

Asphalt Composition and Properties

H. E. SCHWEYER, Professor of Chemical Engineering, University of Florida

The technical material consists of an abbreviated discussion of certain techniques in solvent extraction and adsorption separation procedures for asphalt. It is shown that sharp fractionation is obtained by selective adsorption of methyl cyclohexane solutions on silica gel. These separations produce fractions similar to those from solvent fractionation based on ultraviolet absorption measurements. Additional information is also indicated by infrared absorption studies but the implications at these latter energy levels are not clear at this time. This information provides a basis for evaluating the differences in chemical composition of asphalts which can be valuable in classifying bituminous materials into separate categories.

Based on a gross classification into naphthenic, intermediate or aromatic type asphalts, the paper then discusses the range of physical properties to be expected for each type as a function of processing. The physical properties considered are penetration, softening point, ductility and consistency in absolute units. Generalized charts relating consistency and complex flow and the common physical tests used by asphalt technologists are presented. Comments are made concerning the durability of asphalts as a function of their composition.

● **ACCEPTANCE** of the statement that "knowledge in a field is measured by the brevity with which the concepts can be presented" makes the asphalt technologist pause when the voluminous literature on asphalt is considered. The novice in the field is at first intrigued and finally confused in attempting to deduce simple generalizations regarding asphalt behavior from the numerous empirical relations, incomplete data and conflicting viewpoints found in the art of production and utilization of bituminous materials. To put this art on a scientific basis will require the use of new fundamental concepts to replace obsolete empirical tests and relationships. It is the purpose of this paper to suggest possible improvements in present concepts and to illustrate their application.

Stated briefly the properties and behavior of asphalts are a priori a function of the chemical composition of the material. However, some variation in properties may be expected for a given chemical composition depending upon the history of the material as is the case with metallic alloys where the properties may be altered (for a given chemical composition) by suitable metallurgical treatment. The asphalt technologist's problem therefore reduces to the apparently simple problem of determining the composition of the material, and, considering its history, correlating this composition with the properties and behavior of the material. Unfortunately, such a simple approach is blocked by a lack of suitable methods for determining the composition as pointed out by Csyani and Fong (4) and the recourse is to develop empirical correlations for those properties in which the investigator is interested. These empirical correlations eventually are discarded because further investigations by others prove them invalid as a greater variety of materials is considered.

In general, the properties of asphalt which make it an article of commerce or which control its use can be reduced to one or more of the following: water resistance, resistance to corrosive agents, adhesiveness, stability (or resistance to oxidation or change in physical properties), viscosity, change in viscosity with temperature, emulsifiability, electrical properties, solubility in solvents and a few other special properties, all of which certainly are a function of chemical composition. However, because the physical properties are the most important from the viewpoint of the major commercial uses for asphalt, the principal emphasis has usually been on attempts to correlate them alone. Since most of the physical tests (e.g., penetration, softening point, adhesiveness, etc.) themselves are empirical tests, there result empirical relations among empirical tests for whatever value such relations may have. Fundamental relations be-

tween composition and the individual properties would appear to be more likely to yield valid correlations if a simple logical method for delineating composition could be developed.

The most generally accepted theory regarding the composition of asphaltic materials is that they are composed of a group of hydrocarbons of the general formula $C_nH_{2n+b}X_d$ where n and b vary (b may be negative) and X may be other elements such as sulfur, nitrogen, oxygen and metals (traces of vanadium and other metals are found in many petroleum residuals) (32). O'Donnell (19) presented evidence for empirical formulas of $C_{82}H_{97}N_{0.2}S_{0.5}$ for an asphalt fraction obtained by molecular distillation. The amount present of any individual hydrocarbon may be very small and the value of d is also usually small. Accordingly, the mixtures of these materials, known as asphalt, varies over a range of composition from low molecular weight to very high values with isomers, ring structures, combination of rings, straight chain hydrocarbons, and bridge structures containing other elements as summarized by Gruse and Stevens (10). At the higher molecular weight ranges, polymers and condensation products formed during the processing are also present, but it is doubtful that colloidal carbon exists except as a result of decomposition in certain processing operations as concluded by Katz and Beu (12) from electron microscope studies. Other data refuting the concept of dispersed carbon particles has been presented by Mack (16) based on dialysis. A similar conclusion is presented by Eilers (7) based on X-ray analysis.

Classical methods for determining the composition of asphalt using hydrocarbon solvents such as pentane or propane have never been of any great value for explaining the behavior of asphalts in service although such methods are useful in determining the uniformity of the product. A review of the available data from classical procedures including bibliographies (17, 18) has been given by Neppe. The classical methods fail because they separate on the basis of molecular weight rather than on the basis of chemical composition. It is believed that the proposed Traxler-Schweyer (38) method overcomes some of these difficulties. This method utilized a two step solvent extraction procedure summarized as follows:

	Butanol Extraction	Acetone Extraction
Asphalt	{ Extract Asphaltics (Raffinate)	{ Saturates (Raffinate) Cyclics (Extract)
Sample		
5 grams.		

The n-butanol is employed to extract the low molecular weight oils leaving a residual raffinate of high molecular material called asphaltics. The butanol free extract is subsequently extracted with acetone to yield a cyclic (extract) fraction and a saturates (raffinate) fraction. Typical results for this method of analysis are shown in Figure 1, and experience with over 2,000 analyses has indicated that this procedure is of considerable value. It is not to be inferred that the procedure is a cure-all or a utopian method, but its simplicity and usefulness in explaining asphalt behavior in the experience of the author has shown it to be of merit. (Note: since the acetone raffinate is probably composed of a variety of types of saturated hydrocarbons, the term "paraffinics fraction" used in the earlier paper (38) is somewhat restrictive and hence, in this paper is replaced by the term "saturates" fraction.)

Asphalts exhibit colloidal properties in a variety of ways as has been discussed by Traxler and Romberg (37). It has been recognized that asphalts may exhibit the properties of a gel — examples are highly blown asphalts showing age-hardening characteristics (37), a great propensity to stain paper because of oil exudation or syneresis (13), high elasticity and other complex flow characteristics where deformation is not linear with the applied stress (24). Conversely other asphalts exhibit the properties of sols and show low stain propensity, little change with age and essentially truly viscous flow. Other asphalts may exhibit any of the properties intermediate between those of a true gel and those of a true sol. The term sol as used in this paper indicates a highly solvated material having properties similar to those of a true solution regardless of whether the material is or is not a true solution.

Attempts to explain differences in asphalts by use of hydrocarbon selective solvents

alone is not fruitful because the quantity of "asphaltenes" or high molecular weight material alone is not controlling (37). It is the kind of low molecular weight material associated with the high molecular weight material that is important. This is particularly true where the amount of high molecular weight material separated is critical with the amount of solvent and the conditions employed as is the case for "asphaltenes" and so called "resins."

As an example, two 55 penetration asphalts from different Texas crude oils might have properties somewhat as given in Table 1, where each shows about 24 per cent asphaltenes.

The data illustrate that at some given empirical consistency (55 penetration) the asphaltene content is of no value in distinguishing between the two materials. Furthermore, "homogeneity" as deduced from a negative spot test is also a meaningless term, since Asphalt A is definitely more nearly a mixture of heterogeneous phases having the properties of a gel as evidenced by its higher stain, lower ductility, and greater degree of complex flow.

It is obvious that these variations must be the result of differences in chemical composition. The application of component analysis to these asphalts provides some information concerning these chemical variations as indicated by the data in Table 2.

The higher refractive indices for the components from Asphalt B together with the greater amount of cyclic fraction (acetone solubles at -10 F) are indicative of a higher degree of unsaturation. This unsaturation may be from aromatics or some other configuration and for Asphalt B would be expected to produce a stronger solubilizing action for the high molecular weight asphaltic materials present with less tendency to form a gel. The oils in Asphalt A are, relatively, more naphthenic or more saturated in nature and although the amount of high molecular weight material (asphaltenes) is less, this asphalt has a higher viscosity at a given power input. This higher viscosity and the higher degree of complex flow (smaller values of "c") are manifestations of the gel-like nature of the asphalt which is also indicated by the high stain index resulting from syneresis or exudation of the oily components. Such colloidal phenomena point to partial solvation of the high molecular weight asphaltics by the saturated oils rather than the formation of highly solvated mixtures with aromatic oils of higher refractive index as in Asphalt B.

In order to confirm the relative degree of saturation in the oil fractions obtained by component analysis, ultraviolet absorption analyses have been made on numerous asphaltic materials. Typical results are given in Figure 2 which are for a Gulf Coast petroleum residual. The analyses were made using a Beckman spectrophotometer Model DU with a 15 percent normal butanol-85 percent spectral grade iso-octane as the solvent, using a technique by Schweyer (26) reported elsewhere. The butanol was employed to assist in effecting complete solution of the oils in the solvent since the butanol extract as obtained by component analysis at 122 F apparently contains some colloidal material. The absorption solvent mixture used produced solutions with no apparent turbidity in ordinary light, but a definite Tyndal effect was observed when some of the solutions were exposed in a Tyndallometer. These effects would tend to reduce the sensitivity of the spectral analysis.

The results in Figure 2 may be considered to indicate the following: (a) The component analysis method is partially effective in separating the components consisting of CH = bonds as indicated by the lower optical densities of the saturate fractions for wave

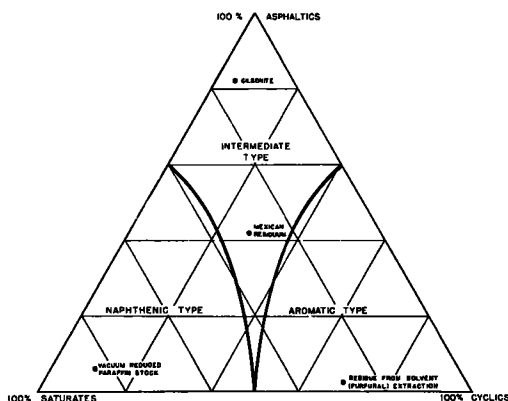


Figure 1. Generalized composition ranges for various bituminous residuals.

TABLE 1
PROPERTIES OF TWO 55 PENETRATION ASPHALTS

	Asphalt A	Asphalt B
% Asphaltenes	24	24
Sp. Gr. at 77 F	0.980	1.035
Pen. 32 F, 200 g/60 sec	27	16
77 F, 100 g/5 sec	55	55
115 F, 50 g/5 sec	135	290
R and B softening point, F	149	125
Ductility, 77 F, 5 cm/sec	6	200
Viscosity at 77 F, megapoises ^a	24	3.0
Complex flow, "c" ^a	0.5	0.9
Stain Index ^b	10	5
Spot Test	N	N

^a See reference 24.

^b See reference 13.

lengths above 220 millimicrons. If the separation had been complete, the saturate fraction would show no appreciable absorption in this range. (b) The peaks shown in the range from 220-240 millimicrons indicate the presence of conjugated acyclic dienes which are separated (partially) in the acetone extraction. (c) The shoulder at 250 to 270 millimicrons indicates the presence of monocyclic aromatics and/or conjugated acyclic trienes which also are partially separated and concentrated in the cyclic fraction. (d) The absorption in the range from 270 to 350 millimicrons indicates a generalized absorption attributable to a variety of compounds such as polycyclics, unsaturated heterocyclics and oxygenated compounds, etc., which are present in relatively small amounts. In general the ultraviolet absorptions confirm the relative naphthencity and aromaticity based on the refractive indices of the fractions separated by component analysis. The average deviation in spectral absorption of the fractions for combined component analysis and spectral analysis is of the order of plus or minus 2 percent. Thus, in comparing different materials a minimum variation of about 4 percent in absorptivity might be considered the minimum for significant differences in composition.

Certain selective adsorption studies (27) using a chromatographic procedure with silica gel have been made on the asphalt shown in Figure 2. The ultraviolet spectral

TABLE 2
COMPONENT ANALYSIS FOR TWO 55 PENETRATION ASPHALTS

	Asphalt A	Asphalt B
Asphaltic content—%	36	44
Saturates—%	54	38
RI at 158 F	1.5000	1.5300
Cyclics—%	10	18
RI at 158 F	1.5500	1.5700

absorptions for two separated fractions are similar to those separated by solvent extraction as illustrated. However, it should be noted that the asphaltic component is present in the chromatographed samples whereas it has been separated out by solvent fractionation prior to the ultraviolet analyses. At this stage of the study no advantage of either method for delineating composition is indicated. In addition to the ultraviolet absorption, infrared absorption data have been reported by Schweyer (26), but here also the data are of a preliminary nature. They appear to confirm information from the ultraviolet studies as shown in Figure 3 for the saturate fraction from a naphthenic asphalt similar to the one shown in Figure 2 and for the cyclic fraction from a so-called aromatic asphalt. To date both asphalts and their components show significant absorption at 3.41, 3.49, 5.85, 6.20, 6.85, 7.28, 9.7, 10.3, 11.5, 12.3, 13.45 and 13.9 microns which indicate the presence of various functional groups. Straight chain hydrocarbons on aromatic nuclei are shown by absorption at the lower wave lengths. At the two higher wave lengths the absorption at 13.45 microns is considered to represent short chain CH_2 groups whereas at 13.9 microns the absorption is attributed to long CH_2 chains. The relative absorption at the intermediate wave lengths and in the ultraviolet region may eventually provide a means for quantitative characterization of asphalts by such techniques. However, the variation for different fractions obtained from the same or different sources are small and at the present time there is some question as to the value of such measurements on these gross mixtures of hydrocarbons and their mixtures with other oxygen, sulfur and metallic complexes. Additional research in this field is indicated.

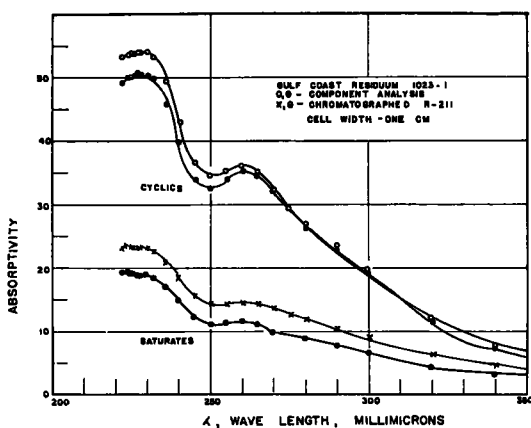


Figure 2. Ultraviolet spectrograms for certain residual asphalt components.

COMPOSITION OF ASPHALTS

Little information is available in the literature on the chemical composition of asphalts since it is expected that any one chemical compound is present in only minute quantities making the separation and identification of individual compounds tedious and difficult. Gruse and Stevens (10) have considered the available data as has also Sachanen (25). Some comments on the chemical composition were presented previously (38) in which it was pointed out that asphaltic residues might be expected to contain higher molecular weight homologues of the materials found in lubricating oils. The problem is more complicated, however, since the high temperatures employed in producing asphalts may result in decomposition with the subsequent loss of hydrogen, sulfur and oxygen originally present in the crude oil and particularly when any of these elements tend to concentrate in the asphaltic fraction as is usually the case for sulfur.

In studying the complex compositions present in asphalt it appears that, as a first step, the most expedient procedure is to consider the types of compounds present and how their presence affects the properties. Following a delineation as to type, subsequent study can be pointed toward further subdivisions of each type. Based on available data and the literature the following appear to be reasonable statements regarding the materials to be found in asphalts.

1. Naphthenic and aromatic ring compounds (with or without side chains) constitute the major chemical types with the probability that the aromatic condensed rings pre-

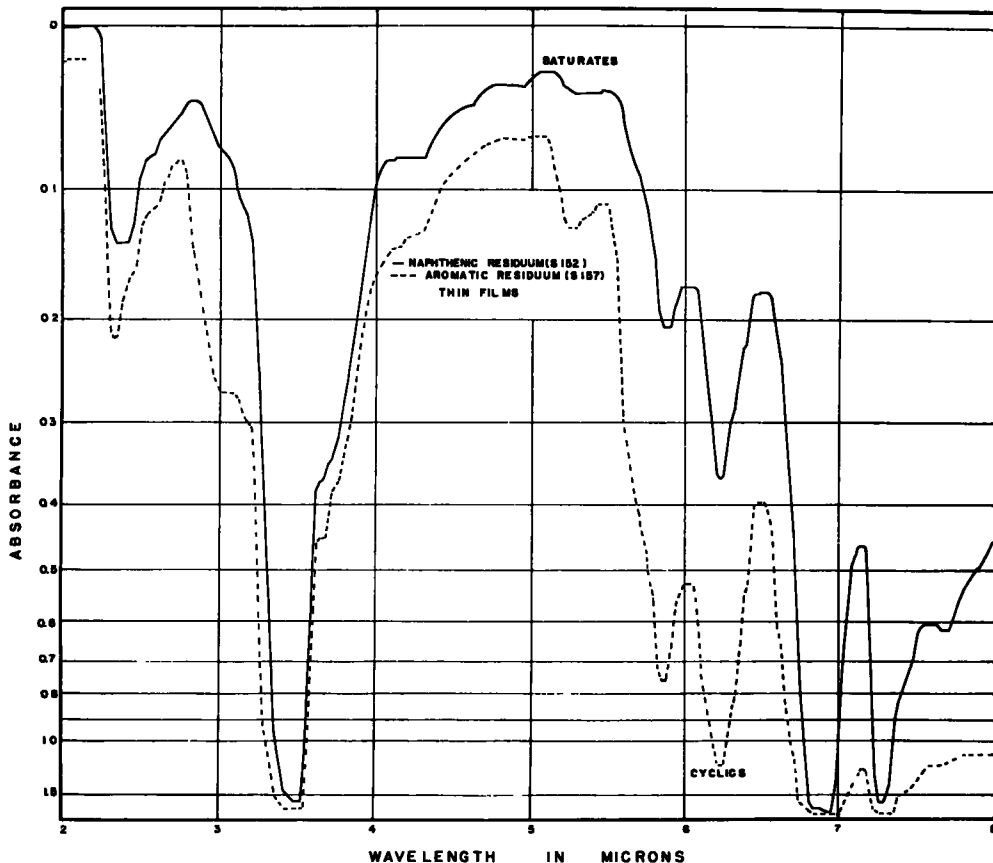


Figure 3. Infrared spectrograms for certain residual asphalt components.

dominate in the cyclic fraction as obtained by the Traxler-Schweyer method.

2. The ring compounds may be condensed aromatic nuclei, or five and six member rings connected by side chains with or without sulfur, nitrogen or oxygen bridges, although these elements also may be present as part of the ring structure. The saturated ring compounds with long paraffin chains are found in the saturates fraction by component analysis. The efficiency of separation will influence the shape of such plots as shown in Figures 2 and 3.

3. Pure aliphatic compounds (paraffin or isoparaffin hydrocarbons) are present only in small quantities with paraffinicity being imparted to the asphalt by the presence of long side chains on the ring compounds, with the cyclic fractions having the shorter chains. Waxes representing solid hydrocarbons, either amorphous or crystalline in nature, are found in the saturates fraction with the waxes being predominately naphthenic in character. Waxes that are insoluble in n-butanol are found in the asphaltic fraction.

4. Unsaturated straight chain compounds are present in minor quantities except where the material has undergone considerable thermal treatment such as cracking.

5. The range of molecular weights encountered for the components for the mixture is wide and varies upward from about 200 for the lighter oils present (8, 11) It is this wide range of materials and the mutual solubility effect of their presence which permits the solution of high molecular weight material in solvents which otherwise would not dissolve the pure high molecular weight material. Partial or selective solvents destroy these mutual solubility effects permitting the separation of the asphalts into components of a general type, that is, high molecular weight, high degree of saturation or high degree of aromaticity.

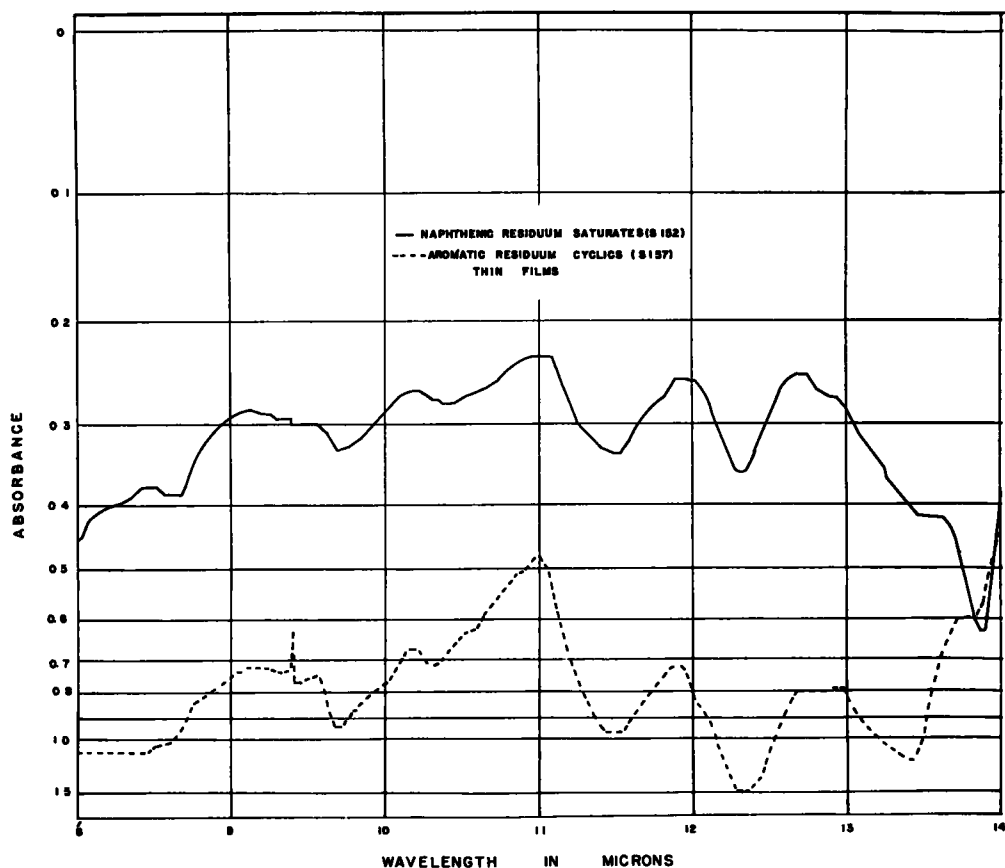


Figure 3. (Continued)

6. The properties of the asphaltic material are controlled by the relative amounts of these types of compounds present with a high preponderance of aromatic rings tending to produce "sol" or aromatic type asphalts where the high molecular weight material is more or less completely dissolved. If the naphthenic rings containing long side chains predominate for the lower molecular weight material, the high molecular weight material is not dissolved but is partially solvated to produce a "gel" or naphthenic type asphalt. The possible presence of organic complexes (33) or metallic chelates (31, 32) introduces additional complications in influencing these mutual solubility effects.

The component analysis method (38) appears to be a logical and simple procedure as the first step in determining the general types of materials present in asphalts. This conclusion is based upon the general application of the results that have been obtained as shown in Figure 1, which is based on a previous article (38) and other confirming data. If gilsonite is considered as a highly asphaltic material, a residual from a naphthenic crude is considered as containing a high content of paraffinic naphthenes and a furfural free residue from furfural refining of a lube oil which extracts the aromatic materials is considered as representing materials of relatively high aromaticity, then these materials should, by analysis, appear near the apices of a ternary diagram such as given by Figure 1. Component analysis shows this to be true and on a purely arbitrary basis it is possible to divide the diagram into segments as shown for the purpose of classifying materials that fall within the defined areas. Starting at the lower right, the area may be considered as that into which will fall the residues from crude residues containing a high proportion of aromatic ring compounds. Similarly residues from thermal and catalytic cracking will show component analysis that fall in this region.

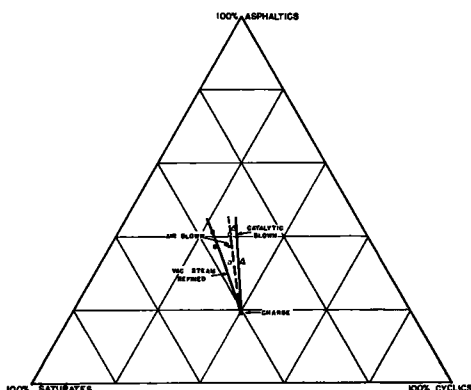


Figure 4. Changes in composition when processing Florida (Sunniland) residuum.

proportion of compounds with conjugated double bonds either aromatic or acyclic with a minimum of side chains. This is confirmed qualitatively by ultraviolet absorption analysis, chromatography and infrared analyses indications.

The residuals that fall in the lower left area of Figure 1 have been called "naphthenic" and may also be considered to consist of ring structures with naphthenic rings predominating, but with relatively long side chains on the rings which distinguish the saturate fraction from the cyclic fraction as obtained by component analysis and chromatography. Evidence for this distinction lies in the lower refractive indices for the saturates fraction. Other confirmation is found in the fact that the separated saturates fraction will polymerize faster (as measured by the increase in viscosity) than the cyclic fraction when processed with air or catalysts. This is in accordance with published results that long chain paraffin hydrocarbons on ring structures are quite susceptible to oxidation. The boundary for this region is shown concave looking from the left because certain asphalts containing a high wax content fall in the concave area. The waxy hydrocarbons may appear in either the asphaltic or the saturates fraction depending upon their molecular weight or solubility in *n*-butanol. The presence of wax as a separate component is not considered important. What is important is that wax, if found, indicates the presence of certain types of chemical compound (solid saturated hydrocarbons probably naphthenic in nature) and the properties of the containing asphalt may be expected to be affected accordingly.

Refractive indices for the saturate fractions vary from about 1.4800 to 1.5600. The higher values for the saturate fraction are found in the "aromatic" type asphalts which show a correspondingly higher refractive index for their respective cyclic fraction. This emphasizes that variations in composition are matters of degree rather than absolute differences. The lower limit of refractive index for the saturates fraction may ex-

Such materials would be expected to show a preponderance of ring structures with only short side chains and with the aromatic type of ring compound predominating.

The refractive index at 158 F for the cyclic components from asphalts range from about 1.520 to 1.600 regardless of source material even over a wide range of consistencies. From some special petroleum residues from cracking operations considerable higher values have been obtained, but these would normally not be considered as asphalts. The refractive index increases linearly with the density of the cyclic fraction(38). Since the variations to be found are primarily a matter of degree, the residuals in this area have been labeled "aromatic" with the connotation that they contain a relatively large

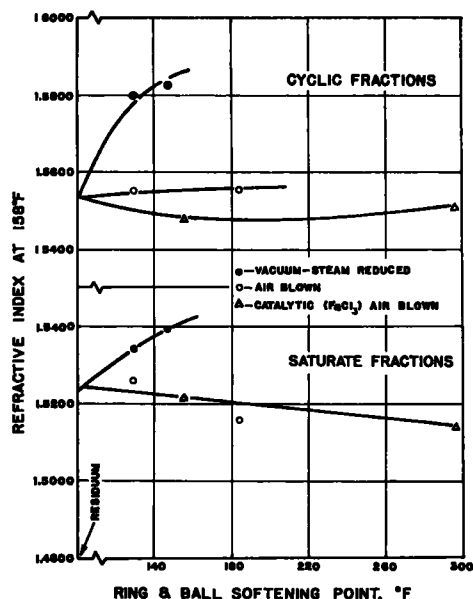


Figure 5. Changes in refractive index of components when processing Florida (Sunniland) residuum.

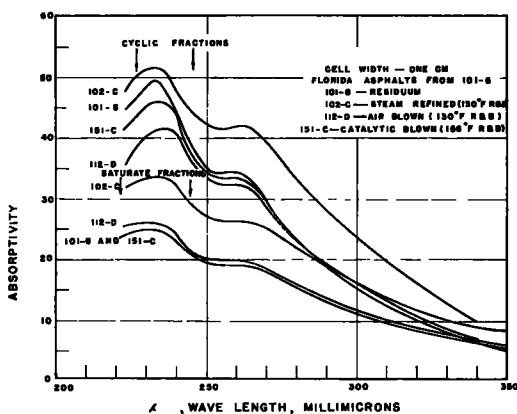


Figure 6. Ultraviolet spectrograms for processed asphalt components.

tend below 1.4800 for some very fluid residuals. (Paraffin wax shows a value of about 1.43 at 158 F.)

Highly asphaltic materials are represented in Figure 1 by the area at the top of the diagram. Materials containing over 50 percent asphaltics usually have a high consistency (of the order of 15 penetration). Certain softer materials may show high asphaltics contents where the peculiarities of composition affect the solubility relationships. Road tars and propane solvent treating residues are examples. In certain cases the asphaltene contents will exceed the asphaltic content whereas normally the reverse is true. This occurs where the solvent has disturbed the bituminous system to such an extent that excessive precipitation occurs at the solvent ratios for pentane employed in the test.

The asphaltic fraction as determined by component analysis is reproducible and when fluxed with the combined saturate and cyclic fractions (in proportion to production) will yield asphalts similar to vacuum reduced products made from the mother stock. Similarly air blowing of the combined saturate and cyclic fractions will produce products similar to air blown asphalts from the mother stock. These results would indicate that the asphaltic fractions as derived from the oily components present are related chemically with differences being account-

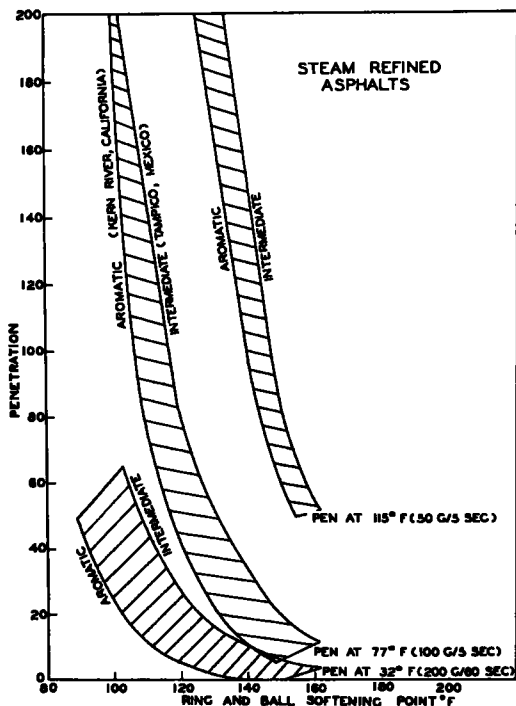


Figure 7. Effect of composition of properties of steam-refined asphalts.

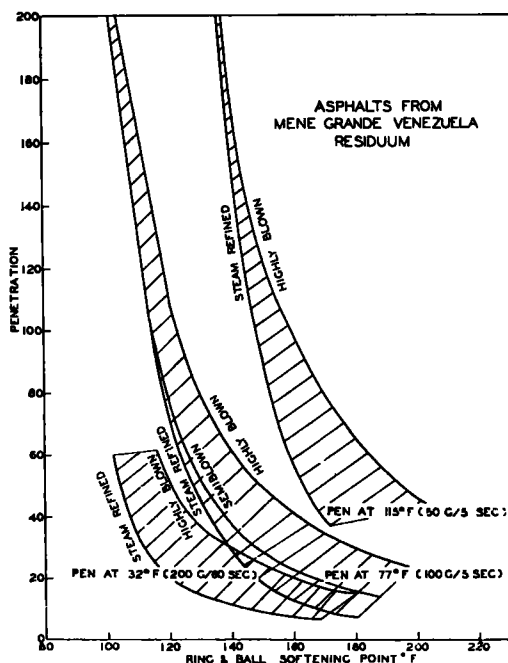


Figure 8. Influence of charge consistency on properties of resulting air-blown asphalts.

able primarily to a higher molecular weight.

An upper center area is shown in Figure 1 which is labeled "intermediate." This section represents a less rigorously defined area of composition where no one general type of component predominates. Many asphaltic materials will fall in this area. Panuco (Mexican) asphalts show analyses which place them in the intermediate region as do many other types that have proven satisfactory for paving purposes. As might be expected the asphaltic materials whose analysis places them in the "intermediate" area will show, in general, smaller variations in refractive index for the cyclic and saturate components. The ranges are intermediate between those for the asphalts found in the lower left area and those that fall in the lower right areas of Figure 1 with some overlapping of the values occurring. Grader (9) found that Mexican asphalts showed relatively fewer paraffinic side chains on the rings.

One other factor in the chemical composition of asphalt that appears significant is the sulfur content. Practically all publications on the subject include consideration of sulfur. O'Donnell (19) has commented on mercuric chloride-sulfur complexes from asphalt and indicated that the sulfur is concentrated in the aromatic fractions and the higher molecular weight material. This is also confirmed by sulfur analyses on fractions separated by the Traxler-Schweyer method. Apparently, the importance of sulfur lies in its ability to form both rings and bridge structures. In the latter form it would permit the combining of long side chains to produce more complex molecules of higher molecular weight (thus increasing the asphaltics content). It is known that the densities of asphaltic materials of similar consistency ranges will increase almost linearly with sulfur content. Similarly as was shown, (38) the density increases with the increased C/H ratios generally expected for the higher molecular weight materials in the asphaltic fraction. This results in the high sulfur content asphalts appearing in the upper intermediate region of Figure 1. The high sulfur contents of Mexican asphalts is well known and their appearance in the intermediate area is an illustration. Certain Californian and South American asphalts are similar in this respect.

The effect of nitrogen and oxygen (32) even though present in only small amounts eventually may be found to affect the composition of asphalts considerably in the high molecular weight ranges. Like sulfur, if they form bridge linkages, the small weight percents present may permit the formation of long side chain polymers which otherwise might not be produced. Ball and co-workers (2) have shown that nitrogen (like sulfur) tends to concentrate in the high molecular weight portions of asphalt. Richter and others (23a) have also studied the distribution of nitrogen.

A consideration of the relations between true chemical compositions and general types of compounds present as indicated by component analysis permits a general classification of asphalts as "naphthenic," "intermediate" or "aromatic" according to the respective areas in Figure 1. Such a classification should not be construed as rigorous since the boundary lines in Figure 1 have been drawn arbitrarily to form a symmetrical diagram and apply relatively for straight run residuals of viscosities of the order of 200 seconds Saybolt Furol viscosity at 210 F. Furthermore, borderline cases obviously will occur and asphalts of different consistencies made from the same

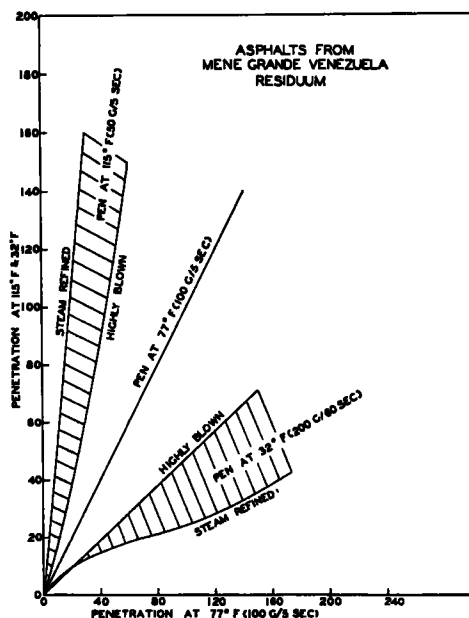


Figure 9. Influence of charge consistency on penetration of air-blown asphalts of an intermediate type.

stock may appear on different sides of a boundary line. The areas shown have been drawn to represent normal asphalts likely to be encountered in commercial practice. The use of this simple system with the connotations regarding chemical composition as previously stated will facilitate the following discussion of the influence of composition on the properties of asphalts. That these concepts are in accord qualitatively with experimental facts regarding asphalts will be demonstrated in the next sections.

COMPOSITION AND COLLOIDAL PROPERTIES

The wide range of chemical compositions found for asphalts would be expected to produce a variety of properties for them and the practice of describing these variations on the basis of colloidal behavior is gaining favor. The concept of "sol" or "gel" type asphalts is not new, and Traxler and Romberg (37) have summarized certain pertinent data useful for classifying asphalts as to colloidal types. Oliensis (20) has discussed the analogous colloidal behavior of asphalts with that for aqueous gelatin mixtures to explain syneresis and compatibility of asphalts. The "solvation potentials" discussed by this author appear to be an attempt to evaluate chemical composition on the basis of physical effects. Reiner (23) has proposed a mathematical analysis as a means of differentiating between a sol and a gel structure based on the relative elastic and non-elastic deformation of asphalts under stress.

In general, any given asphalt produced as a residual in refining operations at high temperatures consists of high molecular weight material which may be considered as being more or less associated as its temperature is decreased according to Krenkler and Wagner (15) and Krenkler. (14) These authors also suggest the build up of a spherical type micelle in contradistinction to long chain polymers because the asphalts do not exhibit the highly elastic properties of chain type elastomers. Pfeiffer and co-workers (21) have considered the asphalt micelle to be built up first with the aromatic portions followed by gradation to the more paraffinic materials, but Krenkler et al. suggest that the association potential rather than progressive chemical differentiation is the controlling factor.

The presence of lower molecular weight materials as the oily portions of the asphalt appears to be the critical factor in controlling the colloidal nature. Whatever the nature or structure of the high molecular weight portions (asphaltenics) it is reasonable to assume that they will imbibe the oils and become solvated to a greater or lesser extent. The degree of this solvation will determine the properties. If the oils are powerful solvents a complete solution of the high molecular weight material results in producing a "sol" type asphalt. An imbibing of the oils with incomplete solution where the oil is the discontinuous phase or the production of a suspension of the "asphaltenics" in the oil will yield a "gel" type asphalt. In this connection it is interesting to note that Oliensis (20) has suggested that the intermediate hydrocarbons (or so called resins) may be considered as solvents or peptizers while contrawise the lighter oils act as desolvents. Chemical type would appear to be more important than molecular weight as a criterion for the solvent ability of the oils. It will be found that those asphalts falling in the "naphthenic" region of Figure 1 will usually exhibit the properties of gels whereas those in the "aromatic" region usually are sols. Asphalts having intermediate compositions on Figure 1 will show some properties of both the sol and gel type with no distinct demarcation indicated. This might be expected since the degree of solvation is a relative rather than a quantitative term and requires that any comparisons be made for asphalts of about the same viscosity.

Where the gel type asphalt persists, the partial solvation (rather than solution) of the high molecular weight material apparently is the result of insufficient solvent power (high interfacial tension, etc.) or the absence of an intermediate mutual solvent as sometimes occurs in blending of two dissimilar asphaltic materials. The relatively weak solvent power of the paraffin hydrocarbons compared to aromatic hydrocarbons would explain why asphalts in the lower left region of Figure 1 are of the gel type. Conversely, the high solvent power of aromatics would explain why sol type asphalts usually show a relatively high cyclic content. In connection with solvation it should be pointed out that the viscosity of the mixture is not a function of the amount of high

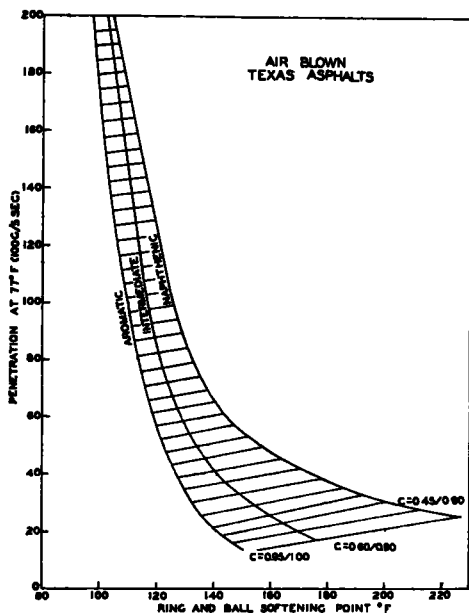


Figure 10. Effect of composition of properties of air-blown asphalts (starting material of 100 to 200 Saybolt Furol viscosity at 210 F).

because of the low degree of solvation even before blending; the latter operation accentuates the effect. Conversely, highly asphaltic materials from solvent refining operations are good blending materials because: first, the relatively high cyclic content acts as a solvent, and second, the high asphaltic content presupposes high molecular weight material of a wide gradation which would exercise a mutual solubility effect on the high molecular weight material in the other asphalt or asphalts making up the mixture. This mutual solubility effect is perhaps the most important factor in making sol type asphalts. A common reverse procedure is the production of gel type asphalts by fluxing a hard asphalt with a light oil. The lack of mutually soluble components produces a mixture showing a high degree of complex flow, staining and other properties of a highly colloidal material. The degree of colloidity will be affected by the molecular weight of the fluxing oil and its relative naphthenicity with the more naphthenic oils producing the gels. Sludging or incompatibility in blending asphaltic materials of low viscosity will be recognized as another manifestation of incomplete solvation of the high-molecular weight material present. The exudation and insudation reactions (20) of asphaltic materials in contact with each other is also a colloidal phenomenon which should be more readily rationalized on the basis of chemical composition than by complicated empirical test procedures.

It is this degree of colloidity together with certain chemical properties (resistance to oxidation, resistance to corrosion, etc.) which in the final analysis determine the suitability of the asphalt for commercial use.

ASPHALT COMPOSITION AS AFFECTED BY PROCESSING

Asphalts are produced commercially by a variety of methods and the composition of the product is affected accordingly. Among the major methods used are:

1. Vacuum reduction by volatilization of the lighter fractions.
2. Air blowing of residues at elevated temperatures (500 F).
3. Catalytic polymerization in the absence or presence of air at elevated temperatures.

molecular weight material present as has been demonstrated in Tables 1 and 2 and by Traxler and Rombers (37) and others. The degree of solvation is the controlling factor since a sol type asphalt may have a considerably higher asphaltic content than some other gel type.

In studying the influence of composition in producing a gel or sol type asphalt, the amounts of the respective components together with their refractive indices both may be considered. It is interesting to note that the "intermediate" type asphalts with high asphaltic contents show smaller differences in the refractive indices for the saturate and cyclic fractions than do other asphalts. This would indicate a continuous phase of less variable composition for intermediate type asphalts. The variations, however, are a function of both the degree of processing as well as the method (i.e., vacuum reduction, air blowing, or catalytic polymerization).

Many of the peculiar effects of blending can be rationalized on the basis of composition of the materials used for the mixture. For example, the use of high consistency naphthenic asphalts usually will not produce satisfactory sol type asphalts

4. Air blowing and concomitant refluxing with low volatility oils or fluxing with fresh feed stock.

5. Blending of products from the preceding operations.

Corbett (3) has presented data showing how the "asphaltene" contents and refractive indices of the pentane soluble portions of asphalt vary with source and process. This author also suggested the possible use of specific refraction evaluations for characterization purposes.

The production of asphalts by vacuum processing in general results in a gradual hardening of the asphalt through loss of volatile vapors. The composition of the asphalt changes primarily as a result of concentration of the asphaltics fraction with the composition varying in several ways in Figure 4 and with progressive increases in density of the asphalt and in the refractive indices of the components of a residue from the Sunniland, Florida field as illustrated in Figure 5. A vertical line in Figure 4 is significant because on a ternary diagram it represents an equal conversion in amounts of both the cyclic and saturate fraction with a corresponding increase in asphaltics. However, a removal of equal amounts of cyclics and saturates without an increase in asphaltics results in a line sloping to the right or left since the percent asphaltics must increase (the line rises vertically if the saturates and cycles are present in the original charge stock in equal proportions). Obviously, combination of changes in any of the components caused by vaporization or chemical changes will produce other configurations on the chart which are not necessarily straight lines. Since the oils present regardless of chemical nature may be considered as having similar vapor pressures (otherwise they would be volatilized and appear in the distillates during the refining operation), it is probable that vaporization of both aromatic and saturated hydrocarbons should occur in essentially equal amounts. In addition polymerization may also occur during the processing to increase the asphaltics content. In Figure 4 the vacuum refining produced a relatively larger loss in cyclic fraction than for the saturate fraction. The resulting residual oils of high molecular weight apparently are good peptizers and solvents for the asphaltic materials since steam or vacuum refined asphalts generally show less tendency to form gels than other products from the same stock. The exception to this are the products from vacuum reduction of highly paraffinic stocks which are difficult to process. In this case the removal of a portion of the aromatic oils from a source material already deficient in them accentuates the deficiency and produces a gel type product. The excess of saturates is difficult to remove by volatilization because of the low (relatively) vapor pressure of saturated hydrocarbons compared to aromatics of the same viscosity.

In the air blowing process a different result is obtained (38) because the refractive indices of the components show a tendency to remain constant or to increase or decrease slightly (Fig. 5) depending upon the extent of the blowing. Volatilization occurs to a limited degree, and the asphalt density is increased considerably less than in vacuum reduction, even though the percent of asphaltics increases appreciably as shown in Figure 4. A reasonable explanation is that the higher molecular weight saturate and aromatic oils are dehydrogenated and polymerized to higher molecular weight asphaltics. This causes a depletion of intermediate molecular weight solvent material and tends to produce gel type asphalts because of the deficiency of intermediate solvent oils. If the remaining light oils are resistant to dehydrogenation the refractive indices of the fractions containing them will decrease progressively. However, sufficient polymerization may occur in the lighter oils also to raise their refractive indices to the original values but the quantity of these materials will now be less than in the original charge. The locus of the composition line tends to move upward on the ternary diagram. When the saturates to cyclics ratio remains constant the line moves toward the asphaltics apex. This would mean that the relative amounts of saturates and aromatics converted to asphaltics depend upon the charge stock composition and that air blowing converts proportionate quantities of each to the higher molecular weight asphaltics. It is known that the naphthenic residues from petroleum crude oils are more amenable to alteration of their properties by air blowing which implies that a higher proportion of the saturate fraction relative to the cyclics is converted (38) to asphaltics.

This is true where the lines on Figure 4 slope upward to the right. Such results also are in accord with the concept that ring compounds with long side chains are readily broken, and are confirmed by the fact that saturate fractions separated from a given stock will process faster than cyclic fractions when subjected to the same operating conditions. However, highly aromatic materials must show a relatively higher loss of the cyclic fraction if the composition line moves upward to the left toward the 100 percent asphaltics apex. This phenomenon usually occurs when the charge stock composition lies to the right of a line projected downward vertically from the asphaltics apex.

Air blown asphaltics exhibit the properties of gels and will have lower asphaltic contents than vacuum reduced products of the same ring and ball softening point in accord with the theory that the degree of solvation rather than quantity of high molecular weight is the critical factor in controlling consistency.

Catalytic polymerization where the petroleum residual is treated with a catalyst in the presence or absence of air must be considered as a separate case where the mechanism is specific with the charge stock and catalyst employed. The catalyst may selectively accelerate the polymerization of either the naphthenes or the aromatics which will alter the slope, accordingly, of the line in Figure 4 indicating composition changes. In some cases the catalyst tends to produce a vertical line, but the refractive indices of the components may be either higher or lower than those of the corresponding fraction for air blown asphalts from a given source stock. The specific results for one residuum are illustrated in Figure 5 and Table 3. In general, the refractive indices usually are higher for the saturates and lower for the cyclics than the indices of the corresponding fractions of air blown asphalts of the same softening points. These differences are less pronounced at higher consistencies. A peculiar result occurs sometimes where an increase in the cyclics content with catalytic processing has been noted with certain residuals. An indicated possibility here is that some low molecular weight saturates are converted (catalytic cracking) to cyclic compounds which would also account for the decrease in refractive index of the composite cyclic fraction and the increase for the residual saturates. These specific results will vary with the charge stock, catalyst employed and extent of processing. The catalyzed product also exhibits more colloidal properties than the straight air blown asphalt of the same softening point although the former may contain fewer asphaltics than the air blown one. These differences indicate a variation in the nature of the high molecular weight material produced by the catalyst which tends to result in reduced solvation by the oils present. The naphthenic and intermediate type asphalts are more amenable to catalytic blowing than the aromatic asphalts with the latter showing some tendency for an increase in refractive indices for both oily components (saturates and cyclics) but not to the extent that results from vacuum reduction.

Certain of the above processed asphalts when subjected to component analysis and the fractions studied for ultraviolet absorption characteristics gave results as shown in Figure 6. The data indicate that the saturate fraction remaining after air or catalytic blowing are but little different from the original saturates of the mother stock but the amounts change.

This is somewhat in accord with the results shown in Figure 5. In steam refining the remaining saturates show a higher unsaturation as do the cyclic fraction confirming the results in Figure 5. Since steam reduction removes oil primarily by vaporization these data indicate that the higher molecular weight materials present in steam refined asphalts may have relatively greater C=C groups.

The different results for air blowing and catalytic blowing indicate that the catalyst tends to control the dehydrogenation or polymerization in such a manner as to produce a residual cyclic fraction less changed than in air blowing but yet producing a more gel-like product. The difference appears to a matter of degree, but the mechanism is not clear. Apparently the remaining cyclic fractions after air blowing are less saturated because the ones of higher molecular weight have been used in making asphaltics or some saturates may be converted to cyclic material. Perhaps the catalyst accentuates the polymerization to produce some type of condensation effect that is different from that obtained with air alone. Thus, the catalytic blown asphalt is more colloidal at a given

TABLE 3
 PROPERTIES OF ASPHALTS FROM FLORIDA (SUNNILAND) RESIDUUM^a

	Steam Refined	Air Blown	Catalytic Blown	
R and soft point — F	150	150	150	- -
Penetration, 77F, 100g/5sec	19	43	98	- -
Asphaltics—%	43.0	37.0	32.0	- -
Saturates—%	36.0	34.5	34.0	- -
RI/158F	1.5400	1.5210	1.5210	- -
Cyclics—%	21.0	28.5	34.0	- -
RI/158F	1.5850	1.5555	1.5495	- -
R and B soft point — F	- -	200	200	296
Penetration, 77F, 100g/5sec	- -	19	33	17
Asphaltics — %	- -	43.0	38.0	42.5
Saturates — %	- -	32.0	32.0	31.0
RI/158F	- -	1.5200	1.5195	1.5140
Cyclics — %	- -	25.0	30.0	26.7
RI/158F	- -	1.5550	1.5480	1.5518

^aData by interpolation and extrapolation from curves for experimental points necessary in order to show properties for comparable softening points.

softening point but the compositions are quite similar (Table 3). A study of the properties of the asphaltic fractions from comparative air blown and catalytic blown asphalts might prove very informative on this point but data are not available. From the foregoing it should be apparent that it is possible to obtain from a given source two asphalts having quite different properties but which show the same composition on a weight basis. Determinations of the refractive indices or ultraviolet absorptiongrams of the saturate and cyclic fractions may be helpful in explaining the variation in properties.

The other commercial methods of producing asphalts require special consideration of the composition of the individual stocks and the specific process employed. As a generalization, the components of blends may be considered additive on a basis of weight percent with the physical properties of the resulting mixture being a function of its colloidal properties. Any subsequent processing of the blend will affect the composition (and properties) in a variable amount depending upon the proportion and susceptibility of the components to the particular processing method used. In connection with blending it is interesting to note that Dengler et al. (5) blended a Mexican asphalt with a cracked residue and through mutual solubility effects were able to increase appreciably the solubility of cracked residue in carbon tetrachloride. This improvement usually is greater the more viscous and/or the more aromatic the blending agent. Other peculiar phenomena (21) of binary mixtures such as blends having softer penetrations or lower softening points than either material making up the blend can be explained readily by the colloidal nature of the blend as a function of the composition of original materials used.

COMPOSITION AND FLOW PROPERTIES

One of the most striking examples of the lack of scientific approach in asphalt technology is the continual use of empirical tests such as penetration, ductility and others. The data from such tests with few exceptions are difficult to correlate quantitatively with the performance of asphalt in service. It is true that such tests have been valuable tools to the technologist in the past, and it is true that they are simple and rapid tests, but as more useful procedures for evaluating the flow properties become available the use of the old methods should be discouraged. A similar attitude should be taken regarding any new empirical tests for evaluating hardness, consistency, etc., which will only add more confusion and result in uneconomic investigations. The position taken by this author is based on experience and the opinion of others. For example, Reiner (22) states "It is

doubtful whether either asphalts or bitumens show plastic deformation, — except perhaps in blown bitumens — this being a deformation connected with the existence of a yield value." The present author would not except blown bitumens since with proper techniques no yield values have ever been shown conclusively for asphalts, although Thelen (34) has proposed such analyses. The discussion of Thelen's paper also raised this question. The study of deformation requires a consideration of time as well as stress and strain and it is believed that most asphalts of commercial use will show deformation at very small stresses if sufficient time elapses. There are two reasons for empirical flow tests being unattractive. First, it is difficult to get two investigators to agree to the same word definition as to what the test measures. Second, and by far the most important, all deformation characteristics of asphalts when subjected to an applied stress are amenable to rigorous mathematical analysis. That such analysis may not have been made does not mean that it cannot be done. The application of sound rheological techniques such as those being studied by Reiner (23) will eventually replace the empirical tests as has been done in the rubber industry and is being done in the plastics industry.

It is apparent from the literature that more and more emphasis is being placed on rheological phenomena where the data are measured in scientific units. In the final analysis the flow properties of an asphalt are a function of its composition, the stress-strain relations, temperature, time and the history of the sample. These variables affect the behavior of the asphalt under stress and by their control and measurement the behavior may be predicted. In general, the major flow tests required are viscosity, the degree of complex flow (the gel-sol evaluation), and the change in consistency with temperature and elasticity. In the following sections the influence of composition on these properties will be illustrated. Data for the commonly used empirical tests are included as a matter of interest along with the more fundamental rheological relations.

The influence of composition on asphalts from the standpoint of standard penetration and softening point tests is illustrated in Figure 7 using various data.(29)

In general, the range as shown may be considered to cover all asphaltic materials obtained by steam reduction of crude petroleums. The range extends from the low values for aromatic types of residues, of which those from Kern River (California) crude oil are an example, to the high values shown for those from Tampico (Mexico) crude oil, which is an example of an intermediate type source of residual. It is possible that there might be found some exceptions to the range shown, but it is not likely, since the two examples may be considered more or less as extremes of their respective types. It should be noted that no steam refined naphthenic residuals are shown. This is because it is difficult to steam reduce residues from paraffinic crude oils to make satisfactory commercial asphalts. The steam refining of asphalts consists primarily of the removal of the more volatile fractions, and it is generally not possible to process paraffinic residuals without causing cracking since the more oily fractions in paraffinic crude oil residues have extremely low volatilities and thus very high temperatures would be necessary to remove any material by steam refining.

The curves indicate that the more aromatic residuals produce asphalts for a given softening point having lower penetrations at all three of the standard temperatures used in asphaltic testing. The characteristic difference between the aromatic type residues and the intermediate type residues are believed to be due to a relatively greater number of aromatic and naphthene rings with short paraffinic chains present in the intermediate type. If steam refined naphthenic residues were plotted on this same chart, the curves would lie upward to the right above the respective curves for the intermediate materials.

The curves in Figure 7 can be considered generally applicable for all straight reduced residuals, since in general the processing of asphaltic residues either by steam alone, or combined steam and vacuum, produces about the same results.

The effects of air blowing upon the flow properties of asphalts made from different consistencies of an intermediate type of source material are illustrated in Figure 8 with the steam refined asphalts from the same source being shown for comparison since it represents the least amount (none at all) of blowing. The curve for the highly blown asphalts made from this particular crude oil source illustrates the properties when a

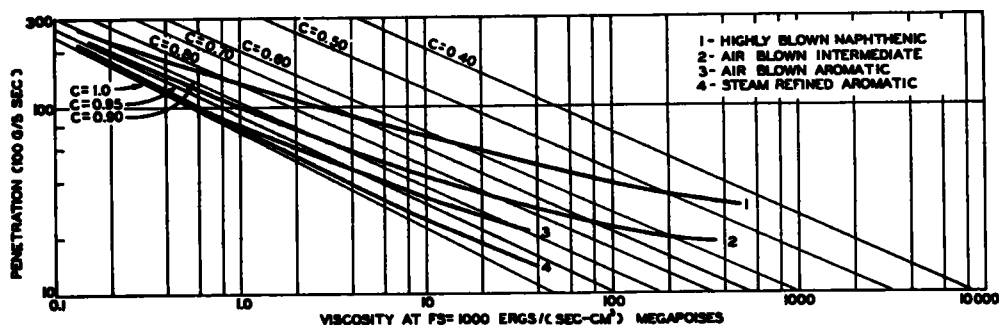


Figure 11. Generalized rheology—penetration curves for asphalts.

residue of about 300 sec Saybolt Furol viscosity at 210F is air blown. The curve for the semi-blown asphalts was derived by air blowing a residue of 100 penetration. As shown, the asphalts made from the softer starting material have a higher penetration for a given ring and ball softening point than the ones made from the 100 penetration starting material. These relative effects are characteristic of air blown asphalts made from different starting consistencies and the relative effects for penetration are shown to be similar for all three standard temperatures at which penetration is measured.

The curve for the highly blown asphalts from this particular source should not be considered as representing the most highly blown asphalts that could be made, since by the use of a still lower viscosity starting material (lower than 300 sec Saybolt Furol at 210 F), very highly blown asphalts could be made and the position of such curves on Figure 8 would be above and to the right of those shown for the highly blown asphalts. Furthermore, the curves for a given starting consistency for all intermediate type residuals will not necessarily superimpose on the curves in Figure 8. This is illustrated elsewhere (28) for Sunniland (Florida) residues, which may be considered a borderline naphthenic-intermediate residual, but which require a starting viscosity considerably below 300 sec Saybolt Furol at 210 F in order to produce highly blown asphalts similar to those shown in Figure 8.

The explanation for these differences in the properties of the asphalts produced by various degrees of blowing lies in the fact that the softer starting materials contain a larger quantity of the less viscous oils. The oils of intermediate molecular weight that are present are converted in the air blowing process to compounds of higher molecular weight through a process of dehydrogenation and polymerization, and it is the combination of these polymers and the low molecular weight oils that yields the peculiar properties of air blown asphalts. The more highly blown asphalts have the properties of gels indicating a partial solvation of the high molecular weight material rather than a solution. A hard semi-blown asphalt when fluxed back with the softer mother stock shows a tendency to have the properties of the highly blown asphalt confirming the partial solvation concept. The tendency is greatest with naphthenic type asphalts. In the case of the semi-blown asphalts, the quantities of the low viscosity oils are less and the air blowing process results in a smaller amount of polymerization with the result that the properties of semi-refined asphalt tend to approach those of the steam refined residues. The refractive indices of the components therefore are intermediate between those of the highly blown and steam refined products.

The penetration data in Figure 8 have been replotted in Figure 9 to illustrate the influence of the degree of blowing upon the tests results. Certain relationships (such as the vertical distance between the penetration at 32 F and 115 F) from these empirical tests are often used to evaluate the susceptibility of asphalts to temperature change. The fallacies of such methods become apparent when the penetration at 32 F is higher than at 115 F. This is not a rare occurrence and results for materials having a high degree of complex flow where the deformation is greater at the lower temperature in a given time with a given load than at the higher temperature in a shorter time with a smaller load.

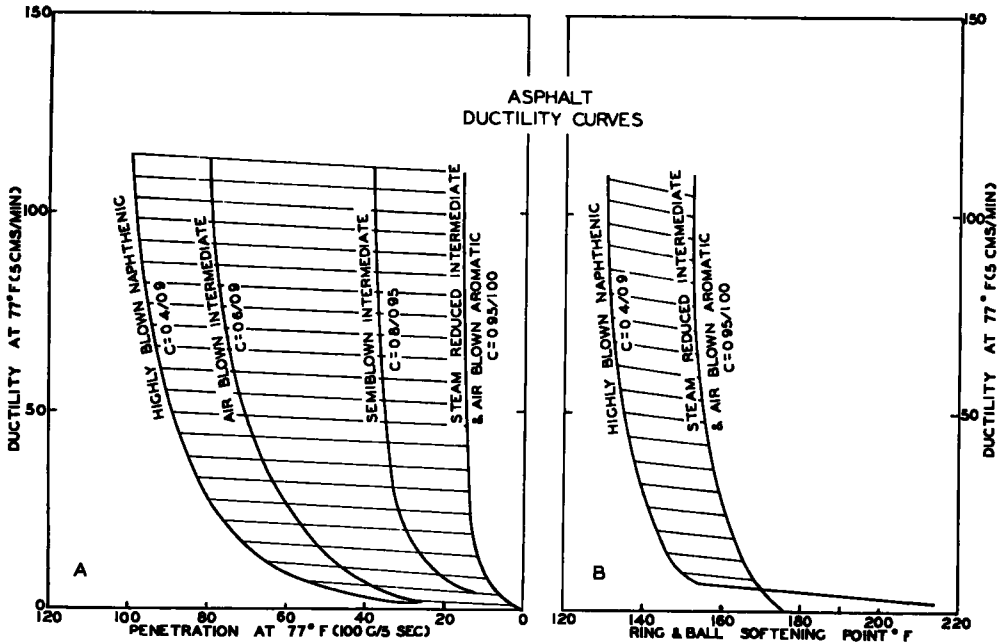


Figure 12. Effect of composition ductilities of asphalts.

Composition exerts a considerable influence on the flow properties of asphalts as might be expected and the remaining illustrations are an attempt to correlate the available information. The wide variations in composition encountered for petroleum residues preclude quantitative relationships at the present state of knowledge, but certain generalizations can be made.

It was shown in Figures 4, 5 and 8 that a given mother stock will yield asphalts of varying composition and properties depending upon the type of processing. The effect of composition on the properties of steam refined asphalts was shown in Figure 7; in Figure 10 the effect of composition on the properties of certain air-blown asphalts is plotted from published data. (39) The variable of charge consistency has been eliminated by comparing the products made from stocks of a similar viscosity. The naphthenic type residues yield asphalts with higher penetrations for a given softening point than the other types. These same relative effects as shown in Figure 10 will apply regardless of the starting consistency used for air blowing, but the range shown does not necessarily encompass the range of penetrations that may be obtained, since certain specific residuals of the same viscosity as used in Figure 10 when air blown, may have still higher penetrations for a given softening point. That is, the curve might be displaced upward

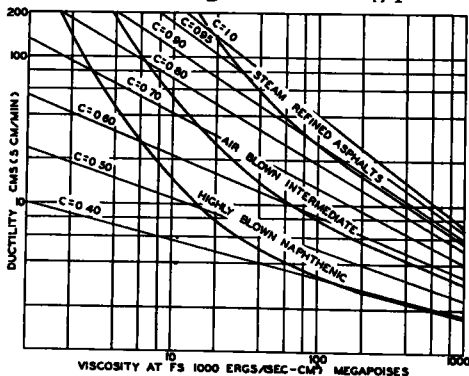


Figure 13. Generalized rheology-ductility curves for asphalts.

and to the right above the naphthenic type curve shown. It is also possible to displace all of these curves upward and to the right when using the same starting viscosity for air blowing by varying the process conditions such as to retard the removal of oils by volatilization. Such processing might be accomplished by air blowing at low temperatures (not commercially feasible because of the extended time required), by air blowing under high pressure (not generally used because of the hazard due to possible explosion), or by refluxing during the blowing operation which has been done commercially. Catalytic blow-

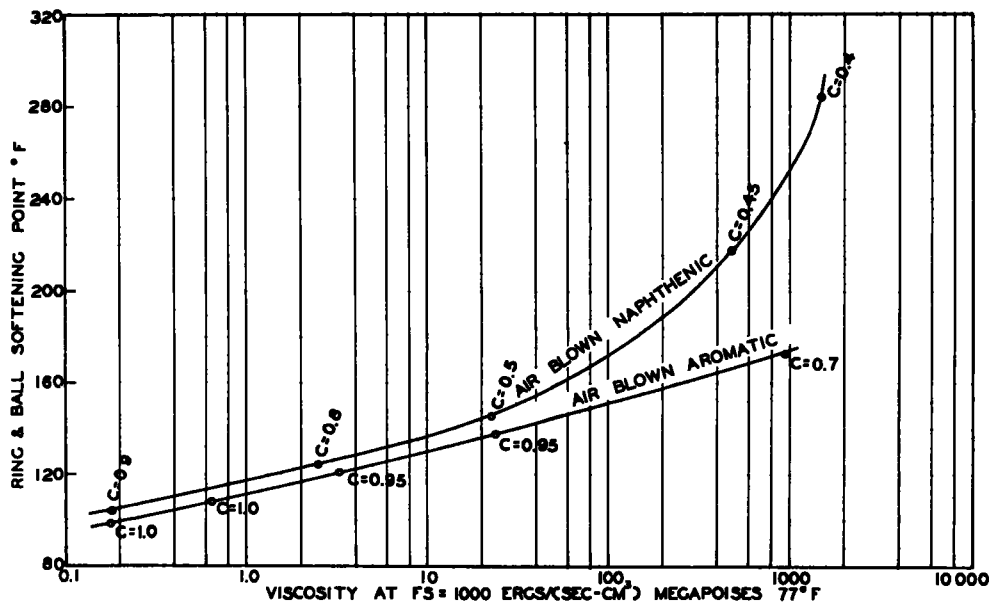


Figure 14. Generalized rheology—softening point curves for asphalts.

ing of a given feed stock will also shift the curves upward to the right.

The data in Figure 10 are typical for penetrations at 77 F and the relative effects will be similar at other standard temperatures for penetration measurements. The ranges to be expected can be estimated from the data in Figures 8 and 9.

The differences in the curves in Figure 10 are attributed to the differences in composition of the residuals with the naphthenic residues being considered to contain a greater amount of side chain paraffinic hydrocarbons on more or less saturated ring compounds. At the other extreme are the aromatic types containing a relatively large proportion of single and condensed aromatic rings with fewer side chains, with the intermediate residuals being intermediate in composition. At the present state of knowledge it is impossible to state that the naphthenic asphalts contain only single naphthenic rings since undoubtedly their high molecular weight indicates condensed rings. Similarly the aromatic asphalts are made up of condensed rings with a larger proportion of C=C bonds or CH groups whereas the naphthenic asphalts have higher proportions of C—C and CH₂ groups with all differences being relative. Such theories are confirmed qualitatively by spectral absorptions but quantitatively an evaluation is difficult.

In order to explain the difference in behavior of the asphalts on a more scientific basis than the relationship of penetration and softening point, it has been found that measurement of the rheological properties such as viscosity, elasticity and departure from true Newtonian flow are quite informative. (24) Some evidence of this is illustrated in Figure 10, where the range of complex flow has been evaluated quantitatively for the three different series of asphalts. This evaluation appears as the value of "c" shown on the plot. The value of "c" is a measure of the departure from true Newtonian flow and indicates whether a material is behaving as a true liquid (c=1), or whether it possesses considerable anomalous flow characteristics (c=0.5). Thus, for a given softening point the anomalous flow exhibited by the naphthenic type airblown asphalts is considerably greater than that shown for the air blown aromatic types. It is these differences in complex flow characteristics that account for the higher penetration at a given softening point obtained for the air blown naphthenic types. The subject of rheological properties as related to standard asphaltic tests will be discussed more completely with respect to the curves that follow.

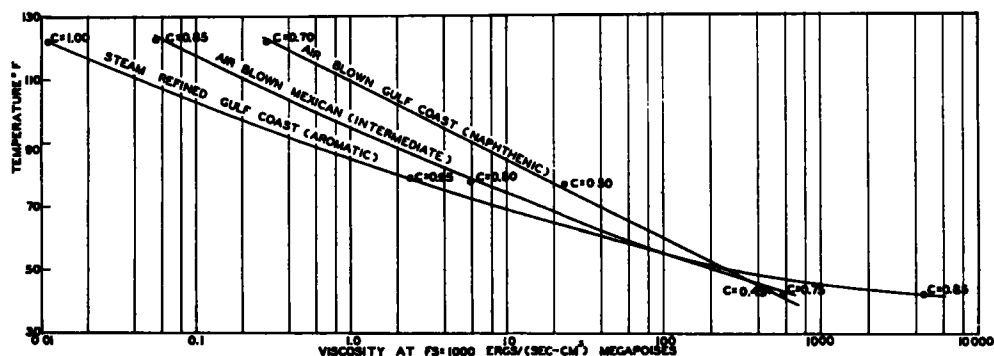


Figure 15. Generalized temperature susceptibility curves for asphalts (50 to 60 penetration at 77 F).

A generalized correlation developed from published rheologic data (39) with the A. S. T. M. penetration is shown in Figure 11 to illustrate the influence of complex flow at a given viscosity on the standard penetration test. The curves show that most low viscosity asphalts (at approximately 100,000 poises) show relatively small amounts of complex flow, whereas the higher consistency asphalts resulting from processing show greater differences in amount of anomalous flow. In all cases the degree of complex flow increases with increase in consistency for any series of asphalts from a given charge stock. The curves should apply generally where the penetration (100 g/5 sec) and viscosity are measured at the same temperature.

The consumer of asphalts who uses the standard ASTM tests (penetration, ductility, softening point) as controlling specifications is in reality attempting to evaluate the rheological properties in a crude, arbitrary manner. It is possible to replace these unscientific tests with fundamental rheological measurements which, after the initial period of confusion because of lack of familiarity with the meaning of the test results, will ultimately prove their value. The methods of measurement are available (36); it is merely a matter of all concerned agreeing on the procedures to be followed.

A basic rheological relationship was proposed by Romberg and Traxler (24) as follows:

$$M = F/S^c \quad (1)$$

where F is shearing stress, dynes/cm²; S is rate of shear, sec⁻¹; M is the value of F when S equals one; and c is the slope of a log F versus log S plot. When c equals one (Newtonian flow), M is the viscosity in poises since for this case Eq. 1 is the integration of the differential equation defining viscosity. For comparing asphalts showing complex flow where c is not equal to one, the "viscosity" in poises is taken as equal to the ratio of F/S arbitrarily at a work input of 1000 ergs/(sec-cm³) or when $FS=1000$ (24). The value of c decreases as the magnitude of complex flow increases where the rate of shear is higher (the usual case) at a given applied stress than prescribed for true Newtonian flow. For the unusual case where the rate of shear is less than prescribed by Newtonian flow the value of c is greater than 1.

The use of Figure 11 in evaluating the penetration from rheological data is satisfactory so long as a given series of asphalts is considered, but when different types of asphalts having the same viscosity and degree of complex flow are compared, they may not have the same penetration, although the chart indicates that they should. Such results raise pseudo objections that the rheological method is not as sensitive as the penetration method (see discussion of Figure 13). This is exactly the point, the penetration test measures a combination of so many properties (including elastic fore-effect and adhesion of asphalt to a steel needle) that it cannot be used for measuring consistency as pointed out by Traxler. (35) The inadequacy of such arbitrary tests is quickly recognized by the consumer when he learns that asphalts showing the same ASTM tests do not behave in the same way when put into service.

Many of the problems concerning the uses of asphalts will be rectified, it is believed, when rheological measurements are used in conjunction with the newer analytical

procedures to explain differences in the behavior of the asphaltic material. Techniques will be developed which will provide means for determining both quality specifications and behavior specifications in order to obtain reasonable duplication of material and "in service" performance.

The influence of composition on the standard ductility tests is illustrated in Figures 12A and 12B. The sharp break in ductility as a function of the penetration and complex flow has been discussed previously (39) where it was shown that the stress in the ductility test increases with deformation, and accordingly materials showing high complex flow yield lower ductilities because of "necking" effects. For Newtonian asphalts high ductility values result even for materials of very high viscosity because these materials flow readily. Photographs of the differences in behavior of asphalt types are given in the reference. These curves illustrate the necessity for interlocking specifications since a ductility specified for a given Ring and Ball softening point range is considerably less restrictive than for the same number of units range in penetration test results. The cross-over of the curves in Figure 12B explains the peculiar fact that high melting point gel type asphalts will show ductilities greater than the sol types in the 0.5 range for test results. The sol types usually are of such a high viscosity that they will fracture rather than flow an appreciable amount as is the case for the gel type products in this viscosity range.

Figure 13 is a generalized curve and more valuable than Figure 12 for studying ductility since the curves apply generally regardless of the temperature of test. The fundamental rheological data predict the ductility result in a semi-quantitative manner and illustrate the influence of complex flow upon the ductility result. Furthermore, Figure 13 covers a range of ductility of 1 to 100 for a 1000-fold variation in viscosity whereas the sensitivity ranges in Figure 12 are much less (about 100-fold for penetration and Ring and Ball softening point).

One factor that limits the rigorous application of Figure 13 is the influence of elasticity on the initial stages of the ductility test (or at low ductilities). This is particularly important for hard materials (usually less than 50 penetration at 77 F). A complete rheological evaluation of asphalts therefore requires consideration of elasticity as well as viscosity and degree of complex flow.

The measurement of elasticity in quantitative terms is difficult, but a method has been proposed (24) for evaluating them in terms of relaxation time after an initial stressing. If a truly elastic material is deformed and then the stress measured to maintain that deformation, the measured stress will remain the same as the initial stress for infinite time, if the body exhibits only a small elasticity, the measured stress will decrease rapidly from the value of the initial stress because of creep. The relation between residual stress and time approximates an exponential relation (Maxwell). For asphalts the measurement of the time required for the measured stress to fall to one-half the initial stress provides a relative measure of elasticity, although this "relaxation one-half time" is a function of sample size, magnitude of initial stress and temperature. The relaxation one-half times (24) of asphalts of different compositions as measured in a rotary viscometer at a power input of 1000 ergs/(sec-cm³) are given in Table 4 for comparative purposes which illustrates that elasticity is associated with a high degree of complex flow.

That the relations among ductility, complex flow and consistency are quite complex is illustrated by these data since high elasticity (relatively) does not necessarily indicate high ductility. Considerably more study of the elastic deformation of asphalts is necessary because of the many service applications of asphalt wherein a knowledge of the elastic behavior would be valuable. Reiner (23) has indicated methods of attack that may aid in this problem.

Figure 14 is a re-plot of data (23) which shows the influence of composition and complex flow on the Ring and Ball softening point for a given viscosity at 77 F. A high degree of complex flow causes a divergence of curves at high consistencies. A study of Figures 11 and 14 explains why air blown asphalts have higher softening points than steam refined ones of the same penetration. The air blown asphalt has a higher viscosity at 77 F from Figure 11 and accordingly the softening point must be higher from Figure 14. Thus, the common evaluation of the susceptibility to tempera-

TABLE 4
COMPARISON OF ELASTICITY AND DUCTILITY DATA

Asphalt	Type	Pen at 77 F (100 g/5 sec)	Rheology at 77 F			Ductility 77 F (5cms/sec)
			Viscosity Megapoises	Complex Flow c	Relaxation one-half time-sec	
A	Air Blown Naphthenic	102	2.5	0.80	3.5	105
B	Air Blown Aromatic	100	0.62	1.0	1	179
C	Steam Refined Aromatic	100	0.55	1.0	1	200
D	Highly Blown Naphthenic	48	94	0.35	66	2
E	Air Blown Naphthenic	53	22	0.5	20	8
F	Air Blown Intermediate	55	5.8	0.80	4.5	114
G	Air Blown Aromatic	50	3.2	0.95	1.6	200
H	Steam Refined Aromatic	52	2.4	0.95	1	200

ture change of asphalts based on penetration — Ring and Ball relations are erroneous because the asphalts may not be of comparable viscosity at 77 F although they show the same penetration at 77 F.

A better comparison of temperature susceptibility can be obtained by plotting the rheology data in the form shown in Figure 15. The degree of complex flow increases as the viscosity is increased by lowering the temperature, which is analogous to the increase in complex flow with increase in viscosity at 77 F for any given series of asphalts as mentioned in the discussion of Figure 11. Asphalts of lower viscosity (higher penetration) than those show in Figure 15 would be expected to show temperature-viscosity curves closer together and vice versa.

COMPOSITION AND OTHER PROPERTIES

The foregoing considered the influence of composition on flow properties which are perhaps the most important group properties of asphalts. However, another property of importance is durability or resistance to change which is definitely influenced by composition. Failure of asphalts is usually measured by changes in physical properties, but outside of age-hardening (37), changes in physical properties are usually a result of composition changes. The oxidation or polymerization of asphalts is catalyzed by ultraviolet and infrared as well as visible energy, and different asphalts are expected to react to the deteriorating agents in different ways. The use of accelerated weathering tests for roofing and paving asphalts has never been found infallible. Other oxidation tests (1,6) have been proposed but their efficacy has not been fully established. The difficulty with accelerated tests is that it is usually impossible to duplicate the service conditions by controlling all the variables in the same way that they apply in actual service. Until a satisfactory durability test is developed it will be necessary to rely on experience in selecting asphaltic materials to give the best performance.

In general, the naphthenic type asphalts are most suitable for roofing purposes. This is true even though the saturate fractions under process conditions at high temperature

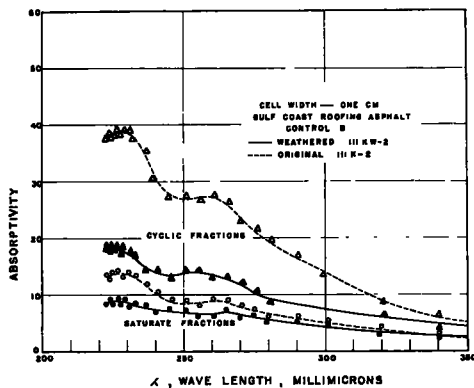


Figure 16. Ultraviolet spectrogram for fractions from a Gulf Coast roofing asphalt.

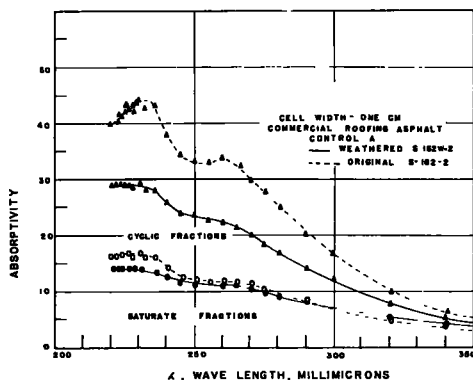


Figure 17. Ultraviolet spectrogram for fractions from a commercial roofing asphalt.

may be more readily polymerized. However, the free energy of the aromatics decreases with lower temperature to a relatively lesser extent than for saturates and paraffinics which may account for the relatively higher stability of the saturates fraction at low temperature service conditions. The suitability of naphthenic asphalts for services requiring a high degree of durability varies considerably and no limits for composition can be firmly established. Data are given in Table 5 on changes in composition with atmospheric weathering as a matter of interest. Recently Hewett and Faid (10a) have proposed a correlation between durability and saturates content where the durability of roofing asphalts was shown to be greater for asphalts with higher saturates content, other things being similar.

Outside of noting the appreciable drop in refractive index on the cyclic fractions after weathering, the data in Table 5 do not appear significant regarding changes in composition and durability. The more stable Gulf Coast asphalt shows a saturates to cyclics ratio of about 4 whereas the ratio for the commercial product is about 2. The available data are insufficient to determine if such ratios are important. However, the relatively higher energy absorption for cyclics would indicate that a low cyclic content is desirable. In Figure 16 certain ultraviolet absorption data are shown for the commercial asphalt and in Figure 17 results for the Gulf Coast coating are given. These data confirm this theory in a qualitative way.

TABLE 5
COMPONENT ANALYSIS OF ASPHALT COATINGS BEFORE AND AFTER WEATHERING^a

	Commercial		Sunniland (Florida)		Gulf Coast	
	Before	After ^b	Before	After ^b	Before	After ^b
Sample No. S	162	162-W	112-I	112-IW	111-K	111-KW
R and B Soft Pt, F	220	--	218	--	221	--
Pen. 77 F, 100g/5 sec	18	--	17	--	20	--
Asphaltenics — %	46.6	55.4	44.0	54.2	39.7	50.1
Saturates — %	36.3	32.2	31.0	28.2	49.1	40.6
RI/158 F	1.5045	1.5015	1.5180	1.5208	1.4976	1.4935
Cyclics — %	17.2	12.5	25.0	17.6	11.2	9.2
RI/158 F	1.5520	1.5230	1.5560	1.5450	1.5496	1.5148
Appearance after weathering 3 years	Large number of cracks extending through coating layer. Failure imminent.		Some cracks extending through coating layer. Fair condition.		No indications of cracks extending through coating layer. Condition good.	
Appearance after weathering 4.5 years	50% of metal surface uncovered.		Large number of cracks. Failed.		Few surface cracks. Good condition.	

^a Atmospheric exposure, 0.025 inch layer on aluminum panel.

^b Analysis based on 4.5 years exposure.

Adhesiveness (for stone, paper, etc.) is another property of asphalts that would be expected to vary with composition, but its evaluation at present requires empirical tests for the specific materials. In general, the naphthenic asphalts lack adhesive properties and are often described as "cheezy." The aromatic and intermediate asphalts usually have good adhesive properties, and are utilized in paving and paperply applications. However, adhesiveness is not an inclusive term since some asphalts will adhere to stone but not to the steel penetrometer needle. Interfacial tension and the nature of the second substance obviously are important factors with naphthenic asphalts exhibiting a better suitability in some instances.

Emulsifiability appears to be related to the chemical nature, since aromatic and intermediate asphalts usually are readily emulsified whereas the naphthenic ones, with some exceptions, do so with difficulty. The ability of Mexican asphalts to emulsify readily is well known and numerous other intermediate asphalts exhibit a similar property. Saponification number or neutralization number apparently will not correlate rigorously with emulsifiability.

Asphaltic materials are used in a variety of applications where their electrical properties (21) are important. These properties are certainly influenced by the composition but few data are available for consideration. Swenson (30) concluded that the asphaltenes and resins were polar compounds whereas the oils showed little activity. The presence of polar compounds probably would have an effect on the electrical properties, and since the naphthenic asphalts would be more likely to contain polar

compounds, they might be expected to show lower electrical resistivities. This has been confirmed in a general way.

Summarizing this paper briefly, it appears that an increasingly greater emphasis in asphalt research is being placed on the application of scientific methods. In the final analysis, the chemical composition will be the criterion in selecting an asphalt for a particular purpose. Improved methods will undoubtedly be developed, but at present the component analysis method is of considerable utility in separating the types of chemical compounds present. This in itself is an improvement in asphalt technology because it helps to explain variations in the colloidal nature of asphalts. The composition together with the colloidal properties will provide for a better understanding of the behavior of asphalt in commercial applications.

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Appendix

The belief that a reasonably simple analytical procedure for characterizing asphalts can be found has been a strong influence in motivating the writer's research. This has been influenced further by the feeling that such a development is necessary if progress in asphalt technology is ever to get beyond the Edisonian technique of "try

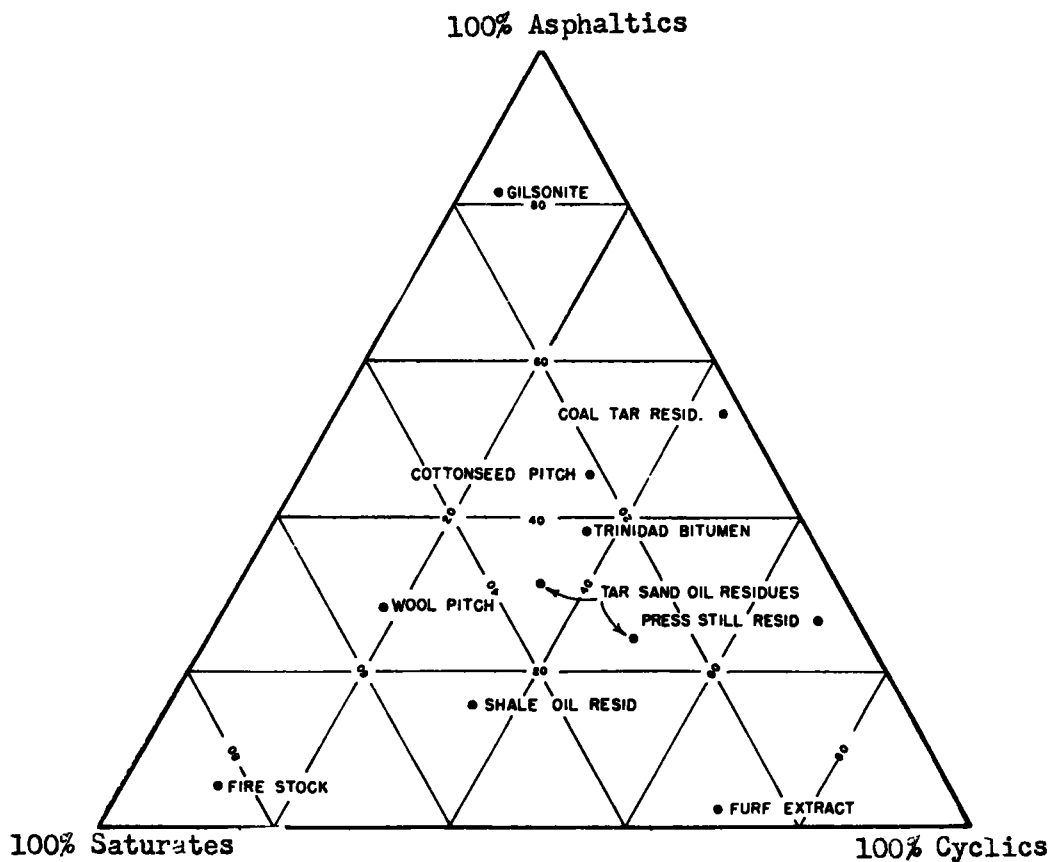


Figure 18. Component analysis of various materials.

this" or "try that." The results summarized in this bulletin are an attempt to apply a scientific approach to composition and to problems in asphalt technology.

A number of years ago the author borrowed a technique used in studying lubricating oils and asphalts, modified it somewhat and applied it to a variety of bituminous materials. The results are shown in Figure 18 taken from a previous article (38). The figure clearly indicated a definite separation of materials of known composition into certain areas on the chart. It showed further that a large group of materials clustered in the center of the chart although it was expected that many of these materials might vary considerably in composition. (The left side apex reads 100 percent "saturates" which is now considered by this author to be more appropriate than 100 percent "paraffinics" as used in earlier diagrams of this type.) These preliminary data served as a motive for an extensive study of a variety of petroleum residues leading to the development of the Traxler-Schweyer solvent extraction method (38) for separating asphalts into three components as mentioned in the bulletin proper and leading to Figure 1 in the bulletin. This latter figure shows a classification system discussed more fully in the bulletin based on the fractions obtained by the solvent extraction technique.

When the acetone-separated fractions of the butanol soluble part of the asphalt were studied by an ultraviolet light absorption technique (26) it was obvious that a separation had taken place but the rejection of pure saturated material by acetone is not rigorous. This is demonstrated by the lower line of Figure 2 which theoretically should be essentially a horizontal line of very low absorptivity. However, there must be something different in the fractions to produce the separation. The question of this difference provided a motivation to keep working on it.

(Note: the following may assist those who are interested in the quantitative values on

the absorption curves as illustrated. The basic absorption relation is:

$$A = \log(I_0/I) = abc,$$

where A is absorbance - sometimes called optical density.

I_0 is transmittance of blank solution.

I is transmittance of the unknown in solution.

a is the absorptivity defined as $A/(bc)$; if the product bc has a numerical value of one, then a and A are equal and the value of a is sometimes called the absorption coefficient, K.

b is the cell thickness, cms.

c is the experimental concentration, gms/L.

Certain of these variations in terminology appear in the literature but the terms and forms of plotting used in the bulletin proper are preferred and vary for ultraviolet and infrared presentations.)

In Figure 2 it will be noted that there is included the results for a chromatographic separation of the asphalt (by adsorption on silica gel from a methylcyclohexane solution) (27) into two parts each of which show ultraviolet analyses to be similar to those for solvent fractionation. This agreement certainly must be more than fortuitous. Actually in the process of separation by adsorption a very sharp break occurs in the refractive index of the solvent free effluent as shown in Figure 19 at 84 percent. This break is apparent to the eye during the processing and definitely indicates a difference in effluents before and after desorption of the adsorbant. Once again the question arises as to what is present to cause the differences in the fractions.

In an effort to establish the magnitude of the range of differences to be expected for bituminous materials, a solvent free furfural extract of a lubricating oil fraction and a pressure still residue (thermally cracked petroleum residue) were subjected to adsorption and the fractions analyzed. The results are shown in Figure 20 compared with the asphaltic residue of Figure 2 in the bulletin proper. The high values for

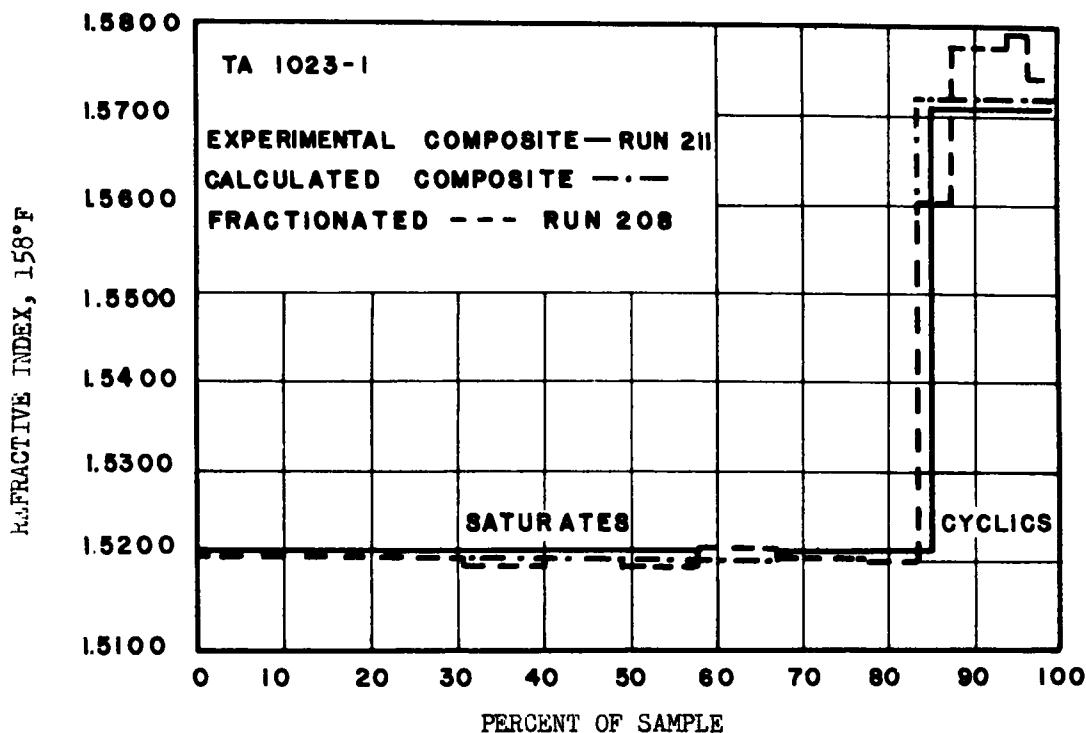


Figure 19. Adsorptogram for TA 1023-1.

absorption in the 230 and 260 millimicron ranges indicate the influence of greater quantities of conjugated acyclic polyenes and aromatics for the cyclic fractions of the furfural extract and pressure still residue. Variations in the saturate fraction are less pronounced and appear to be more a matter of efficiency of separation than real differences.

For further exploration of the composition problem consideration was given (26) to the possibilities of infrared absorption being useful with the results as shown in Figure 3

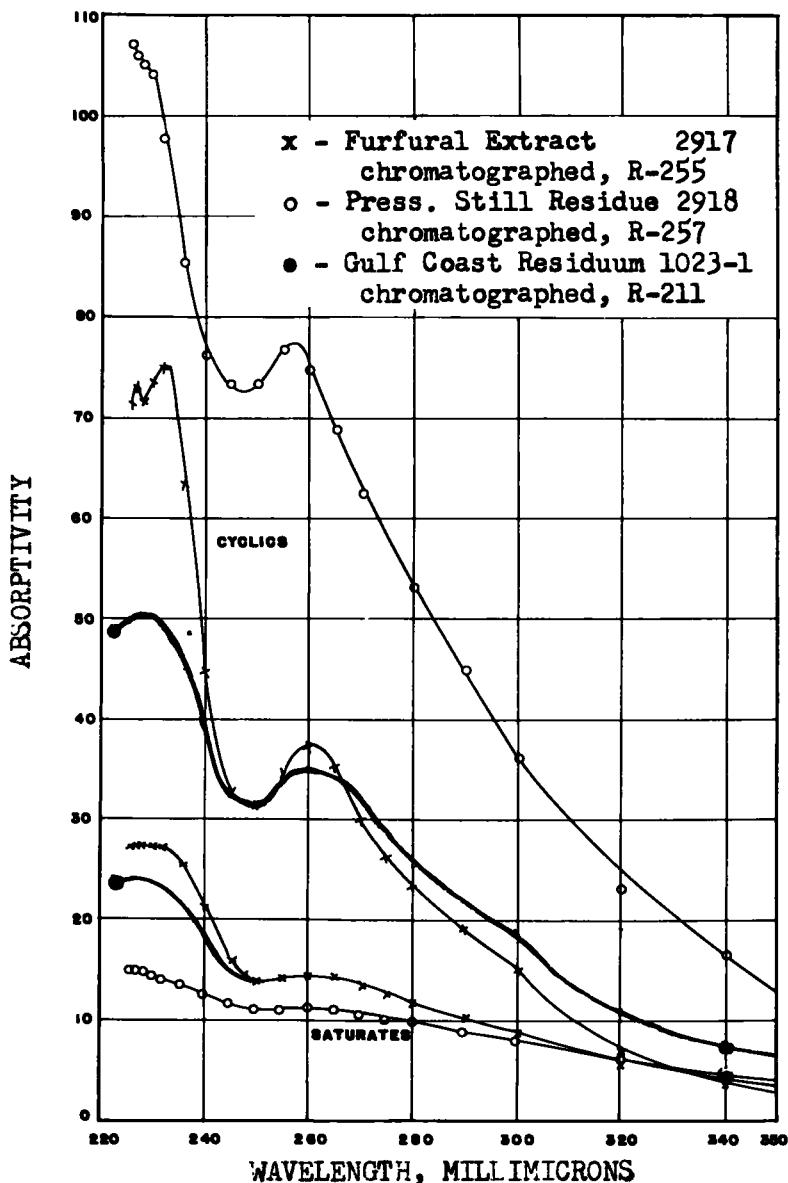


Figure 20. Ultraviolet spectrogram for certain materials.

of the bulletin proper. The spectrograms emphasize differences in absorbance which appear significant. For example, in Figure 3 the aromatic materials have a higher absorbance (lower line in the figures) at 5.85, 6.20, 9.7, 11.5, 12.3 and 13.45 microns; but these relative positions are reversed at 13.9 microns. The writer is not prepared to explain these differences at the present time but they are in qualitative agreement with certain known information concerning the relative saturation of certain hydrocarbons.

These data plus other inferences form the basis for the qualitative assignment of the descriptive terms "naphthenic," "intermediate," and "aromatic" to asphaltic residua as shown in Figure 1 of the bulletin which then provides a means of discussing the asphalts by types. It must be agreed as noted in the bulletin that the symmetrical diagram of Figure 1 is purely arbitrary. Because of overlapping of areas depending upon the consistency of the residuum it would be more realistic for the meeting point of the three areas on the base line to be moved 10 to 15 percentage points to the left to give a skewed diagram.

If the descriptive terminology proposed is accepted, at least for purposes of this discussion it then becomes possible to consider in a general way how the type of asphalt affects the properties of the material. For example, in Figure 7 of the bulletin the properties of steam refined asphalts are shown. These may be expected to cover the range normally expected since processing of naphthenic asphalts is not generally practiced by refiners except for borderline intermediate-naphthenic types which have properties of the intermediate type shown. The point here is that the range of properties available falls within a limited area. However, these areas vary in a specific way as the method of processing or source of the asphalt is changed as shown by Figures 8 and 10.

It is interesting to speculate on what happens during processing and some information is given by Figure 5 where the removal of volatile oils by steam refining is shown by the increase in the refractive indices of oils remaining in the asphalt. Note that this is a different effect from the one found for air blowing. In the latter case the refractive indices do not change much (but the amounts decrease). A reasonable deduction here is that the intermediate molecular weight oils are polymerized to higher molecular weight asphaltic materials producing complex mixtures of high molecular weight material with low molecular weight oils (but void of intermediate oils which might act as mutual solvents) having a variety of colloidal properties as shown by air blown and catalytic blown asphalts.

It is these colloidal properties which are measured by the asphalt technologist's empirical flow tests of penetration, softening point and ductility. A more scientific approach for measuring flow properties is required and is being used in many laboratories as evidenced by recent literature on microviscometers and thin film measurements. The purpose of these new rheological methods is to minimize or evaluate the influence of complex flow on the measurement of consistency. They will certainly lead to more and better information than the empirical methods have yielded in the past fifty years. In Figures 11, 13, and 14 of the original bulletin there are shown generalized correlations of penetration, softening point, and ductility as functions of the absolute viscosity and degree of complex flow shown by the asphalt. The purpose of these charts is to demonstrate the quantitative relations for known measurements which may be used for first approximations when certain data are missing. These charts also illustrate in a general way the range of properties to be expected as the composition of the asphalt changes.

One final property to be mentioned is durability which is definitely of interest to the highway engineer. Unfortunately no test in use at present offers much hope for reliable predictions. Here again, the problem certainly is one of composition. If one ever can determine what types of compounds resist deterioration in service and then find methods for analyzing for those compounds perhaps it will be possible to make some progress on the durability problem. In Figure 16 of the bulletin some data are given for a roofing asphalt with a lower cyclic content which gave better service and had lower ultraviolet absorption than another whose spectrogram is given in Figure 17. These data are much too limited to be conclusive, but others have noted similar results.

In conclusion the writer would like to emphasize that the value of the methods and deductions presented in the bulletin are but one opinion and serve to illustrate potential new fields of study. They are not considered infallible. When something new is shown to be better, the writer would not hesitate to discard any older methods provided it can be demonstrated that the replacement is really an improvement.

Too often a "good idea" is proposed which will not stand the tests of scientific analysis, reliability and logical deduction when applied to a variety of asphalts under different conditions.

A most important immediate goal is to develop the latent desire for scientific tools into a motivating demand for more intensive research in these areas. Such new techniques may become more complex but the highway engineer should be prepared to learn them and apply them if progress is to be made in asphalt technology for road improvement.