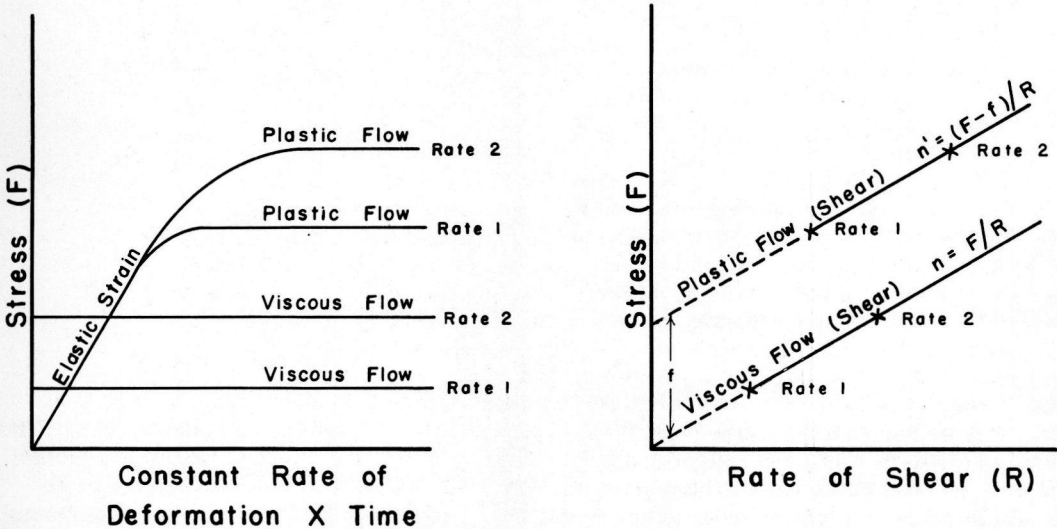


Figure 8. Graphical representation of fundamental-flow characteristics of matter.

a prototype instrument, it would be necessary to preserve a constant shearing area throughout the duration of the test and to

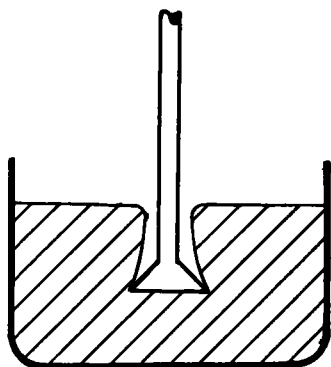


Figure 9. Schematic Drawing of Loading Device.

loads and temperatures. None of these conditions are fulfilled by the standard penetrometer test, although Mack (20) and a number of others (21) were surprisingly successful in applying correction factors in an effort to interpret it on this basis. The rotary viscometer as used by Traxler et. al. (22) and other modifications of the rotary concentric-cylinder types (23) seem to offer the advantage of constant shearing area.

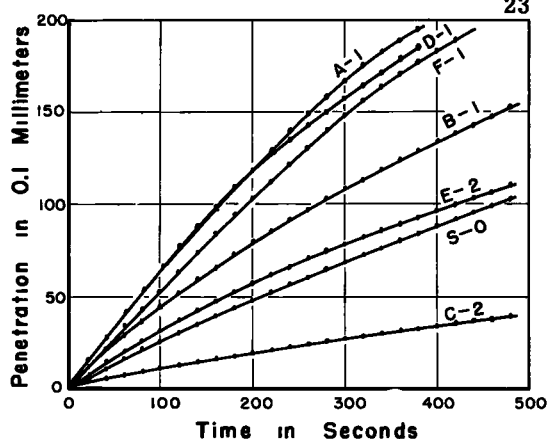


Figure 10. Plot of time versus depth of penetration, for all samples, 62.5 gms. on 1 sq. cm.

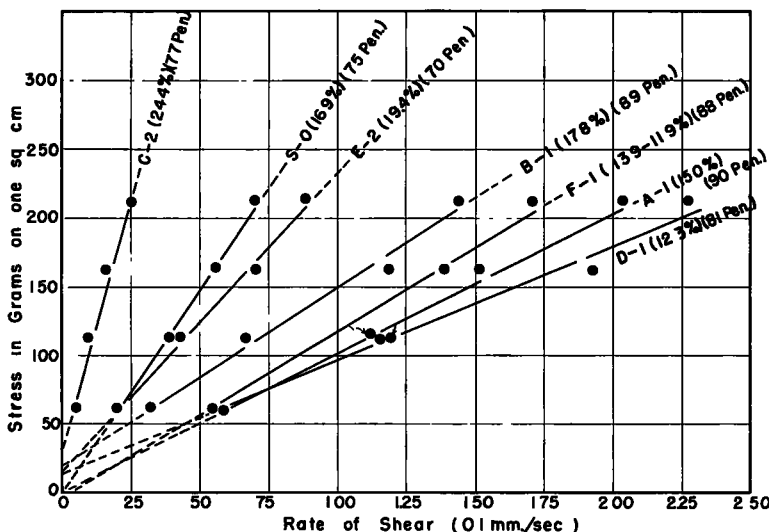


Figure 11. Relationships derived between stress and rate of shear, 77 F., original asphalt. Percent of asphaltene and standard penetration is shown for each asphalt.

In this study, however, the penetrometer was used as a loading and measuring device; but instead of using a standard needle, a truncated cone-shaped bearing-plate type of loading system was used (see Figure 9). All surfaces were amalgamated to prevent adhesion. The loading area was approximately 1 sq. cm. It was not intended to revise the penetration test by this means at all but, rather, to find some expedient means of measuring deformation or shear at somewhat slower rates and to do it in a way that would yield a reasonably linear relationship with respect to depth of penetration and time.

For extremely hard asphalts, a bearing area of approximately 0.08 sq. cm. was used. This was necessary in the case of Samples E-2 and C-2, after hardening in the oven, in order to be able to conduct the test in one day and in order to overcome the threshold stress with a reasonable amount of load on the penetrometer stem.

Thus far these tests have not been made at temperatures other than 77 F. The linearity between depth of penetration and time may be adjudged from the data for one stress level plotted in Figure 10. It was observed that deeper samples and larger sample and larger sample cans yielded linearity over greater depths of penetration. In other words, it was suspected that boundary geometry of the sample may account for some of the departure for linearity.

A mean rate of shear over the approximate range of 5 to 10 mm. of penetration depth was estimated. Mean rate of shear was then plotted against load, as discussed earlier. This was done for the seven asphalts reported in Table 1. The experimental relationships derived (See Figures 11 and 12) are thought to be fundamentally characteristic of the asphalts. It should be borne in mind that these data represent extremely slow rates of shear and involve only about a threefold increase in rate. The resulting linearity is, therefore, not necessarily contradictory to other work reporting departures

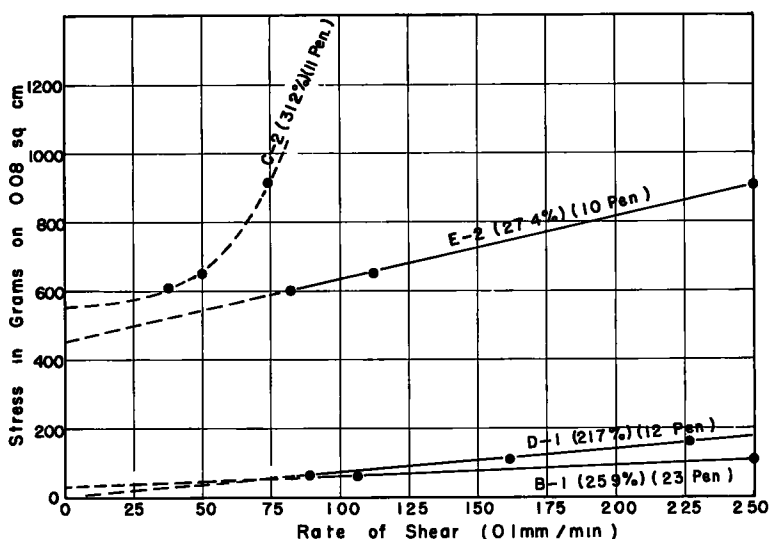


Figure 12. Relationships derived between stress and rate of shear, 77 F., after oven hardening, four asphalts only.

from linearity over ten-to thirty-fold increases in shear rates.

It is quite apparent from Figures 11 and 12 that fundamental rheological behavior of these asphalts is related to, or at least dependent upon, their constitution. It is quite apparent, too, that standard 77 F. penetration fails to differentiate the samples in any intelligible manner. Inasmuch as concentration of the asphaltenes represents the major difference in fractional constitution of the samples studied, it would be expected to reveal attendant rheological manifestations. However, it may not be concluded that these manifestations are not colligative with respect to the resin and oil fractions. The degree of aromaticity of the resins, as considered by Hillman and Barnett (24), may favor a higher degree of dispersion of the asphaltenes, whereas a highly naphthenic or paraffinic disperse medium may tend to flocculate the asphaltenes and reduce their effective concentration.

Samples C-2 and E-2 are purportedly cracked asphalts, the origin of S-O is unknown, and the other four are purportedly straight run materials. Only limited significance can be attached to the extrapolated intercepts in Figure 11, because there was some deviation within the data from which the lines were drawn. Apparently, at least, there is a threshold stress (f) associated with Samples C-2, E-2, B-1, and D-1. The

slopes of the lines, even if considered only as apparent viscosities, tend to increase with increasing asphaltene content.

In Figure 12, the two cracked asphalts are clearly differentiated from the two straight-run materials, the threshold stress is quite unmistakable, and the two asphalts have become more plastic as a result of hardening in the oven. It is not known whether the inflected curve drawn for Sample C-2 is real or spurious. One other observation, however, has a significant bearing on these interpretations:

After these samples had been "dimpled" in the test, it was noted that Samples D-1 and B-1 flowed as a result of the differential "head" surrounding the depression; and there was no trace of the dimple after 24 to 48 hours. The two cracked asphalts retained the dimple in its original shape for several weeks, and the samples had to be melted down in order to restore their original smooth surface. The fact that the two straight-run asphalts smoothed-out means that they flowed under infinitesimal stresses, which clearly characterizes them as viscous liquids.

SUMMARY AND CONCLUSIONS

A cursory knowledge of asphalt constitution enhances basic understanding of their rheological behavior and susceptibility to age hardening. Collectively, these factors are capable of describing the fundamental character of near-solid asphalts and are essential considerations in the development of quality criteria and in establishing specification requirements. This study reemphasizes the need for testing methods that directly reflect fundamental properties of the asphalt and which may eventually afford a rational interpretation of the significance of these properties in paving mixtures. If the mechanical properties sought in a bituminous pavement were sufficiently delineated on an equally fundamental basis, then the criteria for judging the significance of binder properties would be much clearer.

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