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THE CONVERSION OF PETROLEUM RESIDUES
TO ASPHALT BY AIR OXIDATION

A

Thesis

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I. SUMMARY

The known chemistry of asphalts is reviewed, including the concepts of the colloidal state, the proposed structures for the resin and asphaltene molecules, and the oxidation reactions taking place in asphalts on air blowing and on weathering.

Experiments on the blowing of Lloydminster reduced crude with nitrogen, air and oxygen are reported. Results of the fractionation of the asphalt residues obtained into oils, resins and asphaltenes are recorded. The oxygen content of these three fractions for each of the blown residues is reported.

From these investigations, evidence is presented to show that with the blowing conditions used, the primary oxidation reaction is one resulting in dehydrogenation of the asphalt molecules. An increase in asphaltene content on blowing at the expense of the oils and resins is observed. The oxygen determinations indicate that the asphalt increases in oxygen content. Of the three fractions, the resins are the only bodies to increase in oxygen content, the oil and asphaltene content remaining essentially constant. This is regarded as indicating instability of oxidized oil molecules, and the formation of asphaltene molecules containing oxygen in the same proportion as the original asphaltenes. Based on the comparison of the observed oxidation characteristics to the oxidation characteristics of pure hydrocarbons, the suggestion is made that the molecules undergoing oxidation are polynuclear aromatic or aromatic naphthenic compounds.

Suggestions for further investigations following this method of attack on the study of this oxidation reaction are outlined.

II. INTRODUCTION

It may truthfully be said that in producing asphalt products the art is far ahead of the science. Hence, the fundamental problem underlying all asphalt investigations has been that of ascertaining the characteristics of any given asphalt with respect to a given application.

To this end, considerable research has been carried out on asphalts and bitumens during the past forty years. These investigations may be roughly classified into two main methods of attack; these are: the behavior of asphalts in the presence of the other components of the finished product, and the behavior of asphalt itself as a complex natural product.

The former method of investigation has led to the formation of many empirical tests; however, correlation of most of the data from these procedures with observed performance has been extremely difficult and, in many cases, inconclusive. In such studies the investigator cannot overlook the variables introduced by the other components of the finished product.

The second classification, the investigation of the fundamental chemistry of asphalts, excludes these variables. Nevertheless, the study is complex for the reason that asphalts are complex products; in addition

correlation of individual results is hampered by the deviation in chemical nature of petroleum crudes from one another, and from natural asphalts. In spite of these obvious difficulties, it is believed that a thorough knowledge of the chemistry of asphalts will permit an appreciation of the behavior of such products, and permit evaluation of an asphalt or specification of asphalts for commercial application. It is the purpose of this thesis to outline the known chemical properties and the present conception of the asphalt system, and to present research data which will, it is hoped, assist in the complete solution of the problem.

1. Fractionation of Asphalt

To facilitate the study of their chemical nature, division of asphalts into general fractions, more or less physically or chemically distinct from one another, is to be desired. Solvent fractionation with or without the addition of adsorbing mediums has been employed in nearly all procedures reported, although recently the principles of chromatographic separations have been applied.

a. Solvent separations

It has been repeatedly observed in petroleum refining operations that gasoline and naphtha fractions will cause flocculation of reduced crudes when added in large excesses; this observation has been applied to the fractionation of asphalts. It will be seen later, however, that the

colloidal nature of asphalts is such that solvent methods are essentially arbitrary. In fact, due to the arbitrary nature of such separations, correlation of analysis data by the many different procedures and modifications can only be made in general terms; and although standard procedures have been suggested from time to time, no entirely reproducible method has been reported.

The most widely accepted procedure was outlined by Marcusson (1,45,63) in 1916. This worker defined that portion of asphalts which is not soluble in 88°C petroleum ether as the asphaltenes. The soluble extract from the petroleum ether precipitation containing the malthenes or petrolenes was dispersed on Fuller's earth or florigine. The fraction which could be extracted in a soxhlet extractor with 88°C petroleum ether was defined as the oils or oily constituents. The remaining fraction, the resins, was desorbed from the agent with carbon disulfide.

The asphaltenes recovered are dark brown or black amorphous bodies which have no definite melting point but swell on heating and finally decompose. The resin fraction is a sticky brown resinous mass, while the oils resemble lubricating oils in nature and may be fluorescent.

In addition to these three main bodies which are generally accepted as the major constituents of bitumen, Marcusson made provision for the estimation of free asphaltous acids and anhydrides utilizing alcoholic sodium hydroxide.

Generally this refinement is neglected since most asphalts contain less than 0.5% of these fractions.

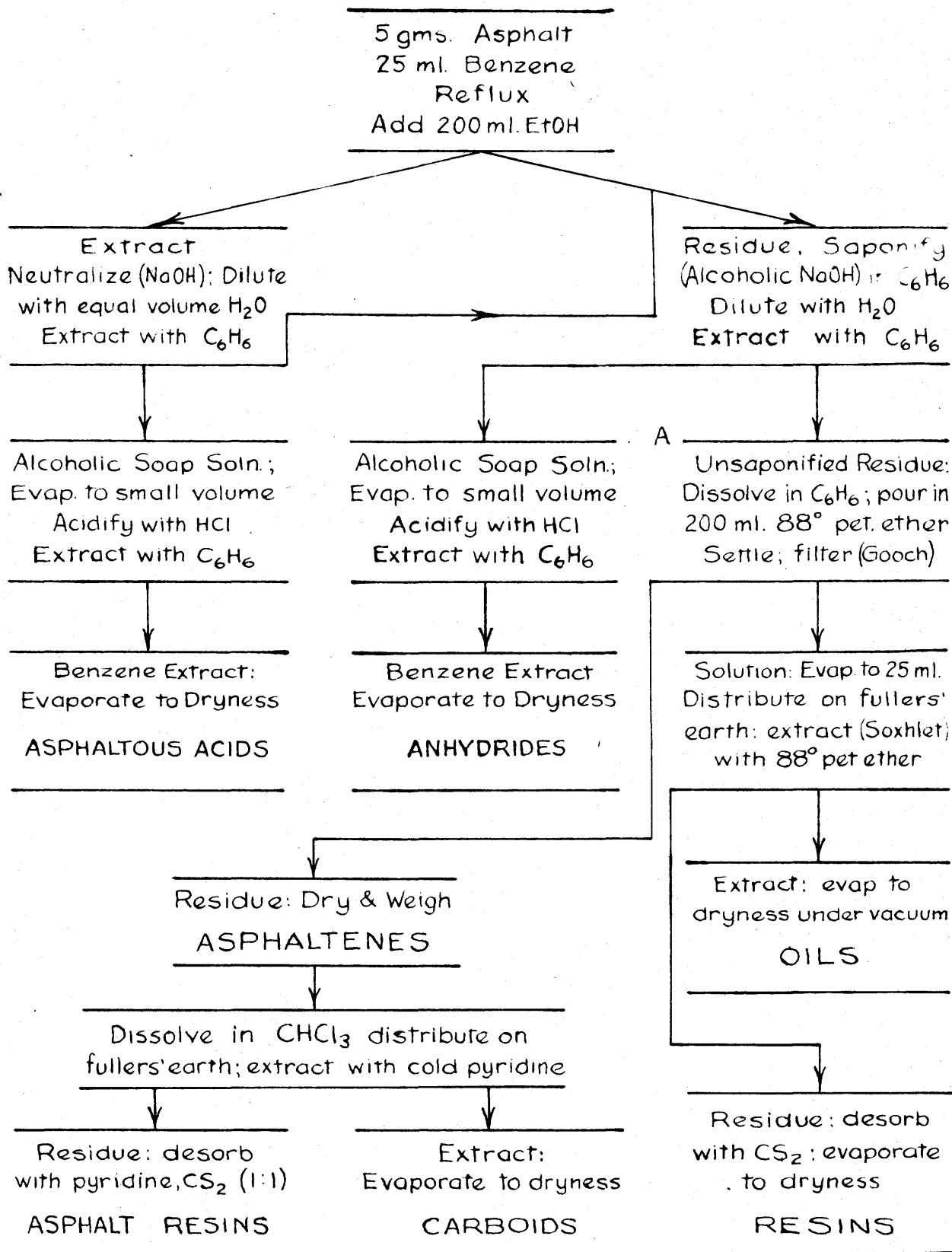
Pöll (88,103) added the determination of carbenes or carboids (carbon-like material) which is effected by dissolving the asphaltenes in chloroform and dispersing on fuller's earth. The carboids are desorbed with cold pyridine leaving the hard asphalt resins adsorbed; these are in turn removed with carbon disulfide. A schematic diagram of Marcusson's procedure with this modification is illustrated in Figure 1.

Many modifications of Marcusson's method have been used. Lang and Thomas (52) used Skellysolve (28°-30°C) in place of 88° petroleum ether; Rosmung used a hexane fraction for precipitation of asphaltenes and extraction of oils from the adsorbent. Some workers have attempted to make the determination more reproducible by substituting pure solvents for petroleum ether fractions whose composition cannot definitely be reproduced. Strieter (102) and Nellensteyn (71) have suggested the use of diethyl ether; Nellensteyn points out that in addition to its homogeneity, ether has excellent flocculation properties for asphalt precipitation.

Suida and Motz (104) have, in contrast to Marcusson's procedure, utilized an entirely different set of solvents. In their method, the asphalt is dispersed on

FIGURE 1

Marcusson's Fractionation of Asphalt
(After Abraham (1))



A: Start from this point if acids & anhydrides not required

fuller's earth and successively extracted with chloroform, pyridine at 20° and finally pyridine at 50°C. These fractions are specified as petrolenes, residual asphaltic resin and residual hard asphalt. These extractions were carried out in an oxygen-free atmosphere.

Doubt has been expressed (32,45,61) that the resins adsorbed on fuller's earth can be recovered without chemical change; consequently, some use has been made of other adsorbing media. Alternatively other procedures have been outlined using fractional precipitation by selected solvents, permitting division of the asphalt into component parts without use of solid agents. With respect to use of adsorbents other than fuller's earth, Cattell et al (16) distributed the malthenes on asbestos fibre. These investigators have suggested removal of wax from the adsorbed malthenes by extraction with acetone. Their second modification involves extraction of asphaltene and resins with benzene to yield "light asphaltenes" and the remaining asphaltenes with pyridine to give "hard asphaltenes". Zapata (118) has also used asbestos fibre. Hubbard and Stanfield (43) have suggested replacing fuller's earth with anhydrous alumina.

Mack (61) overcame the use of adsorbing media by precipitating the resins from the malthene fraction with a petroleum naphtha fraction. Similarly, propane at 140°F has been used (42) to precipitate the asphaltenes; following addition of more propane and heating to 180°F, a resin

fraction is obtained. However, sharp differentiation is not realized by this method and the recovery is not complete.

In apparatus designed on a pilot plant scale, Høiberg, Hougen and Zapata (39) have removed asphaltenes with hexane, and resins with propane; all precipitations take place in an atmosphere of carbon dioxide. Thurston and Knowles (106) flocculated asphaltenes with pentane and the resins with propane. A modification was made to remove paraffinic oils (wax) by refluxing the oil fraction with acetone according to the paper by Cannon and Fenske (15). Another method has been outlined by Knowles and Levin (49) for determination of wax. This method comprised of separating the asphaltene-resin fraction with hot liquid propane under pressure, and removing the wax from the oil fraction by crystallization at low temperatures from a solution in methyl-isobutyl-ketone (hexone).

Chernozhukov (17) reported the fractionation of Russian synthetic asphalts (i.e. petroleum asphalts) by treatment with isopentane to remove asphaltenes; extraction of the malthenes with phenol results in division into "naphthenic" and "aromatic" portions.

Høiberg and Garriss (40) removed asphaltenes with hexane, and defined "hard resins" as that fraction insoluble in cyclohexane-isobutyl alcohol at 37.8°C. Wax fractions were removed from a solution of the remaining components in acetone-methylene chloride by crystallization at 0°C.

The fraction insoluble in isobutyl alcohol at 37.8°C was defined as the soft resins. The soluble fraction remaining in this solution was regarded as the oil fraction. Similarly, alcohol was used by Parr (85) to precipitate resins from the malthe fraction. A variation of this procedure has been used by Grant and Hoiberg (32). Following precipitation of the asphaltenes with pentane, the malthenes were dissolved in a 3% solution of 27% ammonium hydroxide in isobutyl alcohol. This solution was centrifuged at 130°F to remove the resins. Again wax was removed from the oils by precipitation at 0°C from an acetone - methyl chloride solution.

Fractionations based on the use of solvents of increasing power of flocculation or increasing internal pressure have been made by several workers. Zwergal (121) discussed the use of methyl, ethyl, propyl, butyl and amyl alcohols as precipitating agents; the amyl and butyl alcohols removed asphaltene-like bodies from the asphalts studied; propanol removed resinous bodies; and the lowest alcohols removed oil fractions. Multiple fractionation of the malthenes was undertaken by Hillman and Barnett (37,38). Isopentane soluble components were taken up in propane, and fractions were flocculated by addition of successive increments of methanol. The asphaltenes were extracted in a large-scale soxhlet with hexane, carbon tetrachloride, benzene, carbon disulfide and pyridine. Bestorigeff (13)

attempted isolation of families of compounds utilizing benzene extraction at increasing temperatures. A similar isolation was undertaken by Mabery (58) who separated components of reduced crudes by fractional solution with hot ether - alcohol solvent pairs.

In nearly all research, however, fractionation into oils, resins and asphaltenes has been considered sufficient for subsequent investigation. Variations of these methods have been used for separation of single components, such as resins, on a plant scale (31). Attempts have been made to devise specification tests based on the oil, resin or asphaltene contents of asphalts (8,29). More complete methods of identification based on the relative amounts of oils, resins and asphaltenes have been outlined, notably by Batchelder (7) and by Nüssel (82). From his work Nüssel concluded that generalizations could not be made between fractionation data and observed performance. This has been confirmed by Hillman and Barnett (38) who have observed that the stability of an asphalt cannot be determined by fractionation unless the character of the asphaltenes and the relation of this character to bitumen stability is known in advance.

The procedures reviewed above will serve to indicate the difficulties encountered in any attempt to correlate the data published in this field. The variation in results is well illustrated by Nellensteyn's experiments (75) which

show that lower surface tension liquids cause a greater precipitation of asphaltenes than liquids of high surface tension. Petroleum ether, b.p. 40°-60°C, with a surface tension of 17.5 dynes per centimeter, flocculated 38% of one asphalt under investigation, while a higher boiling petroleum ether, 100°-130°C, with a surface tension of 24.3 dynes, yielded only 21% of this fraction from the same bitumen. Corlew (20) also reports a large divergence (9-18%) in results depending on the specifications of the solvent. The reason for these deviations is closely allied to the colloidal structure of the asphalt, which will be discussed later.

Consequently the asphaltene, oil and resin fractions must be rigorously defined according to the method of fractionation employed. Although correlation of such data with other published data may not be possible, the determination of oil-resin-asphaltene content may serve two purposes within the particular problem being investigated; these are, the use of this information as a means of following the changes occurring in the asphalt under observation and the use of these isolated fractions to facilitate further studies of the chemical nature and reactions of asphalt.

In a recent paper, Hubbard and Stanfield (43) have outlined a procedure which is reported to be entirely reproducible. The method employs pure n-pentane as a flocculating agent for asphaltenes. The malthenes are divided into oils and resins by distribution on anhydrous alumina and extrac-

tion of the oils with n-pentane in a special constant temperature extractor. The resins are desorbed with benzene. This procedure was adopted for the experimental investigations reported herein, and will be discussed fully in the experimental section.

b. Chromatographic separations

A method of fractionating asphalts into oils, resins and asphaltenes by the principle of chromatographic separation (117) has been described by Grader (30). It is the opinion of this investigator that when a weak adsorbing agent, such as alumina, is used, especially at low temperatures, there should be no chemical change in the constituent parts.

In chromatographic adsorption the most polar bodies are most tenaciously held; hence it was foreseen and then shown experimentally that the oils are most weakly held and the asphaltenes most strongly adsorbed. To obtain a stable column, Grader found it necessary to conduct the separations by fractional elution. All of the solvents used must be chemically homogeneous and be capable of dissolving the asphalt completely; carbon tetrachloride, benzene and chloroform, used in that order, were found to be most suitable.

Merck alumina activated with calcium oxide was used in these investigations. The elutions were effected at constant temperature. The asphalt was taken up in carbon tetrachloride and passed through the column, the oils being

eluted in this step. After sucking the column dry, the second solvent was passed through. The hard asphaltenes remaining in a thin ring at the top of the column could not be desorbed by any of the known asphalt solvents, and were therefore calculated by difference. Grader has suggested the removal of the asphaltenes by solvent precipitation preliminary to chromatographic separations in cases where this fraction is required for further study.

2. The Physical Structure of Asphalt

a. Evidence of a colloidal state

Asphalt has been recognized as a colloidal system primarily through solvent fractionation studies, rheological properties and ultra- and electron-microscopic investigations. Mack (61) points out that the large excesses of solvents required to precipitate the asphaltenes indicate the stability of the colloid and the variation in flocculating powers of different solvents is closely related to the structure of the sol. Hubbard and Stanfield (43) have shown that precipitation of asphaltenes from n-pentane continues for eight to ten hours after initial dispersion. This is taken as evidence that the asphaltenes are present as a protected disperse phase, and may be held in suspension for some time after addition of the solvent before the protecting bodies are completely dissolved and coagulation takes place.

The rheological properties of hard asphalts (low

penetration) were studied by Traxler and Coombs (109,110) using falling coaxial cylinders and conicylindrical rotation viscometers. It was observed that although some asphalts are truly viscous, quasi-viscous flow under stress may be observed in many cases, indicating rigidity in the system. In addition, elastic return was noted even after the application of high shearing stresses over considerable periods of time. The phenomenon of thixotropy or breakdown of structure under mechanical working was also demonstrated. As the asphalts were worked it was observed that the viscosity was reduced. Thixotropy is observed in many colloids, especially those in which the concentration of the disperse phase is appreciable.

It is well known that in "age hardening" the penetration values of asphalts decrease; that is, the asphalts become harder. This hardening may be observed within a few hours after the asphalt has cooled. The asphalt may, however, be restored to its original penetration by heating to the original temperature and cooling. Traxler and Coombs regard this as evidence for the formation within the asphalt of a second structure which is not stable to heat and work.

Saal (95) showed by similar experiments on the rheology of asphalts that these bitumens are likely a mixed gel - sol system in which the degrees of structure vary widely with composition.

Nellensteyn (70) reported that solutions of asphalts in benzene, carbon disulfide, nitrobenzene and

other asphalt dissolving solvents, contain colloidal particles which are easily seen under the ultra-microscope. It appears that the particles in artificial asphalts are more easily seen than those in natural asphalts, although the addition of fine inorganic powders to the latter makes them more easily observable. This same worker later observed (67,74) coarse nuclei in the form of black particles by means of a microscope fitted with an apochromatic lens. Similar microscopic studies by Benson (12) on thin asphaltic films have shown the presence of dark particles within the asphalt.

The study of thin washed films under an electron microscope was undertaken by Katz (48). Typical examples of Katz's findings are reproduced in Table I. The largest particles observed at a magnification of 25,000 X were measured as 65 \AA in diameter.

Chromatographic adsorption indicated (30) that of the three general fractions, oils are the least polar and asphaltenes the most polar. Swanson (105) has shown that asphaltenes and resins are polar while oils are non-polar; this was determined for representative asphalts, the components in relatively dilute solutions, utilizing the heterodyne beat method (11). Katz (48) found that solid material can be deposited electrolytically from freshly filtered crude oil. Platinum electrodes, one millimeter apart and at a potential of 220 volts, were used. After several days the positive electrode was found to be coated with material

TABLE I

Electron Microscope Patterns of Thin Washed Films
(After D. L. Katz and K. E. Beu (48))

Sample	Softening Point	Thin Film Washed In:		
		Benzene	Pet. Ether	Carbon Disulfide
Topped Crude	-	-	-	Hazy, a few large particles
Reduced Crude	-	-	Diffuse particles	Diffuse areas
Vacuum Residue	160	Diffuse particles	Rings, diffuse areas, particles	Webs
Air Blown Residue	214	Sharp particles	Small particles	Webs and particles

which resembled asphaltenes in all respects. These electrolytically separated asphaltenes gave an electron microscope pattern identical with the pattern obtained for asphaltenes flocculated from the same crude by the action of solvents.

A streaming potential of 39 millivolts for crude forced through a silica plug has been recorded by Katz; this potential is attributed to the charge on the asphaltenes since electron microscope patterns of the crude passed through the plug indicated a large number of particles had been removed. This conclusion has been confirmed by Preckshot et al (89) who conducted streaming potential experiments through sand beds. The Zeta potential indicated by this streaming potential is regarded by these authors as being responsible for the formation of the asphalt colloidal

system.

"Sweating" of asphalts has been likened to syneresis in gels by Pfeiffer and Saal (86). Removal of the continuous phase was effected by sprinkling suitable powder evenly on the surface of the asphalt, then removing the powder and extracting the adsorbed liquid. This oily material was shown to be free of asphaltenes and resins.

b. Concepts of the colloidal structure

It is generally agreed that asphalts are colloidal substances in which the oils are the continuous phase and asphaltenes are the disperse phase. However, there is considerable disagreement as to whether the system is a lyophilic colloid or a highly protected lyophobic sol.

The six general criterion for lyophilic sols are:

- a) High stability of the colloid
- b) The disperse phase swells on contact with the continuous phase and dissolves on heating
- c) High relative viscosity of the colloid for a given concentration
- d) Viscosity increases rapidly with increasing concentration
- e) Temperature - viscosity coefficient of sols higher than that of pure solvent
- f) Particles difficult to detect under the ultra-microscope.

Mack (59,60) has shown that asphaltenes are soluble in resins, and on addition to oil fractions swelling occurs. The asphaltenes will in some cases dissolve in the

oil fraction if heat is applied. It was found from viscosity - gravity constants and from refractive indices of the oil fractions investigated that asphaltenes will dissolve in those oils which are rich in aromatic components. Some oils low in aromatic content but rich in sulfur were also found to dissolve asphaltenes.

Asphaltenes are found to have molecular weights of less than 2000 by cryoscopic and viscosimetric methods. Mack suggested that they be classed as semi-colloids, since typical lyophilic colloids have molecular weights greater than 5000. If they are semi-colloids, they should dialyze and diffuse through gel systems. Mack found this to be the case. Experiments were conducted showing that one percent solutions of asphaltenes will diffuse into gels of 20 percent aluminum naphthenate in benzene. This work has been confirmed by Zaharia and Lactau (45) who separated the asphaltenes from resins and wax by diffusion through porous membranes. Mack pointed out that these experiments clearly indicate asphaltenes may be considered as a group of compounds with common general characteristics.

To study the effect of concentration of asphaltenes on the viscosity of asphalts, Mack prepared synthetic asphalts by mixing oils, resins and asphaltenes in the desired proportions. It was shown that the relative viscosities increase rapidly as the concentration of asphaltenes is increased, again indicating a lyophilic system.

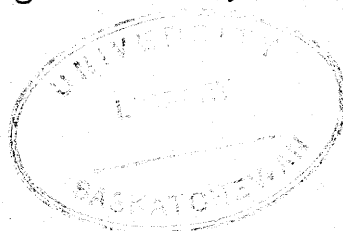
Gel formation and the relatively high viscosity of lyophilic colloids is generally attributed to solvation. Such solvation can only occur through chemical combination or some form of attachment of solvent to disperse phase. In the latter case both components must be charged. Since only the asphaltenes and resins are charged, Mack investigated the adsorption characteristics of resins on asphaltenes (59, 60). He found that Freundlich's adsorption isotherm was obeyed. It was shown from viscosity measurements that the log. of the relative viscosity was directly proportional to the concentration; for this Mack wrote the equation:

$$\text{Log. relative viscosity} = ckM \dots\dots\dots(1)$$

where c is the concentration, M the particle weight and k a constant. If the increase in viscosity with increasing concentration of asphaltenes is due to solvation, then the concentration c and the molecular weight M^1 must both be multiplied by a solvation factor f to give the correct concentration of solute plus solvent. Equation (1) then becomes:

$$\text{Log. relative viscosity} = cf^2 k M^1 \dots\dots\dots(1a)$$

In his studies of adsorption of resins by asphaltenes, Mack found the maximum quantity of resins adsorbed on the asphaltenes to be 23% of the weight of the asphaltenes present; hence, the solvation factor was taken to be 1.23. Assuming an asphaltene molecular weight of 1000, Mack sub-



stituted for M^1 and f in equation (1a) and found the calculated relative viscosity to be less than the observed relative viscosity. Consequently, solvation alone could not account for the increase in viscosity, and some association of the asphaltene particles must have taken place.

Using this equation Mack (61) was able to estimate the degree of association of asphaltenes in his synthetic asphalts. It was concluded that the type of oily constituents present determined the dispersion of the asphaltenes. However, the maximum particle weights observed for viscous asphalts were less than 5000 and Mack classified these systems as falling between true and colloidal solutions, that is, semi-colloids. Plastic asphalts were observed to exhibit high particle weights, hence are to be regarded as truly lyophilic in nature. This colloidal asphaltene particle is referred to as the asphalt micelle.

The electron microscope studies by Katz and Beu (48) indicate that in thin films the asphalt micelle does not occur with a diameter of greater than $65 \overset{\circ}{\text{A}}$, although in thicker films the apparent size is $100\text{--}200 \overset{\circ}{\text{A}}$. Assuming that the density of the micelle is one gram per milliliter, and that these particles are spherical, the micelle gram molecular weight would be approximately 90,000. Since the lowest average asphalt molecular weight is estimated at 1000, this would indicate that a maximum number of 90 asphaltene molecules are aggregated in a micelle.

Saal (95,96), through studies of rheological properties and molecular weight determinations, has reached the same conclusions as were drawn by Mack. Saal regards soft asphalts as semi-colloids, with particle weights of 2000, and highly reduced asphalts as a mixed gel - sol system, with particle weights approaching 30,000.

Pfeiffer and Saal (86) determined the relation of the carbon hydrogen ratio (C/H ratio) to the ability of the asphaltene to adsorb aromatic compounds. A study of relative viscosities of asphaltenes in benzene indicated that micelles formed from asphaltenes with a C/H ratio of less than 0.9 occupy four times the volume of the asphaltenes alone. Those having a C/H ratio of over 1.1 occupy only twice the volume of the original asphalts. (This conclusion is based on the assumption that the asphalt micelles are spherical.) Hence, carbenes and carboids, which have a high C/H ratio, are regarded as special micelles with the power to adsorb only small quantities of resins; due to this property they may be separated from the bulk of the asphaltenes by solvent action.

According to Pfeiffer and Saal, the average particle weights of the asphalt micelle, determined by Langmuir's monomolecular film method, range from 80,000 to 140,000. This is in reasonable agreement with the electron microscope data reviewed above.

These workers believe that the peptizing power of

the malthenes depends on the proportion of aromatic rings present and on their molecular weight. By the study of synthetic asphalts, that is, asphalts prepared by mixing oils, resins and asphaltenes in various proportions, it was shown that a certain optimum aromatic concentration is required for complete peptization. Asphaltenes having a relatively low C/H ratio are easily solvated and hold the resins firmly except when the malthenes are low in aromatic constituents; in this case, gels form. Asphaltenes having a high C/H ratio requires malthenes of high aromatic content to prevent flocculation. Again it was observed that malthenes having a high sulfur content are good peptizing agents.

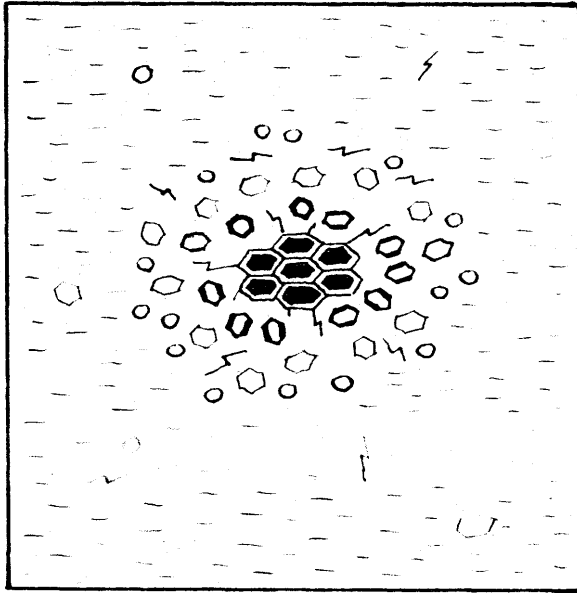
According to the investigators who regard asphaltenes as lyophilic colloids, the structure of the micelle is such that the bulk of the substances with the greatest molecular weight and most pronounced aromatic nature are arranged at the center of the nucleus. This nucleus is surrounded by components of lower aromatic content in such a manner that nearly continuous transition from the disperse to continuous phase is realized. When the system contains sufficient constituents for the complete peptization of the micelles, these particles will be able to move as freely as the viscosity of the intermicellar liquid will permit. Under these conditions, almost purely viscous flow will be observed. If, however, due to the nature of the resins or asphaltenes, or the action of some external agent, there is a shortage

of resins or the aromatic substituents required are not present, the micelles will coagulate. In the extreme case, a gel structure will be formed, the spaces of which will be filled with intermicellar liquid.

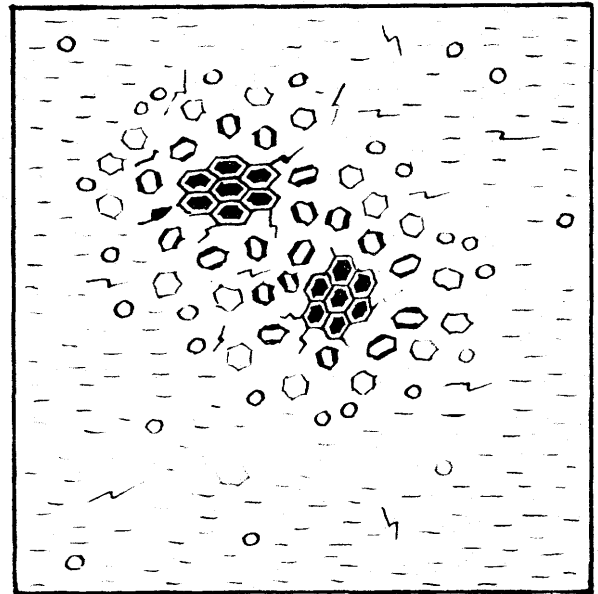
A schematic diagram of this concept of the colloidal structure of asphalts is shown in Figure 2.

In direct contrast to this concept of a lyophilic colloid, Nellensteyn (67,68,73) regards asphalts as belonging to a class of highly protected lyophobic sols. Nellensteyn points out that the lyophilic concept depends upon the peptization of the micelle by aromatic or near-aromatic compounds. However, it has been observed that benzene, toluene and other aromatic solvents are flocculating agents for coal tar, a system allied to asphalt and highly aromatic in nature. Hence, in asphaltic systems the peptizing property may be due to the fact that aromatic compounds usually have a surface tension higher than the critical surface tension (26 dynes per centimeter) of asphaltic bitumens. This is demonstrated by the effect of reagents of different surface tensions in the separation of asphaltenes by flocculation (cf. solvent separations). Reagents with surface tensions of less than 24 dynes/cm. cause flocculation, those over 26 dynes/cm., peptization; those with intermediate surface tensions may cause peptization or flocculation according to the stability of the sol.

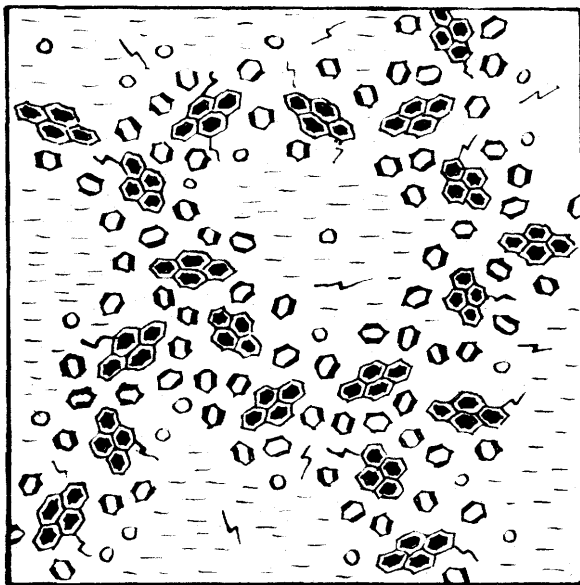
As additional proof, Nellensteyn gave experimental









Peptized Micelles



Flocculated Micelles



Gel Structure

-  Central part, Asphaltenes
-  Compounds of high molecular weight, predominantly aromatic
-  Compounds of lower molecular weight, predominantly aromatic
-  Compounds of mixed aromatic naphthenic nature
-  Compounds of mixed naphthenic, aliphatic nature
-  Compounds of predominantly aliphatic nature

COLLOIDAL STRUCTURE OF ASPHALT (After Pfeiffer & Soal (86))

FIGURE 2

evidence that the oxidation products of asphaltenes are the same as those obtained from carbon black. Also, there is evidence of similarity between the X-ray diffraction patterns of asphaltenes, coke from asphalt and graphite (114). Consequently, Nellensteyn regards the asphalt micelle as composed of a kernel of carbon particles with graphitic structure surrounded by protective substances.

Nellensteyn drew further support for this theory from tar studies. Since hardening of tars is not accompanied by polymerization, hardening of asphalts would not be expected to be the result of polymerization of resins to form more asphalt micelles, as would be necessary if the lyophilic concept is correct. Although the kernel is crystalline, it is not expected that the pattern from X-ray diffractions of asphalts would indicate solid material, since anthracene in tar is completely masked from diffraction by protective bodies.

Later studies by Saal (94) on temperature - surface tension effects and by Rodiger (91) on viscosity measurements would seem to indicate that no semi-crystalline state exists within the asphalt micelle.

Without making reference to either a protected lyophobic or to a lyophilic state, the following generalizations may be made with respect to the colloidal nature of asphalts:

a) Asphaltenes exist in the molecular state in crude oils

- b) In asphalts a colloidal state exists in which the asphaltenes form micelles with the malthenes acting as the continuous phase
- c) Asphaltenes and resins are polar, and the asphaltenes may be precipitated electrolytically
- d) The colloidal properties of an asphalt are determined by the Zeta potential of the asphaltene - malthene interface
- e) The asphalt micelle has a particle weight of the order of 100,000
- f) Rheological studies indicate that in hard asphalts a gel structure exists
- g) Solvent fractionation is essentially arbitrary since the components precipitated will depend upon the extent to which the solvent used attacks the micelle.

c. Quality tests based on colloidal structure

It has been pointed out (82) that quality tests or specifications based on fractionation of asphalts to oils, resins and asphaltenes are not to be favored because of the arbitrary conditions involved in solvent separations. However, since asphalts are colloids of varying stability, it has been the purpose of several investigators to devise specification tests based on the relation between colloidal stability and observed stability in practice. There can be little doubt that such a relation exists (105).

The best known test designed to indicate the

stability of the internal phase is the Oliensis spot test (83,84,115). In this test, the asphalt under investigation is dispersed in naphtha with the addition of xylene as a retarding agent. The dispersion is assisted by shaking and heating. The naphtha - asphalt solution is permitted to come to equilibrium, then a drop of the solution is applied to a filter paper or a glass slide. Homogeneity of the spot is taken as an indication of stability. Benedict (10) substituted normal heptane for naphtha as a dispersion agent in an attempt to make the test more quantitative for distinguishing cracked asphalts from straight-run products. According to this investigator, the presence of as little as 3% cracked stock could be identified. Nevertheless, some asphalts known to contain cracked stock have been shown (54) to give a negative (homogeneous) spot; hence, the value of the test as an indication of stability is in doubt.

Batchelder and Wellman (6) have shown that the percent cyclohexane insolubles less the percent benzene insolubles is an almost quantitative measure of the cracked stock present. Such data are important if flocculation is to be avoided in blending the asphalt base with large quantities of cutback (gasoline or naphtha).

C. F. Williford (114) has conducted X-ray studies on asphalts and was able to draw some conclusions from the diffraction patterns obtained. Intensity curves (i.e. curves relating the change of intensity of the scattered

X-ray beam with the sine of the angle of scattering) were obtained from the patterns developed. It appeared from the intensity of small-angle scattering that discrete particles exist in the asphalt, which is additional evidence for the presence of micelles. It was also evident that the peak in the intensity curves for asphalts which are satisfactory road oils occurs at a constant position, representing an interplanar distance, from Bragg's equation, of 4.8 to 4.9 Å. Asphalts known to be unsatisfactory showed values above 4.9 Å, approaching the value observed for paraffin wax. Williford infers that in such cases the sample contains an excess of resins not yet polymerized to asphaltenes. It would seem from these studies that it is possible to gain valuable information on the stability of an asphalt through diffraction studies. Comparison of the diffuse halo with those obtained for asphalts of known quality would be necessary until the reasons for stability or lack of stability are more clearly understood.

3. The Chemical Structure of Asphalt

a. Average molecular weights

Average molecular weights typical of the values reported for the three main asphalt constituents, the oils, resins and asphaltenes, are reviewed in Table IIa. The majority of these determinations were made by cryoscopic methods. The mathematical equations arising from the Clausius Clapeyron equation relating molecular weight to

TABLE IIa
Average Molecular Weight of Asphalt Fractions

Methods

C(a) - Cryoscopic freezing point and boiling point;
C(b) - Cryoscopic freezing point; V - Viscosimetric.

Solvents

1 - Benzene; 2 - Naphthalene; 3 - Camphor; 4 - Cyclohexane

Fraction	Stock	Method	Solvent	Av. Mol. Wt.	Reference
Oils	Straight run	C(a)	1	293-616	37
	Cracked	C(a)	1	270-483	
	-	C(a)	1	370-710	24
	-	C(b)	1	500	96
	-	C(b)	1	350	34
Resins	Straight run	C(b)	1	1630	
			2	850	37
	Cracked	C(b)	2	800-860	
	-	C(b)	1	540-900	24
	-	C(b)	1	500	34
Asphaltenes	-	C(b)	1	4300-5600	
			3	2219-5160	48
	Straight run	C(b)	1	2400	
			2	1600	36,37
	Cracked	C(b)	2	860	
	-	C(b)	1	1400	34
	Straight run	V	1	1000-1200	
	Air blown	V	1	1200-1600	24
	Cracked	V	1	700	
	-	V	1	500-1800	61
Asphalt	-	C	4	650-1600	61

TABLE IIb

Comparison of Cryoscopic and Viscosimetric Methods
of Determining Molecular Weights (24)

Asphaltene Conc. Weight %	Cryoscopic in Benzene	Viscosimetric
4.7	1892	1433
6.6	2418	1549
8.1	2713	1649

freezing point lowering and boiling point elevation are derived with the assumption that the solution is ideal. It is doubtful if any suitable solvent exists with a structure similar to that of the asphalt fractions, hence it is not likely that the solutions studied approach ideality. Additional doubt on the validity of cryoscopic determinations has been raised by Katz (47) who observed two phases in benzene - asphaltene mixtures at the freezing point.

The molecular weights which were obtained by viscosity methods are the results of attempts to apply viscosity - molecular weight equations of the type used in high-polymer studies. Such equations have the form (24):

$$M = \frac{K \log. \frac{\eta}{\eta_{\text{solvent}}} \frac{\text{solution}}{\text{solvent}}}{C} \dots\dots\dots (2)$$

where M is the molecular weight, η the viscosity and C the concentration. Equation (2) is, in effect, the equation derived by Mack (equation (1)) for viscosity - molecular weight relationships. It was found that the cryoscopic molecular weights of many oils and resins, on substitution in equation (2), did result in a constant value for K. It was this value of K which was used to determine the molecular weights of the asphaltenes.

Comparison of cryoscopic and viscosimetric determinations is made in Table IIb.

These average molecular weights are regarded as

representing the oil, resin and asphaltene molecules as individual entities, in contrast to the micelle particle. As recorded previously, the particle weight of the micelle is estimated by electron micrograph (48) association studies (61), and Langmuir's monomolecular film method (86), as being of the order of 4,000 to 100,000 depending upon the degree of association.

b. Types of structure in asphalt fractions

The structure of synthetic (petroleum) asphalt fractions must be related to the type of crude from which they have been refined. The existence of paraffin, naphthene and asphalt base crudes has been recognized by operators, primarily according to the type of residues obtained. Lane and Barton (51) have suggested the classification of crudes in nine possible brackets based on the gravities of two key boiling fractions. The crudes are classified as naphthenic and paraffinic, with seven intermediate classes. This does not account for crudes which are predominantly aromatic in nature. In view of the complexity of the crudes themselves, it is hardly likely that all asphalts contain compounds of the same structure.

Study of individual compounds which exist in petroleum residues is particularly difficult since asphalts cannot be distilled without cracking, even under vacuum (57). Bestorigeff and Darmois (13,14) found that fractional extraction with benzene was not sufficient to isolate families

of well-characterized components. Separation of petroleum fractions using hot mixtures of ether and alcohol was undertaken by Mabery (58). The heaviest fractions obtained in the series which were asphaltic in the heavy ends were found to have the following average compositions, based on cryoscopic determinations.

<u>Crude</u>	<u>Molecular Weight</u>	<u>Empirical Formula</u>
Cabin Creek	1700	$C_{122}H_{232}$
Rosenbury	1734	$C_{125}H_{234}$
Mecca	1668	$C_{122}H_{204}$
Sour Lake	1240	$C_{90}H_{160}$
Baku	1100	$C_{80}H_{140}$

Oxygen, sulfur and nitrogen contents were not reported.

Several methods for the estimation of aromatic, naphthenic and paraffinic content of asphalts have been discussed. Eisner et al (25) have shown that successive extractions with 86% and 98% sulfuric acid give a good indication of the olefins and aromatics present. The 86% acid will sulfonate olefins, and the 98% acid, the aromatics; the difference between the total sample and the sum of these values indicates the naphthene and paraffin content.

The Waterman determination (112) of naphthenic and aromatic content by refractive indices before and after catalytic hydrogenation was utilized by Hillman and Barnett (36) in a study of malthene fractions. The results from

TABLE III

Waterman Analysis of Malthene Fractions (112)

Stock	Molecular Weight	Aromatics %	Naphthenes %	Paraffins %
Straight run	293	14	35	51
	448	27	24	49
	616	53	1	46
Cracked	270	36	16	48
	344	47	1	52
	350	51	2	47

these analyses are indicated in Table III. Kreulen (50) has indicated, however, in a similar study of Utah Gilsonite (a natural asphalt) decreases in molecular weight after hydrogenation, hence, the Waterman analysis as applied to asphalt fractions may not be reliable.

Grant and Hoiberg (32) have indicated that physical constants may be used in estimating the predominant components in oils and resins. Briefly, this involves the determination of the specific dispersion, the refractive intercept and the bromine number of the malthene fraction under study. The specific dispersion is defined by the equation (33)

$$\delta = \frac{n_{\alpha} - n_{\beta}}{d} \cdot 10^4 \dots\dots\dots (3)$$

where δ is the specific dispersion, n the refractive index for the α and β hydrogen lines, and d is the density. The refractive intercept is calculated from the equation

$$I = n_d - \frac{d}{2} \dots\dots\dots (4)$$

where I is the refractive intercept, n the refractive index for the d line of sodium and d is the density. Values for these constants are known within certain ranges for paraffinic, aromatic and naphthenic compounds. Neither this procedure nor the Waterman analysis has been applied to asphaltenes.

The malthenes from eleven asphalts studied by Grant and Hoiberg all showed definite predominance in aromatic constituents. The Waterman analysis reviewed in Table III, however, indicates that in some cases the resins and oils are predominantly paraffinic in nature. Grader (30), on the other hand, has shown that natural asphalts are particularly rich in cyclic hydrocarbons, and conversely, less suitable synthetic asphalts have correspondingly high paraffin content.

Williford's work (114) on electron microscopy of asphalts also indicates that asphaltenes of proven value are not paraffinic in nature. Although there is similarity between the diffraction patterns obtained for asphalts and those for petroleum vaseline, there is considerable divergence from the pattern observed for paraffin wax.

There is direct evidence for condensed aromatic nuclei in asphaltenes. Cropper and Strafford (21) have isolated small amounts of anthracene by chromatographic methods using alumina as an adsorbent. The anthracene was recognized by characteristic fluorescence and its subsequent

solution in chlorobenzene. Other polynuclear aromatic compounds have been identified in asphaltic bitumen which had been heated just below cracking temperature. Nellensteyn (78) has isolated picene, chrysene and anthracene. The presence of picene in reduced California crude was confirmed by Hillman (37). In all cases the quantity of these compounds isolated was very small.

c. Reactions of asphalts and asphalt fractions

Asphaltenes and asphaltic resins react with fuming nitric acid giving nitro compounds which are soluble in acetone (59). Treatment of these nitro compounds with alcoholic potassium hydroxide converts them to water soluble derivatives. Asphaltenes are sulfonated by fuming sulfuric acid, and oxidized to acids with potassium permanganate. None of the three fractions (oils, resins and asphaltenes) react with diazo compounds, nor with phosphorus pentachloride. Further, they cannot be saponified and show only small acetyl numbers. It would appear from these data that acids, esters and lactones are not present in appreciable amounts, nor do the molecules contain alcoholic-, phenolic-, or oxy- groups. Hillman and Barnett (59) have found that the calcium salts of sulfonated derivatives of the three fractions are qualitatively identical, which suggests close chemical relation between these fractions. Although carbenes and carboids react with nitric and sulfuric acids as do asphaltenes, the calcium sulfonates indicate different

structures.

Contrary to Mack's observations, Jachzel (44) has recorded the treatment of asphalts with 4% NaOH for three to six months and recovering a saponified product. The "resin acids" liberated with sulfuric acid showed acid numbers of 630 to 1250 with 5 N alcoholic potassium hydroxide. Treatment with potassium iodide for the same period of time gave no reaction.

Evolution of hydrogen bromide and iodide following treatment with bromine and iodine indicated (87) that substitution of these halogens rather than addition takes place, and consequently few, if any, aliphatic double bonds exist. Marcusson (63) suggested that any iodine adsorbed without evolution of hydrogen iodide may have gone to the formation of iodonium compounds. Nametikin is quoted in a review of the Russian literature (45) as having found that the amount of benzoyl peroxide decomposed by asphaltenes decreases with the age of the asphalt, while the same determination, the so-called "Oxygen Number", increases for resins.

Chlorination of asphaltenes was effected by Nellensteyn (79) at temperatures from 200°F to 500°F. Hexachlorobenzene was isolated from the reaction mass as fine needles; the remaining oil product, containing 43.1% chlorine, could not be further crystallized. Free sulfur was recovered as well as an amorphous residue.

The oils have been found (100) to contain no active hydrogens. The resins, on the other hand, contain 0.11%

to 0.13% active hydrogens and the asphaltenes 0.06% to 0.08%.

The carbon hydrogen ratios (C/H ratio) for resins and asphaltenes are high; the former have C/H ratios approaching 9 and the latter as high as 13.5. This is in itself indication of cyclic character. Since it has been shown that few olefinic linkages exist in asphalt fractions, sulfonation must occur on aromatic nuclei; and since asphaltenes and resins may be sulfonated to completely water soluble products (36), the cyclic compounds present must be, at least in part, aromatic in nature. Additional evidence for aromatic nuclei has been presented by Abraham (1), in the formation of "formalite" by the action of formaldehyde on asphaltic constituents in the presence of sulfuric acid. Abraham found this reaction to be typical of aryl compounds.

It has been stated previously that these fractions are, like most complex organic compounds, not stable at high temperatures. It would seem that asphaltenes are less stable to heat than are malthenes; Hillman (36) has found that the proportion of carbenes and carboids increases with the degree of cracking but that the conversion of asphaltenes to carbenes is more rapid than the conversion of resins to asphaltenes. Abraham (1) considers the paraffin side chains as being the least stable entities in the asphaltene molecule and has suggested that these are lost on cracking. If this is the case, asphaltene side chains must be less stable than malthene side chains, since the Waterman

analyses indicated in Table III denote no loss in aliphatic constituents during cracking. Since water and hydrogen sulfide are by-products of asphalt processing, Murphy (66) has interpreted the Waterman analysis as indicating that dehydrogenation of existing naphthenic groups has occurred.

d. Oxygen, sulfur and nitrogen in asphalt

All asphalts contain oxygen, sulfur and nitrogen in varying quantities. Total analysis of numerous asphalts by Lang (52) and by Williford (114) indicates the following ranges for these elements:

Oxygen	0.12% - 2.20% (by difference)
Sulfur	0.26% - 6.73%
Nitrogen	0.05% - 2.90%

Lang observed considerable difference between nitrogen values determined by Kjeldahl and Dumas methods. The latter procedure gave higher results than the former, but no constant difference or trend was observed. Ellis (66) has reported that nitrogen may occur as isolated quinolinic or pyridinic bases. In most cases, however, nitrogen has been ignored as being inert or as being present in quantities too small to be effective.

Hillman and Barnett (37) have reported the following distribution of oxygen and sulfur in a cracked asphalt sample:

	Oils	Resins	Asphaltenes
Oxygen (by diff.)	0.4 - 1.2%	1.3%	3.7 - 6.7%
Sulfur	0.7 - 0.9%	1.3%	0.3 - 0.9%

Like nitrogen, little is known about the role of oxygen in asphalt. Kalichevsky (45) and Williford (114) state that due to the small quantities of oxygen present in asphalts it is likely that it is of minor importance. However, as will be seen later, oxygen is absorbed during oxidation and hardening of asphalts, and oils can be converted at lower temperatures to asphaltenes only in the presence of oxygen; consequently, the assumption of its minor importance may not be valid.

It has been shown (61,114) that the sulfur content of the resins has a direct effect upon the colloidal state assumed by the asphalt. There can be little doubt that some asphalt residues contain sulfur in the elemental state; Ariano (5) has obtained crystals of sulfur from Abruzzi reduced crude. Nellensteyn (72) has shown that kerosene, paraffin and lube oils heated in the presence of colloidal sulfur yield asphaltene-like bodies, not observed when sulfur is absent. Hydrogen sulfide was recovered during the heating period. Similarly, Gruse (66) found that octylene and colloidal sulfur on heating yielded a fraction, $C_{64}H_{32}S_5$, which was similar to asphalt. If sulfur is heated with asphalt below the temperature of hydrogen sulfide evolution, considerable change in the physical properties of the asphalt is observed (9).

Colloidal sulfur is present in many crudes as

obtained from the well. Friedmann (26) and Williford (114) support the hypothesis that this colloidal sulfur is incorporated by the hydrocarbon molecules as processing proceeds; from the known chemical activity of sulfur and its oxidizing effect on hydrocarbons, it is highly probable that some type of carbon to sulfur bond is formed at high temperatures. Mack's suggestion (59) that sulfur so included is present as a heterocyclic compound or as a bridging unit is verified by Garner's isolation (28) of thiophenes from malthene fractions. Spielman (66) found that the oxidation of asphalt samples rich in sulfur with persulfuric acid yields sulfoxides and sulfones; this also suggests that sulfur occurs in thionaphthene-type compounds.

e. Proposed structures for asphalt fractions

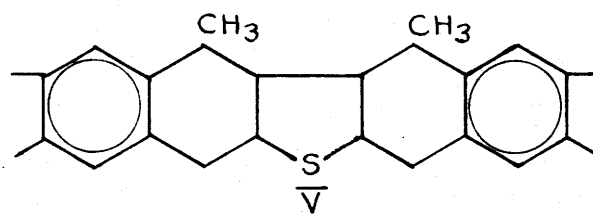
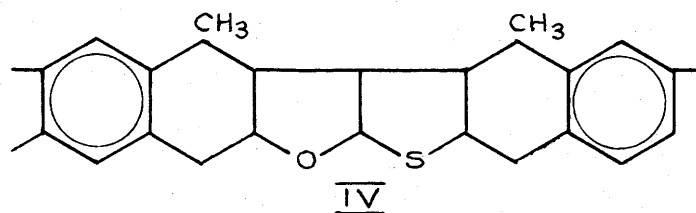
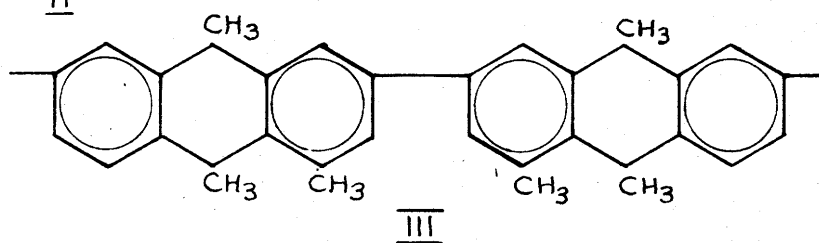
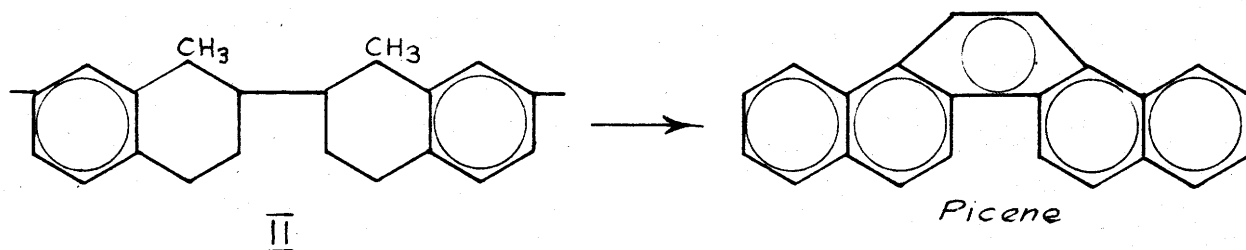
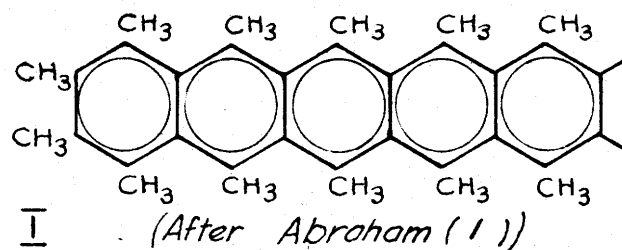
The investigations reviewed above indicate that asphalt fractions in all probability are aromatic and/or naphthenic compounds with heterocyclic components or bridges and paraffinic side chains of uncertain length. There is some disagreement in the structure types proposed by various investigators, primarily due to the uncertainty of the quantity of aromatic and naphthenic nuclei present in the molecules.

Abraham (1) states that the presence of aromatic compounds with long side chains in cracked stock is not likely because of their instability at cracking temperatures; hence an accumulation of naphthalene derivatives and other

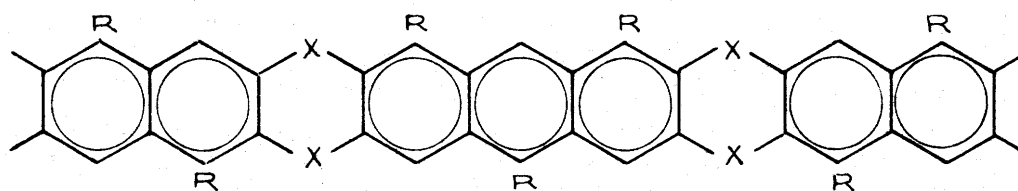
condensed aromatic hydrocarbons is to be expected. (In Figure 3, Abraham's concept of the asphaltene structure, as well as those of the investigators quoted below, have been drawn for reference and comparison.)

Hillman and Barnett (37) do not agree with such a structure, pointing out that picene, crakene and truxene, known polynuclear aromatic hydrocarbons, are extremely insoluble, while asphaltenes are soluble in benzene and carbon tetrachloride. As was stated earlier, these workers observed that the calcium sulfonates of the asphaltenes and resins are qualitatively identical in appearance and solution behavior. They have assumed from this that types of building blocks exist which are common to oils, resins and asphaltenes; in the case of asphaltenes, these must be easily split by hydrogenation into smaller units as exist in the oils and resins.

Since it is not likely that many paraffin side chains exist in cracked asphaltenes, Hillman and Barnett have conceived structures conforming to observed C/H ratios by linking small partially hydrogenated naphthalenic molecules together through carbon to carbon, or carbon to sulfur, oxygen and/or nitrogen bonds. (See II, III, IV, V, Figure 3.) Hillman draws additional evidence for formula II by the suggestion that on cracking it would be feasible for this molecule to polymerize and dehydrogenate to picene, IIa, which has been isolated in small quantities from cracked



(After Hillman & Barnett (37))



R = C₃H₇ or C₄H₉; X = O or S (After Murphy (66))

PROPOSED STRUCTURES OF ASPHALTENE MOLECULES

FIGURE 3

asphalts. Nellensteyn (77) also stated that $-CH_2-$ groups are apparently predominant in the protecting bodies (resins) supporting the presence of naphthenic nuclei.

Mair et al (62) reached the following conclusions regarding the ring structure of Mid-continent lubricating oil:

- a) 60% of the molecules are naphthene rings, with one to three rings per molecule,
- b) 15% consist of molecules of one aromatic ring and one to three naphthenic rings, associated with some sulfur and oxygen,
- c) 14% of the molecules are composed of two aromatic and two naphthenic rings associated with a small amount of oxygen and sulfur,
- d) 11% consist of molecules with more than two aromatic rings.

Murphy (66) has suggested that during processing the aliphatic rings in the oil fractions are dehydrogenated to aromatic nuclei. Murphy also points out that if the Waterman analysis (Table III) is to be accounted for, 50% of the molecules must be paraffinic side chains. Furthermore, if sulfur is to cause increase in molecular weight by polymerization of oils to resins and asphaltenes, the building blocks must be linked by suitable bridges. From these considerations, Murphy has suggested that asphaltenes are condensed nuclei linked by sulfur and oxygen bridges with aliphatic side chains of three to four carbon atoms. (See VI, Figure 3.)

None of these proposed basic units is compatible

with all the observed properties of resins and asphaltenes. Presumably Murphy's structure would be insoluble in solvents which dissolve asphaltenes but not picene, truxene and crakene; further, Hillman and Barnett's elemental analysis of asphalt fractions indicates that the sulfur content of asphaltenes is lower than that of resins. Consequently, it would appear that conversion of resins to asphaltenes must be possible without sulfur bridging and/or with the loss of sulfur.

Hillman and Barnett's proposals account for the increase in C/H ratios if the oil - resin molecules are predominantly naphthenic and are dehydrogenated during conversion to asphaltenes. Sulfonation data and refractive index experiments indicate that resins are predominantly aromatic. In addition, the absence of aliphatic substituents to the rings of this proposed structure is not in agreement with Waterman analyses.

It should be noted that Waterman analyses supply the only evidence for the presence of numerous aliphatic members; and the value of such analyses has been questioned, when it was found that hydrogenation was accompanied by a decrease in molecular weight. All results, however, indicate an increase in aromaticity as the molecular weight of the asphaltic bodies increases; whether this is due to dehydrogenation of existing naphthenic bodies or to polymerization and dehydrogenation, is not clear.

It has been shown that the aromatic nature and the C/H ratio of the asphaltenes and resins have a profound effect upon the colloidal state and stability exhibited by the asphalt. Since asphalts have varying stability, arise from different sources and may undergo completely different procedures in refining, it is possible that a fundamental unit such as suggested may be present in some asphalts and entirely lacking in others. As yet there is little evidence to indicate that all asphalts have the same basic structure. However, the following generalizations, based on the research done to date, may be made:

- a) It would appear that malthenes are polynuclear aromatic and naphthenic hydrocarbons, predominantly aromatic in nature, which may have aliphatic side chains of uncertain length
- b) The conversion of malthenes to asphaltenes is accompanied by dehydrogenation and polymerization, the former may be the result of reduction of naphthenic to aromatic nuclei
- c) Sulfur and oxygen may be present as bridging units
- d) Sulfur is chemically included into the asphalt fractions as processing is carried out
- e) The colloidal structure assumed by the asphalt is closely related to the chemical structure of the malthenes and asphaltenes.

4. Oxidation of Asphalts

The oxidation of asphalts is of particular interest for two reasons; first, air blowing of reduced crudes and asphalt is common refinery practice for adjusting the physical properties of asphalts and for producing extremely hard products; second, the oxidation reactions are undoubtedly responsible for many of the characteristic changes observed during exposure and weathering. Of the two, weathering is more complex than controlled blowing since moisture, humidity, temperature and sunlight are found to have considerable effect on bitumens.

a. Weathering and film oxidation

The majority of investigations on asphalt weathering have involved the use of apparatus designed to accelerate the reactions, hence reduce the time factors involved in natural exposure. Nisikawa (81) has found that thin films weathered under natural conditions harden and increase in weight; an increase in weight was also observed for films submerged under water for considerable periods of time. Nisikawa concluded that both oxygen and water may be absorbed by asphalt; however, sunlight and air had the greatest effect on the films. Mitchell (65) observed that weathering of road binders gives rise to a tough protecting skin which is apparently less susceptible to further oxidation and protects the underlying surface.

Thin films of 0.001 inches thickness were pre-

pared by Benson (12) on glass slides and subjected to natural weathering, various types of artificial weathering, and to heat. The weathering was conducted in a celluloid-covered box in which maximum temperatures of 185°F were observed. Artificial methods included heating at 140°F and 325°F, and also radiation with infra-red lamps at 140°F and cold-quartz lamps. In some cases, microscopic examination of the film indicated that coagulation had taken place, the amount of coagulation being dependent on the weathering procedure used. Carbon dioxide atmospheres were found to inhibit coagulation while oxygen accelerated the separation. No correlation was found between coagulation and the serviceability of the asphalts as road binders.

Lewis and Welborn (55,56) have shown that after thin film oven tests, the ductility of nearly all asphalts is reduced, and suggest that the ability of an asphalt to retain its original characteristics in an oven test may indicate its durability. Thurston (107) irradiated synthetic asphalts (i.e. asphalts prepared by mixing oils, resins and asphaltenes in the desired proportions) by arc lamp, with periods of water-spray and intervals at freezing temperatures. Observation indicated that asphalts with high resin contents are less susceptible to weathering. Anderson et al (4) found that deterioration of cracked asphalts is more pronounced than that of straight run (steam refined) fractions.

Asphalts which have been exposed to ultraviolet light form brownish, chalky films when immersed in water.

Strieter and Snoke (101) found this film to be resin-like and acidic in nature. It has been found that the asphaltene content increases during natural and artificial weathering. Zapata (118) recorded an increase in "hard asphaltenes" of 30% to 100% after 15 hours exposure to ultraviolet radiation. Samples exposed to natural weathering did not show such a marked increase, although a similar trend was evident.

More fundamental studies of this photooxidation have been described by Thurston and Knowles (108). These authors oxidized asphalt components (separated according to Cannon and Fenske (15)) in sealed tubes and erlenmeyers containing oxygen at slightly over atmospheric pressure. The tubes were irradiated with a standard sun lamp, a temperature of 77°C being recorded. Gaseous products of the oxidation were recovered as well as the residues. Of the constituents identified as asphaltenes, resins, naphthenic oil, paraffinic oil and wax, it was observed that the resins and naphthenic oils absorbed slightly more oxygen than the other fractions. Approximately 50% of the oxygen used was absorbed by the sample, 35% evolved as water, and 10% as carbon dioxide. The data for three asphalts indicated that all constituents are susceptible to photooxidation, although relative sensitivity is dependent on the source of the asphalt.

The evolution of carbon dioxide and water from thin heated films in the presence of oxygen had been observed previously by these investigators (106). In these studies,

the asphalt was fractionated according to Marcusson (63) and the constituents dispersed on fine sand. The samples were oxidized at 200°C in a closed system which permitted determination of the rate of disappearance of oxygen and collection of the carbon dioxide and water evolved. No provision was made for recovery of volatile products. It was found that the asphaltenes were the only constituents which gained in weight; the asphalt itself lost weight. Further, the rate of disappearance of oxygen was greatest for the asphaltenes. Approximately 60-70% of the oxygen used was recovered as water; in the fractions other than the asphaltenes as much as 19% of the oxygen was not accounted for.

It was suggested that the oxidation might take place by three mechanisms:

- a) Formation of unstable compounds on addition of oxygen which lose water and polymerize
- b) Oxidation to carboxyl derivatives from which carbon dioxide is lost, followed by polymerization
- c) Loss of unstable oxidation products other than carbon dioxide, followed by polymerization.

Considerable carboids were formed on oxidation of asphaltenes, a phenomenon not usually noticed in the oxidation of asphalts. Hillman and Barnett pointed out that the products of oxidation of separated asphaltenes will not likely be indicative of the products to be expected from the protected asphaltene micelle.

It is not possible to say whether or not the dif-

ference in oxygen susceptibility observed in these two experiments is due to the presence or absence of ultraviolet light, since they were conducted at different temperatures. Two main differences are evident however: the asphaltenes are less stable at 200°C than the resins, while at 77°C, under ultraviolet radiations, the reverse is true; also no volatile oxidation products were observed at 77°C other than carbon dioxide and water, as were observed at 200°C.

Ebberts (23) has outlined a quality test for asphalts based on the oxidation of thin films with potassium permanganate solutions. It has been pointed out (64), however, that although there is some correlation between reagent absorbed and observed behavior, it is not likely that potassium permanganate reacts with asphalts in the same manner as free oxygen.

b. Bomb oxidation

Bomb oxidations have been studied by May (64) using benzene solutions at 25°C under an initial oxygen pressure of 100 pounds per square inch. A relation between penetration susceptibility and oxygen consumed was observed. Similar oxidations were conducted by Haus (34) at temperatures of 150°-250°C. Haus found that the quantity of asphaltenes increased on oxidation and the C/H ratios and oxygen contents of all fractions also increased. Sulfur was found to remain divided between oils, resins and asphaltenes. It was concluded that aging and oxidation are accompanied by

conversion of oils to resins and resins to asphaltenes, the rate of conversion being dependent on the conditions.

c. Air blown asphalts

Asphalts are produced from all types of crudes by blowing with air at elevated temperatures. According to present practice (1), temperatures of 525°-575°F are used, with 30-50 cubic feet of air per minute per ton of asphalt charged. Volatile oils, carbon dioxide and water are removed. The products obtained are less susceptible to temperature change than steam refined products of the same penetration and have higher softening points. Although often resilient and rubber-like, blown asphalts have poor ductility characteristics. Nevertheless, crudes which would otherwise give poor asphalts or none at all by vacuum or steam distillation often yield suitable products. Asphalt base crudes give a higher yield of asphalt of the desired penetration by blowing. It is often possible to obtain products, by the judicious coupling of distillation and air blowing, which would otherwise not meet all of the required specifications.

Several qualitative tests for asphalts have been outlined involving the measurement of physical properties before and after blowing. Nicholson (80) blew asphalt samples of 225 grams at 425°F with 0.33 cubic feet of air per minute for fifteen minutes. The ductility and penetration after this test were compared to the original values. As an alternative, Nicholson blew the asphalt under investi-

gation until a penetration of 20 was obtained, and recorded the quantity of air used and the resulting ductility. Two asphalts investigated by these methods were observed to retain their original ductility, while six others became "short". Raschig and Doyle (90) have reported similar tests with slightly varied conditions. Although data from Nicholson's and Raschig's experiments checked for identical asphalt samples, the information is limited and inconclusive. Skidmore (99) has found some correlation between decrease in penetration and ductility on air blowing and the decrease in these properties observed in asphalt - aggregate mixing plants.

Studies on the chemical changes occurring when asphalt is blown have been made by Katz (48). Samples of Alberta bitumen were blown in a steel reactor equipped with a stirrer and reflux condenser, and maintained at 270-275°C by an oil bath. Air was introduced at six milliliters per minute per gram of sample. The major part of the volatile oils was returned to the asphalt by the reflux condenser; no provision was made for collecting the carbon dioxide and water evolved.

Katz fractionated the asphalts into asphaltous acids and anhydrides, oils, resins and asphaltenes by Marcusson's method (63). It was observed that the quantity of asphaltenes present increased on blowing accompanied by a decrease in the other constituents. The molecular weight of the asphaltenes (determined by the Rast method) increased

from 2,200 to 4,700 over the blowing period. Similarly, the resins increased in molecular weight (cryoscopic, in benzene) from 700 to 1,000; no increase was observed for the oil fraction.

Ultimate analysis of the constituents of original and blown bitumens indicated that the sulfur content of each remained essentially constant. The oils contained no oxygen even after blowing and the oxygen in the asphaltenes increased only slightly in the latter stages of blowing; the oxygen content of the resins, however, increased from zero to 2.65%. Nitrogen contents remained the same for asphaltenes and resins but decreased for oils from 0.28% to 0.06% (Kjeldahl Method).

Katz concluded that asphaltenes are not as susceptible to oxidation as the resins, and that nitrogen and sulfur in asphalt are stable entities. The net result of air oxidation was regarded as the gradual polymerization of the asphaltene molecules. However, it also appears from these data that the quantity of asphalts has increased at the expense of the oils and resins; apparently, the resins have also undergone polymerization.

Kamptner and Maas (46) conducted similar blowing experiments on a paraffin, a naphthene and an asphalt base crude. Microscopic examination of the blown products indicated that of the hardest asphalts obtained, only those from the asphalt base crudes were homogeneous; the residues

from the other crudes contained fine to coarse grained material, regarded as "free carbon". Again the increase in asphaltenes and decrease in oils and resins was observed for all three asphalts. Kamptner and Maas concluded that, on blowing, resins are formed from oily fractions and these are in turn converted into asphaltenes. A part of the asphaltenes is, in the case of paraffin and naphthene base stocks, converted into carbenes and carboids. Hence, it appears that the asphaltenes from these crudes are particularly susceptible to oxidation.

It has been seen that aromatic constituents are essential for peptization of the asphalt micelle. These investigators have suggested that aromatic resins are rapidly converted to asphaltenes and only in the case of asphalt - base residues are there sufficient aromatic resins left after oxidation to continue effective peptization. The naphthene and paraffinic base residues, on the other hand, quickly lose their protective bodies, and the asphaltenes are open to oxidation to carboids and are free to flocculate.

Support for this hypothesis may be drawn from Hicks-Bruun's studies (35) on the oxidation of lubricating oils. In these investigations, it was found that oils containing 19% aromatic constituents form a sludge three times more rapidly than oils containing only 3% aromatics. Further, Thurston and Knowles' studies (106) of thin film oxidation indicated that separated asphaltenes oxidize rapidly to carboids, absorbing oxygen more readily than resins under

the same conditions.

Hoiberg (41) and Rossi (93) have also observed a decrease in acids and anhydrides, and an increase in asphaltenes at the expense of oils and resins. Davis et al (22) have shown that the sludge resulting from oxidation of lubricating oils may be fractionated into resins and asphaltenes by solvent methods. Oxidation of asphaltenes at 180°-190°C yields humic acid-like material according to Zabavin (116). Similar oxidation of resins yields asphaltenes differing from the original asphaltenes in that they will react with methanol in the presence of hydrochloric acid, and with diazomethane, and are apparently resistant to further oxidation.

According to Kalichevsky and Fulton (45) only those resins which are soluble in sulfuric acid may be converted to asphaltenes, unless sulfur is present. Further, these authors indicate that asphaltous acids and anhydrides are quickly converted into resins and asphaltenes on heating. Hence, the present concept of conversion of oils to resins and asphaltenes involves the formation of acids and anhydrides, which, after losing water or carbon dioxide, polymerize.

The unique physical properties of air blown asphalts may be attributed to the formation of a gel structure due to the decrease in protective bodies and an increase in the quantity of asphaltenes present (see Figure 2). The extrusion of oily material, the counterpart of syneresis

in aqueous gels, has often been observed in blown asphalts. However, the properties appear to be due to two structures, one of which is not stable to work and heat (110). Abson (2) has shown that oxidized asphalts become softer after they have been heated to temperatures above those used in blowing, but below the cracking point; the degree of softening is proportional to the maximum temperature reached in heating. No such change is observed for steam refined asphalts. As yet, no theory has been proposed to account for the changes occurring in blown bitumens when this procedure is carried out.

III. EXPERIMENTAL

The plan of attack adopted in these investigations of the oxidation reactions occurring in asphalt, involves the blowing of reduced crude under controlled conditions designed to permit recovery of all oxidation products. Although carbon dioxide and water are known to be evolved, their quantitative determination has not been reported; hence, it is one of the main objects of this research to ascertain the relation, if any, between the quantities of these products produced and the changes occurring in the asphalt. Further, the effect of blowing with an inert gas at elevated temperatures has not been recorded.

It was decided to fractionate the recovered residues into oils, resins and asphaltenes to determine the extent of conversion of the constituents and to facilitate further study of the asphalts produced. Tests planned for these fractions included determination of the oxygen content (by direct determination) and sulfur content, as well as their relative average molecular weights. In this manner, the oxygen absorbed by each fraction with time might be determined and the course taken by the sulfur followed. Molecular weights would serve to indicate the extent of polymerization taking place within each fraction. However, it was not possible to complete determination of sulfur contents and

molecular weights for inclusion in this thesis.

The stock used in these investigations was a commercial reduced Lloydminster crude of 12° A.P.I. gravity. This crude is particularly rich in asphaltic constituents and produces straight run asphalts which are considered to be of high quality.

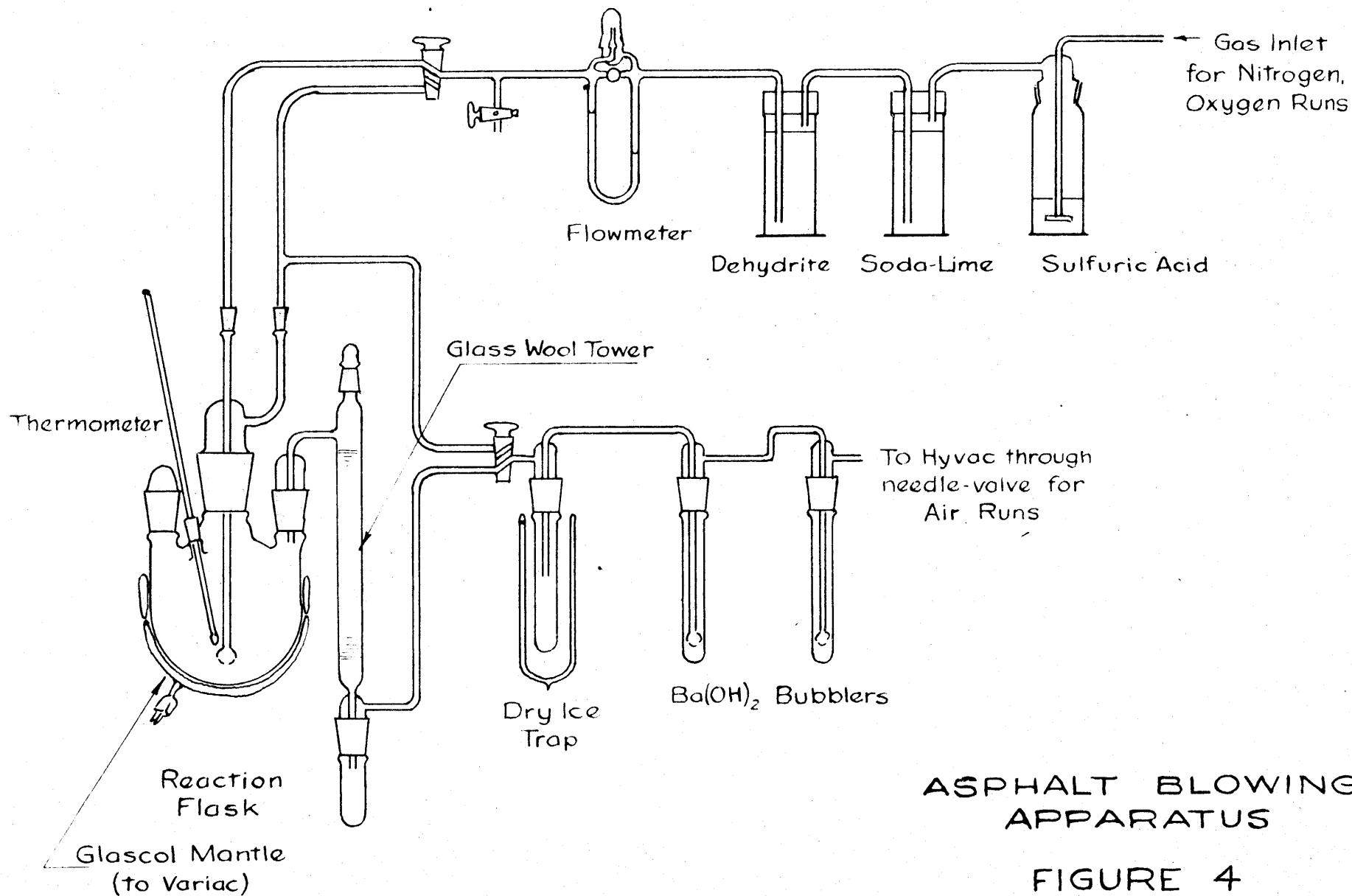
1. Air Blowing of Reduced Crude

a. Blowing procedure

For the blowing experiments, a moderate temperature and a slow blowing rate were adopted, at the expense of time, so that water, distilled oils and carbon dioxide might be easily recovered. In addition to blowing samples with air, oxygen runs were conducted under identical conditions as well as nitrogen runs, the latter serving to indicate the effect of heating with agitation at the elevated temperature.

The apparatus used was constructed of pyrex glass (see Figure 4). The purification train, consisting of a sulfuric acid bubbler, a soda-lime absorber and a dehydrite absorber, was designed to remove extraneous matter, carbon dioxide and water from the incoming gas. For nitrogen runs, hot copper wire maintained at 600°C preceded this purification train to remove traces of oxygen (not shown in Figure 4). The indicator liquid selected for the flowmeter was n-butyl phthalate.

The reaction vessel was a three neck, standard taper, 500 ml. round bottom flask, fitted with a standard



taper opening for a thermometer. The bubbler contained five 3/32 inch holes for dispersion of the gas stream. Since sufficient agitation was supplied by the gas, no special stirrer was used. Heat was supplied by a glascol mantle controlled by a variac.

The distilled oils were removed by the effluent gas as a fine mist and it was necessary to use a tower lightly packed with glass wool to effect their recovery. A dry ice - acetone cooled trap was used to condense the water produced, and bubblers filled with saturated solutions of barium hydroxide removed the carbon dioxide evolved. Barium hydroxide was used instead of askarite, since traces of oil were observed to deposit on the latter during blowing. Provision was made for by-passing the reaction flask and for sweeping out the flask with the gas stream.

The tared reaction flask was charged with 200 ± 5 grams of reduced crude weighed to the nearest 0.1 gram and placed in position. The temperature was brought to $200^{\circ} \pm 3^{\circ}\text{C}$ as quickly as possible (about twenty minutes) with the system open to the air until a temperature of 100°C was reached, at which time blowing was commenced to prevent spot heating in the flask. The blowing rate was adjusted to give 300 ml. of gas per minute, or 1.5 ml./gm./min. For oxygen and nitrogen runs, the gas was supplied from high pressure cylinders; for air runs, the gas was drawn through the system by a rotary oil (Hyvac) pump to ensure a constant blowing rate.

The flow of air was controlled by a needle valve situated between the pump and the apparatus.

The nitrogen runs were continuous. During oxygen and air runs, however, it was necessary to stop the blowing for five minutes periodically (every eight hours for air, every four hours for oxygen) to melt the ice blocking the neck of the dry ice trap and to remove the precipitate in the barium hydroxide traps. At the same time fresh barium hydroxide was introduced.

At the completion of the blowing period, heating was stopped, and in the case of air and oxygen runs, the flask was swept with nitrogen to remove the last traces of water and carbon dioxide. This operation required 30 minutes for air runs and up to three hours for oxygen runs. The flask was removed, weighed, and the product poured, while still hot, into a glass storage bottle. The oils adhering to the glass wool were washed through with benzene, and the solvent removed on a steam bath. The products in the dry ice trap were removed by pipette, centrifuged to separate the oil and water; the oil thus recovered was weighed with the portion removed by the glass wool. The water was measured by volume.

The precipitate in the barium hydroxide traps was recovered by filtration and washed with water. The separated solids were dried for three days in a vacuum desiccator and weighed. A blank was necessary to correct for the precipitate formed during filtration.

In this manner, samples of reduced crude were blown with nitrogen for 60 and 120 hours; with air for 10 hours and at increasing 10 hour integrals to 60 hours; and with oxygen for 10, 15 and 20 hours.

b. Physical tests

The physical tests: softening point, penetration and ductility, were determined according to standard A.S.T.M. procedures. It was necessary to use one sample for these three tests in order to conserve the asphalt recovered. After penetration determination, the samples were warmed and the ductility molds and softening point rings filled.

2. Fractionation into Oils, Resins and Asphaltenes

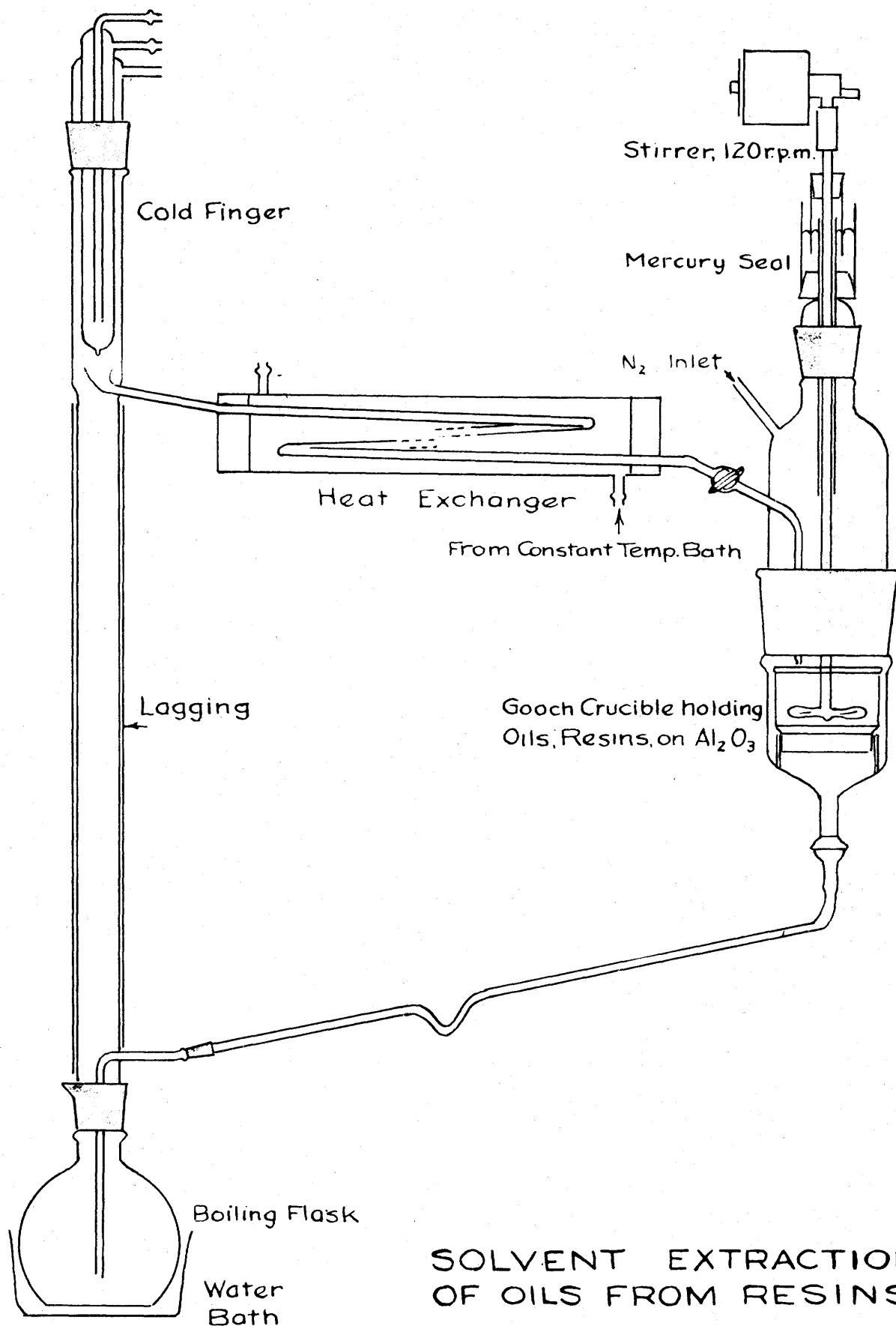
The method of fractionation used in these studies was developed recently by Hubbard and Stanfield (43). The method has the advantages of being short and of being conducted as much as possible in an atmosphere of nitrogen, a precaution against further oxidation. In addition, Hubbard and Stanfield claimed complete reproducibility.

In this fractionation, the asphaltenes are defined as that portion of the asphalt which is not soluble in n-pentane. The soluble portion, the malthenes, is distributed on anhydrous alumina. That portion of the malthenes which can be desorbed in one hour in a constant temperature extractor with n-pentane is defined as the oils. The remainder, the resins, is desorbed by a methanol - benzene solvent pair.

a. Procedure

Approximately 1.5 grams of asphalt was weighed into a 100 ml. petroleum centrifuge tube. For each gram of asphalt, 40 ml. of n-pentane was added and the asphalt dispersed by stirring at high speed for ten minutes. This solution was allowed to stand in the dark overnight. The precipitated asphaltenes were then dispersed by hand, stirred for ten minutes, and centrifuged. The supernatant liquor was decanted through a filter paper into a 300 ml. standard taper (S.T.) boiling flask. The residue was washed with 25 ml. of n-pentane by stirring for ten minutes, centrifuging and decanting the washings into the original solution of malthenes. The washing was repeated three times. The asphaltenes were dissolved in benzene, and the solution filtered through the filter paper used above into a tared 300 ml. S.T. boiling flask. The solvent was distilled off in an atmosphere of nitrogen on a steam bath, and the final traces removed in a vacuum oven. The flask was cooled, weighed, and the asphaltenes chipped out and stored.

The solution containing the malthenes was evaporated on a steam bath, in the presence of nitrogen, to 5 ml., and distributed on 25 grams of previously prepared (see below) 100 - 200 mesh anhydrous alumina in a 50 ml. pyrex gooch crucible. The gooch was then placed in the extraction apparatus (see Figure 5), constructed of pyrex glass. A 300 ml. S.T. boiling flask with 100 - 150 ml. of n-pentane



SOLVENT EXTRACTION
OF OILS FROM RESINS

FIGURE 5

was put in position and the oils desorbed with constant temperature n-pentane with stirring for one hour. The flow of n-pentane from the heat exchanger was controlled by the stopcock so that the alumina in the gooch was just covered with solvent. At the end of the extraction period, the boiling flask, now containing pentane and desorbed oils, was removed and the contents filtered into a tared 300 ml. S.T. boiling flask. The liquid remaining in the return line and the lower section of the extraction chamber was washed into the tared flask. Removal of the solvent was carried out as described for the asphaltene fraction.

The resins were desorbed from the alumina with 90% benzene - 10% methanol. One hundred and twenty milliliters of this solvent pair was added portionwise to the alumina in the gooch crucible, the adsorbent stirred, and the resulting solution drawn through into a 250 ml. suction flask under vacuum. This solution was transferred to two 100 ml. centrifuge tubes and centrifuged to throw out the alumina particles which were washed through the sintered disc. The clear liquor was filtered into a tared 300 ml. S.T. boiling flask, the solvent removed as described for asphaltene recovery, and the residue weighed. Both oils and resins were warmed to effect their transfer to storage test tubes.

The alumina was recovered and reactivated for subsequent determinations.

b. Preparation of alumina

According to Hubbard and Stanfield, the alumina may be regenerated by heating at 700°C for two hours and cooling in a desiccator. The effect of variation of this temperature and the method of cooling was studied. The solvent used was a petroleum ether fraction, b.p. 38-42°C, and the asphalt was the 120 hour nitrogen blown sample. Table IV contains a summary of these results.

TABLE IV

Effect of Alumina Reactivation of Fractionation of L-120-N₂

Solvent: Petroleum Ether, b.p. 38-42°C

Adsorbent: Alcoa Alumina, 100-200 mesh

Asphalt: L-120-N₂

Blown 120 hours with Nitrogen

No.	Oven Temp.	Cooled at	% Oils	% Resins	% Asphaltenes	% Recovery
1	700°C	Atmospheric	51.9(a)	30.5	18.0	100.3
2	700°C	"	52.4(a)	28.8	18.2	99.3
3	800°C	"	34.9(a)	45.0	18.4	98.3
4	800°C	10 mm. Hg	33.8(b)	40.1	18.1	92.0
5	700°C	"	38.1(b)	42.1	18.4	98.6
6	700°C	"	40.0(a)	41.6	18.0	99.6
7	700°C	"	39.7(a)	41.4	18.5	99.4

(a) Dried at 110°C, atmospheric pressure

(b) Dried at 110°C, under vacuum.

Fractionations 1 and 2 were conducted with alumina prepared by heating at 700°C in a muffle furnace for two hours. Comparison of the oil fraction recovered in these runs with the oil obtained from alumina heated at 800°C for two hours (No. 3) indicates that the alumina in the latter run was much more active. For Nos. 1-3, inclusive, the alumina

was cooled at atmospheric in a desiccator over calcium chloride, while Nos. 4-7 were conducted with alumina cooled in a vacuum desiccator over the same drying agent. Comparison of 3 (atmospheric) and 4 (vacuum) and more markedly 1 (atmospheric) and 6 (vacuum) show increased alumina activity when the adsorbent was cooled under vacuum. Due to the precision obtained in fractionations 5, 6 and 7, the alumina used in subsequent determinations was activated by heating for two hours at 700°C and cooling in a vacuum desiccator.

The poor recovery obtained in runs 4 and 5 was attributed to the drying of oils under vacuum resulting in the loss of some of the lighter fractions. All further oil fractions were therefore dried at atmospheric.

c. Choice of solvent

Although this procedure specifies C.P. n-pentane (b.p. 36.10° to 36.15°C), this solvent was not available. Technical n-pentane (b.p. 33°C - 36°C) and a petroleum ether fraction (b.p. 38° - 42°C) were compared to determine the effect of the solvent on the quantities of the fractions obtained. The results obtained have been summarized in Table V.

The oil fraction recovered using n-pentane was 3% less than the oils recovered using petroleum ether, while the resin fraction was 1% greater and the asphaltene

TABLE V

Petroleum Ether vs. n-Pentane
 Fractionation of L-120-N₂
 Extraction at 25°C Alcoa Activated Alumina

No.	Solvent	% Oils	% Resins	% Asphaltenes	% Recovery
6	Petroleum ether, 38-42°C	40.0	41.6	18.0	99.6
7	Petroleum ether, 38-42°C	39.7	41.4	18.3	99.4
	Average	39.9	41.5	18.1	99.5
8	n-Pentane (tech.), 33-36°C	36.6	43.2	20.3	100.1
9	n-Pentane (tech.), 33-36°C	36.8	42.9	19.9	99.6
	Average	36.7	43.1	20.1	99.9

fraction 2% greater. The difference in results obtained was too great to justify substitution of petroleum ether for pentane; the latter was used in fractionating the blown residues.

The effect of varying the temperature of the solvent extracting the oils from the resins was also investigated. The variation in oils extracted at n-pentane temperatures between 20°C and 25°C was found to be less than the experimental error. Although the specifications laid down by Hubbard and Stanfield called for desorption at 16.5°C, this temperature was difficult to maintain; hence, the reactions were conducted at 25°C.

d. Effect of alumina used

In view of the difficulty experienced by analysts

using chromatographic techniques (117) in obtaining consistent results with aluminas from different sources, it is reasonable to suppose that the source of alumina may also have some effect on the fractions obtained in these separations. To ascertain the extent of any variation due to this factor, experiments were conducted comparing Alcoa (Aluminum Company of Canada) activated alumina and Norton "R.R." alumina. The results have been tabulated in Table VI.

TABLE VI

Comparison of Alumina from Different Sources

Alumina prepared by heating 2 hours at 700°C,
cooling in vacuum desiccator.

Extraction at 25°C

Solvent, n-Pentane

No.	Alumina (100-200 Mesh)	% Oils	% Resins	% Asphaltenes	% Recovery
8 & 9	Alcoa	36.7	43.1	20.1	99.9
12	Norton	80.0	0.0	19.9	99.9

It will be seen that the Norton alumina absorbed none of the malthene fraction which is sharply fractionated by Alcoa alumina. Unfortunately, these were the only alumina samples available for studies of this type; however, it would appear that the method is reproducible only when the alumina is rigorously defined and the same stock used in all experiments.

The conditions followed in the fractionation of the residues were selected on consideration of the tests of

the scope and limitations of this procedure reviewed above. The solvent was n-pentane, technical grade, b.p. 33°-36°C. The alumina used was Alcoa activated alumina, screened to 100-200 mesh, and activated by heating in a muffle furnace to 700°C for two hours and cooling in a vacuum desiccator. The extraction of oils from resins was conducted at 25°C. The oils were given a final drying for 30 minutes at 110°C under atmospheric pressure, the other fractions under vacuum at 110°C.

The precision obtained in the separation of oils, resins and asphaltenes in twenty fractionations representing nine asphalts is indicated in Table VII.

TABLE VII

Precision in Fractionation of Asphalts

Twenty determinations, Nine asphalts, Lloydminster crude

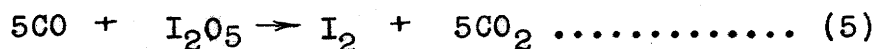
	Oils	Resins	Asphaltenes
Average Deviation from Mean:	0.24%	0.36%	0.16%
Maximum Deviation from Mean:	0.50%	0.70%	0.30%
Average Recovery:		99.7%	

3. Direct Determination of Oxygen

To date all data on the oxygen content of asphalt fractions have been obtained by difference; i.e. the remainder of the sample not accounted for by carbon, hydrogen, sulfur

nitrogen and ash content has been regarded as oxygen. It has been shown, however, that nitrogen determination by the Kjeldahl and the Dumas methods do not agree; consequently, the oxygen content in reports using the former method for nitrogen analysis is subject to uncertainty. A direct method for oxygen determination is to be desired since it would eliminate the necessity of determining total elemental analysis.

Methods for the direct determination of oxygen have been reviewed by Chrones (18) and by Clark (19). The most recent techniques of pyrolyzing the sample in a stream of inert gas and converting the oxygen containing fractions evolved to carbon monoxide by hot carbon, was introduced by Schütze (97) and modified by Zimmermann (119) and by Unterzaucher (111). In these methods, the carbon monoxide formed is oxidized to carbon dioxide by iodine pentoxide according to the equation:



Schütze and Zimmermann collected the carbon dioxide evolved while Unterzaucher recovered the iodine which may be measured by titration with standard thiosulfate. While the procedure of collecting the iodine gives more accurate results, Aluisse et al (3) and Chrones (18) found that the blank obtained is variable and too large to be neglected. This blank value is a serious source of error, particularly in micro determinations, and results in less accuracy than the difference

method for samples containing only carbon, hydrogen and oxygen.

Walton et al (113) have suggested that the high blanks are due to impurities in the iodine pentoxide. To eliminate this error, they replaced the iodine pentoxide oxidation tube by a carbon monoxide indicator consisting of ammonium molybdate and palladium sulfate deposited on silica gel (98). The gases containing the carbon monoxide to be determined are collected and a measured quantity passed through a tube containing the indicator gel. The color of the gel is then compared with standards to determine the carbon monoxide content of the gas. Excellent results are reported, especially for small samples low in oxygen. The preparation of the gel is, however, critical and involved, and for accurate results, standards must be prepared for each determination.

Unterzaucher's method was adopted for these investigations and the apparatus constructed by Chrones (18) was used.

a. Procedure

The apparatus used is illustrated in Figure 6. Nitrogen, the inert carrier-gas, was fed to the system from a high pressure cylinder at 14 ml./min. through a purification train consisting of heated copper wire (at 400°-500°C), to remove traces of oxygen, and an askarite-dehydrite tube,

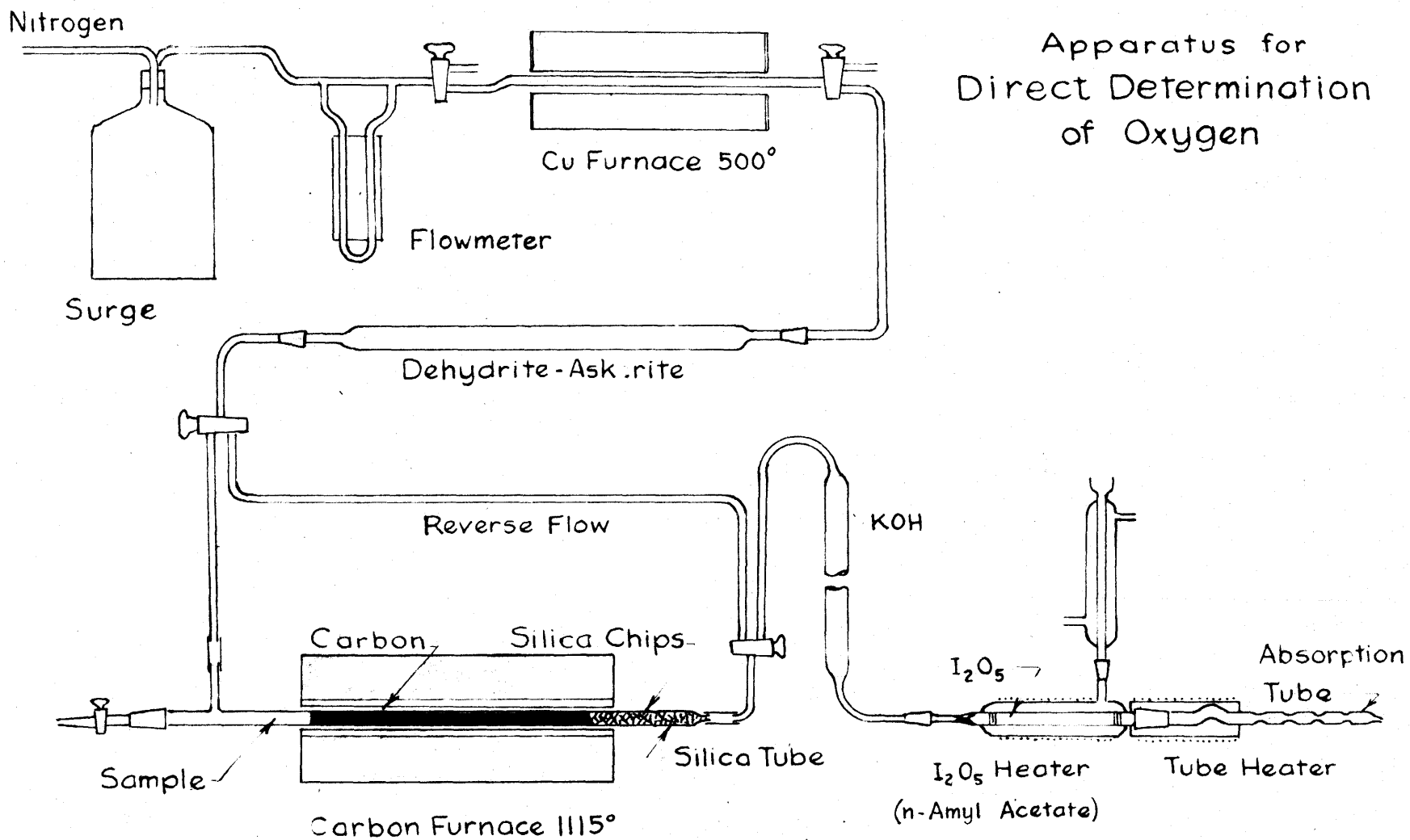


FIGURE 6

to remove carbon dioxide and water. A sample of the product under investigation, sufficient to give a titre of 15-30 ml. of 0.02 N sodium thiosulfate, was weighed into a platinum boat and introduced into the silica tube through the ground taper joint by means of a platinum boat-carrier (left in position during the determination to facilitate removal of the sample boat). Oxygen in air which might be introduced with the insertion of the sample was expelled from the system by passing nitrogen through the silica tube under reverse flow at an elevated rate (24 ml./min.) for fifteen minutes.

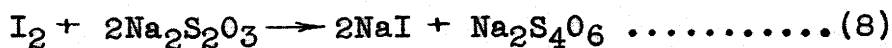
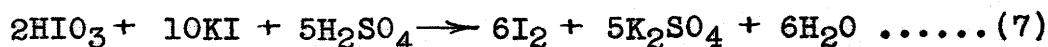
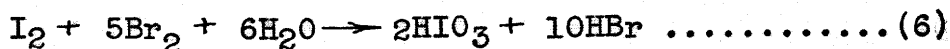
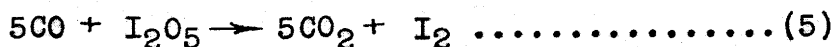
At the conclusion of this purging period, the absorption tube was moistened with 20% sodium hydroxide and put in position. The nitrogen rate was restored to 14 ml./min. and the flow directed over the sample and into the carbon packed section of the silica tube. The carbon was maintained at 1125°C to 1130°C. The sample was pyrolyzed by a heating unit consisting of two air - gas blast lamps; this heat was applied first to the inlet end of the tube and advanced slowly to the carbon furnace. This heating period was five to ten minutes. The carbon monoxide and nitrogen leaving the furnace were passed through the potassium hydroxide pellet tube to remove sulfur and halogens. The iodine pentoxide, maintained at 118°C by refluxing glacial acetic acid, served to oxidize the carbon monoxide to dioxide (Equation 5) and the iodine expelled was absorbed in the sodium hydroxide. The total time allowed for heating the sample and collecting

the sample was 35 minutes.

For blank determinations, this procedure was followed except that an empty boat was introduced into the silica tube.

The contents of the absorption tube were washed with distilled water into a 60 ml. test tube containing 10 drops of bromine dissolved in 10 ml. of 10% potassium acetate in glacial acetic acid. This was in turn washed into a 250 ml. erlenmeyer containing 10 ml. of 20% sodium acetate solution, and 10 drops of 90% formic acid were added to dispel the excess bromine. The resulting solution was shaken and permitted to stand for 5 minutes. Two grams of potassium iodide were added together with one ml. of concentrated sulfuric acid previously diluted to 15 ml. The liberated iodine was titrated with standard sodium thiosulfate, using 2% starch solution as an indicator.

The equations for the reactions involved may be written as follows:



From these equations it will be seen that five gram-atoms of oxygen are equivalent to 12 equivalents of thiosulfate. Hence, for a 0.02 N thiosulfate solution, one milliliter is equivalent to

$$\frac{0.02}{1000} \times \frac{5}{12} \times 16 \times 1000 = 0.1333 \text{ mg. of oxygen.}$$

Then for a sample weighing w grams, requiring a ml. of thio-sulfate with a previous blank of b ml.,

$$\% \text{ Oxygen} = \frac{(a - b)(\text{Normality Na}_2\text{S}_2\text{O}_3)(0.1333)(100)}{(0.02)(1000)(w)} \dots\dots(9)$$

b. Analysis of pure organic compounds

The analysis of several pure organic compounds was undertaken to check the accuracy and precision of the method. Considerable difficulty was encountered in these investigations before the above procedure was evolved and adopted. The carbon which was found to give the most accurate results was a commercial product, Wyex Compact Carbon Black. A summary of analyses made using this carbon and procedure is contained in Table VIII.

There can be little doubt that much of the error in these determinations was due to the blank value. It will be seen from Table VIII that the variation is considerable, the blanks ranging from 0.26 to 1.85 ml. of 0.024 N sodium thiosulfate. The blanks between consecutive runs varied widely in some cases; the question arose whether to use the blank value obtained before the determination or after. For the sake of uniformity, the blank value obtained before the analysis was used. There is no reason to believe, however, that the blank during the determination was considerably different from either the blank value before or after the run.

TABLE VIII

Direct Determination of Oxygen in Pure Compounds

Wyex Compact Carbon Black

Flow: 14 ml./min. I₂O₅ Temp.: 118°C
Furnace: 1125-1130°C Time of Run: 35 min.

Compound	Sample Weight gm.	Blank ml.	Titre less Blank ml.	N	% O Found	% O Calc.	% Error
Benzoic Acid	0.01856	0.75	29.51	a	26.13	26.22	-0.34
β-Naphthoic Acid	0.02878	0.84	32.71	a	18.67	18.58	0.48
	0.03328	0.88	37.75	b	18.59		0.05
Benzoin	0.03359	1.15	30.76	a	15.05	15.09	-0.27
	0.03975	1.85	36.41	a	15.05		-0.27
Benzophenone	0.06985	1.09	37.61	a	8.85	8.78	0.79
p-Hydroxy-azobenzene	0.05678	0.93	27.98	b	8.09	8.07	0.25
	0.07073	1.25	34.95	b	8.11		0.50
Cinchonine	0.06765	0.62	26.79	b	6.50	6.45	0.84
	0.07448	0.26	29.28	b	6.45		0.00
Triphenyl-carbinol	0.07059	0.92	26.52	a	6.17	6.15	0.32
	0.07528	0.82	28.86	b	6.29		2.28
	0.07123	0.82	28.57	b	6.35		3.26
Triphenyl-amine	0.17528	1.25	5.50	b	0.11	0.00	-

a: Normality Na₂S₂O₃: 0.02465 N

b: Normality Na₂S₂O₃: 0.02462 N

With respect to the analysis of the asphalt fractions, smaller samples were used for two reasons: in some cases the quantity of oil, resin or asphaltene available was limited; in those cases where sufficient fraction was available for a large titre, it was found that large samples led to abnormalities in gas flow through the system when the

sample was pyrolyzed. It was found that even on slow pyrolysis (10 minutes) when the burners approached the furnace during oil or resin analysis, a sudden back-pressure was developed, sufficient to reverse the flow on the sample side of the carbon furnace. This is believed to be due to high boiling point of these fractions, causing them to distil down the tube rather than vaporize and be carried into the furnace. Consequently, a large fraction of the sample, still intact, was trapped between the furnace and the advancing burners until cracking temperature was reached. At this point the sudden increase in the volume of gases in the tube caused the momentary reversal of flow. To avoid this phenomenon, smaller samples were used, for which the back-pressure developed was not sufficient to reverse the flow of nitrogen.

IV. RESULTS AND DISCUSSION

1. Results of Blowing Experiments

For simplicity, the asphalts recovered from the various blowing experiments with nitrogen, oxygen and air, have been assigned code numbers. These numbers are defined in Table IX.

TABLE IX

Identification of Blowing Experiments
and Blown Residues Recovered

Lloydminster Reduced Crude, blown at 200°C,
at a rate of 1.5 ml. of gas/gm. charge/min.

Symbol	Blowing Time	Blowing Agent
L-10-A to L-60-A	10 hrs. to 60 hrs.	Air
L-10-O ₂ to L-20-O ₂	10 hrs. to 20 hrs.	Oxygen
L-20-N ₂ to L-120-N ₂	20 hrs. to 120 hrs.	Nitrogen
Original	Original Reduced Crude	

The experimental figures obtained, by the blowing investigations, on the production of water and carbon dioxide, the distillation of oil, and the asphalt recovered, have been reduced to a common basis of 100 grams of Reduced Crude as charged. These data have been summarized in Table X. The quantity of oil distilled has been plotted against

TABLE X

Material Balance, Blowing of Lloydminster Reduced Crude
at 200°C, 1.5 ml. gas/gm. charge/min.

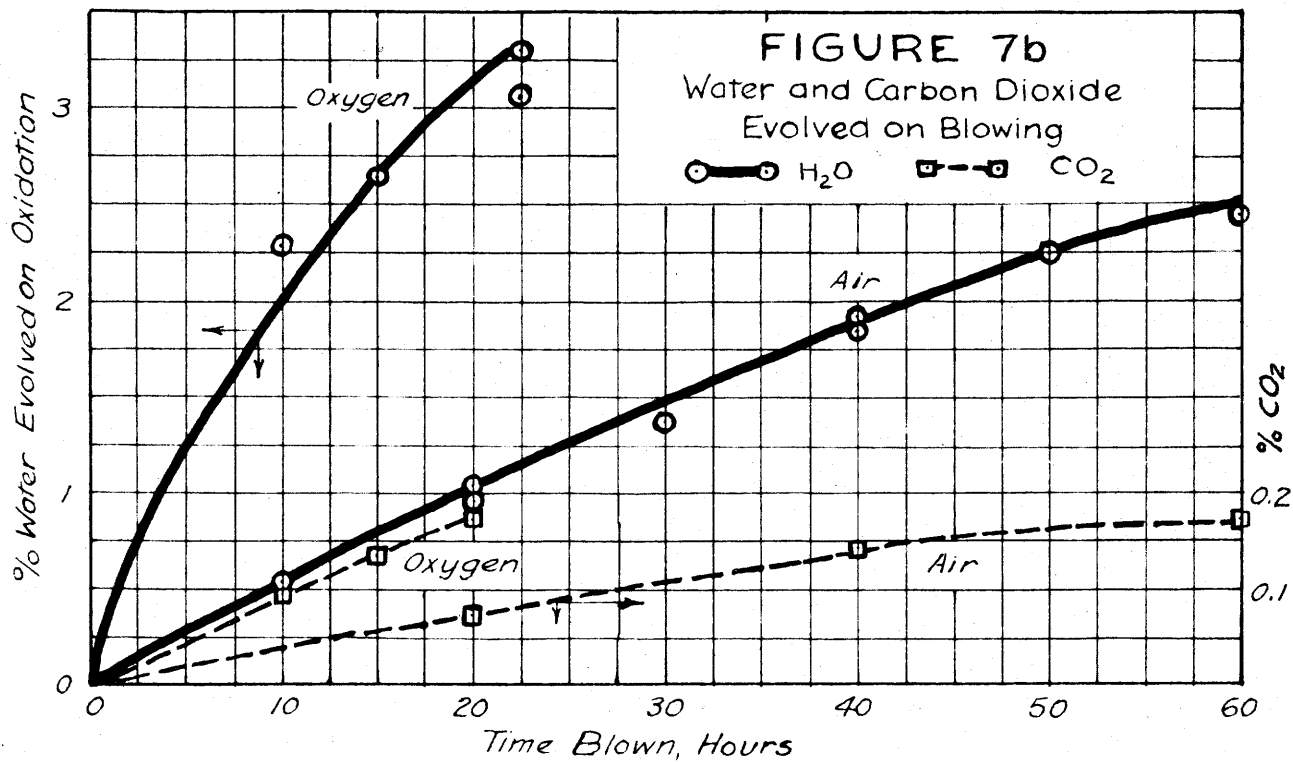
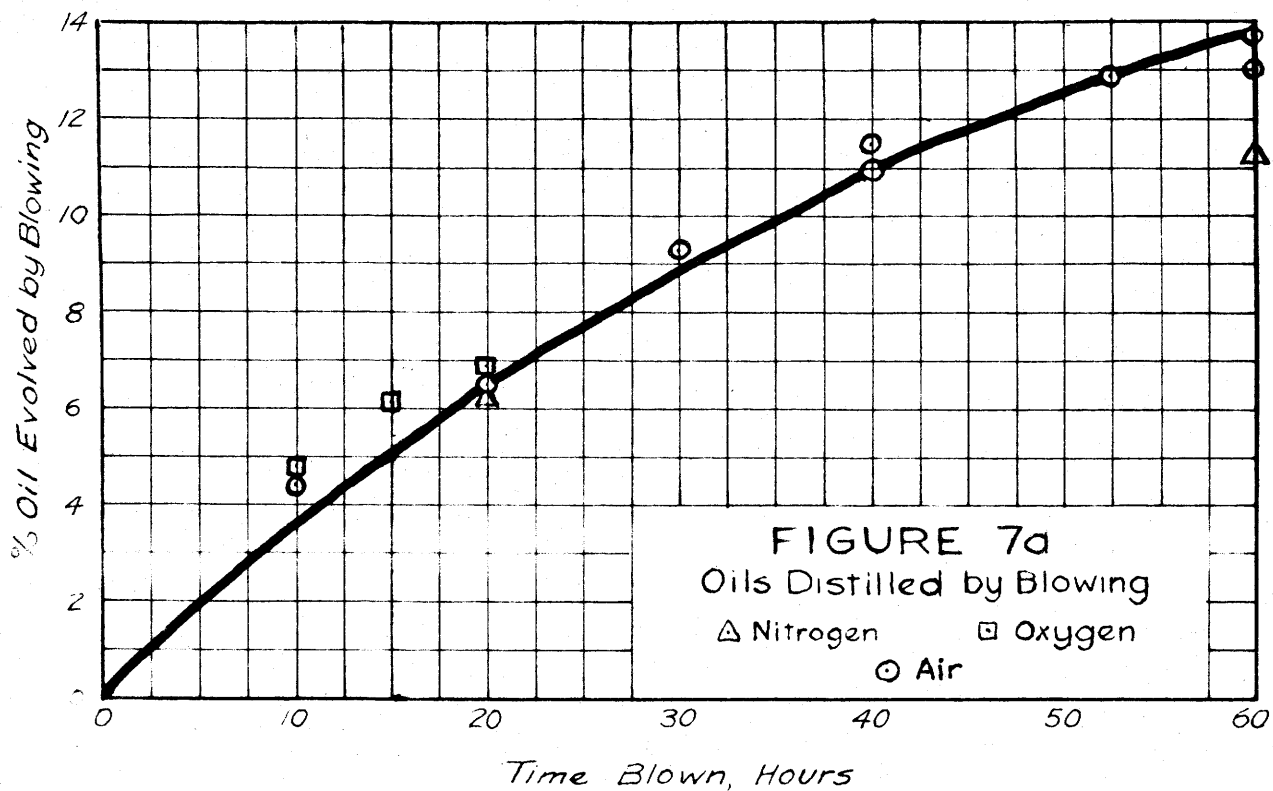
Basis: 100 gm. Reduced Crude as charged

Blowing Run	(1) % Oil	(2) % H ₂ O	(3) % CO ₂	(4) % Asphalt Residue	(5) % Gain
L-20-N ₂	6.28	0.05	0.000	93.33	-0.33
L-60-N ₂	11.17	0.05	0.000	87.60 [ⓧ]	-1.08
L-120-N ₂	19.00	0.05	0.000	80.94 [ⓧ]	-0.06
L-10-A	4.45	0.54	-	95.23	0.22
L-20-A	6.45	0.98	-	93.40	0.39
L-20-A	6.43	1.05	0.072	94.07 [ⓧ]	0.55
L-30-A	9.29	1.38	-	90.51	1.18
L-40-A	11.00	1.90	-	88.35	1.25
L-40-A	11.52	1.89	0.146	88.26 [ⓧ]	1.67
L-50-A	12.91	2.25	-	87.34	2.50
L-60-A	13.72	2.46	-	85.37	1.55
L-60-A	13.05	2.45	0.175	87.47 [ⓧ]	3.15
L-10-O ₂	4.85	2.28	0.100	94.85 [ⓧ]	1.98
L-15-O ₂	6.08	2.65	0.135	93.78 [ⓧ]	2.64
L-20-O ₂	6.70	3.08	-	92.91	2.63
L-20-O ₂	6.72	3.31	0.171	93.29 [ⓧ]	3.49

[ⓧ] Asphalt residues fractionated

the time of blowing in Figure 7a. This figure indicates that the oil recovered is dependent on time only and is independent of the blowing agent used.

It is evident that no carbon dioxide and only small amounts of water are produced by nitrogen blowing. The traces of water recovered are presumably due to water already present in the reduced crude. On the other hand, considerable quantities of water and some carbon dioxide are evolved during air and oxygen blowing, due to the oxidation reactions



taking place. However, it will be seen that the water recovered is much greater than the carbon dioxide obtained; that is, the removal of hydrogen from the asphalt by oxidation under these conditions is more extensive than the removal of carbon. For example, in the course of the twenty-hour oxygen run, 3.31 per cent of water was obtained while 0.17 per cent of carbon dioxide was realized. This indicates that 47 moles of hydrogen were removed as water for each mole of carbon as carbon dioxide. This would indicate that at this temperature the volatile oxidation products are due predominantly to dehydrogenation. The relative amounts of the products resulting from air and oxygen blowing are indicated in Figure 7b.

Partial qualitative analyses of the barium hydroxide precipitate indicated that while the majority of this salt was carbonate, small amounts of another component were shown by the power of a dilute HCl solution to reduce permanganate solution. This component has not been identified, although it is known that sulfate, sulfite and sulfide are not present. For these calculations, the precipitate will be regarded as barium carbonate.

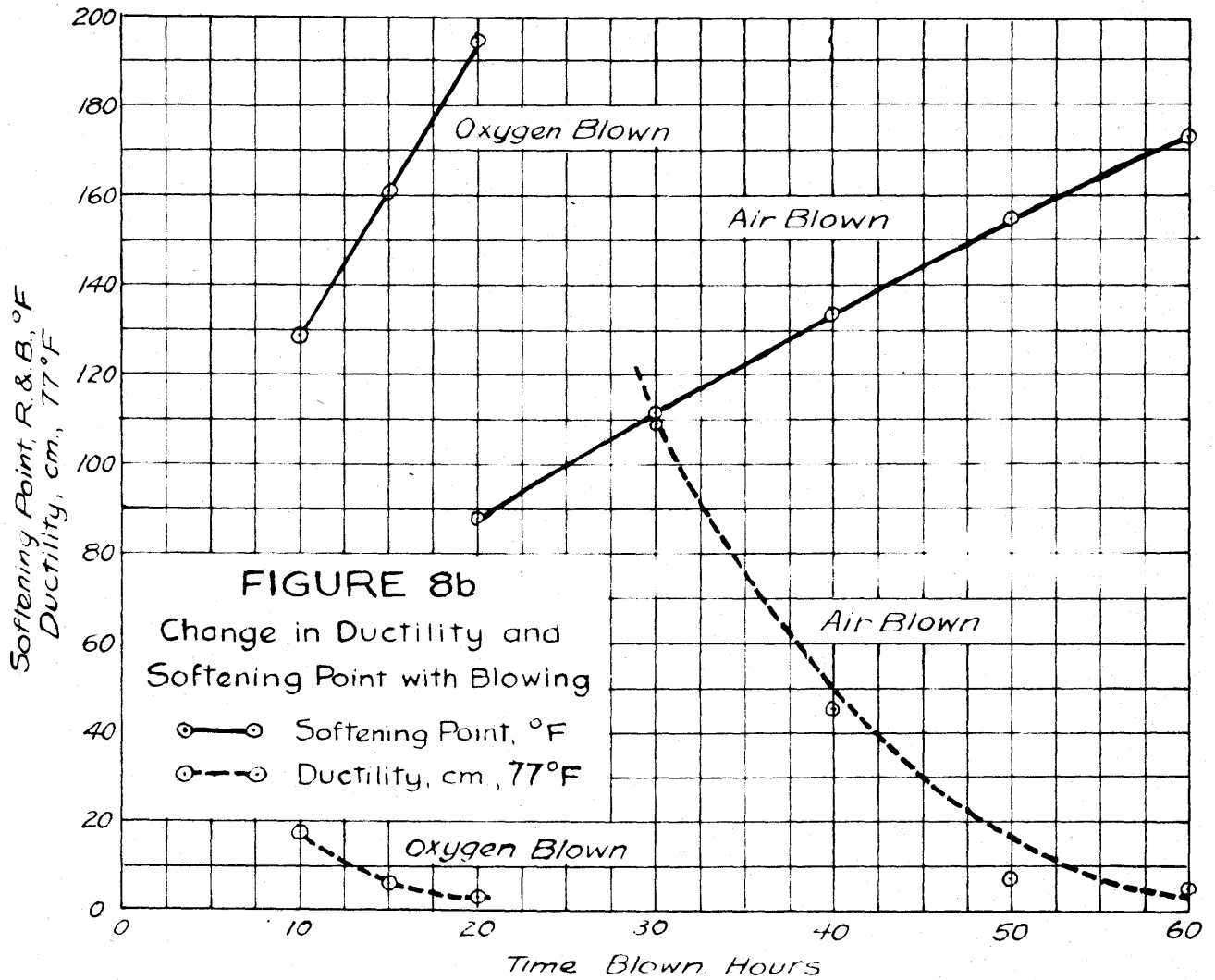
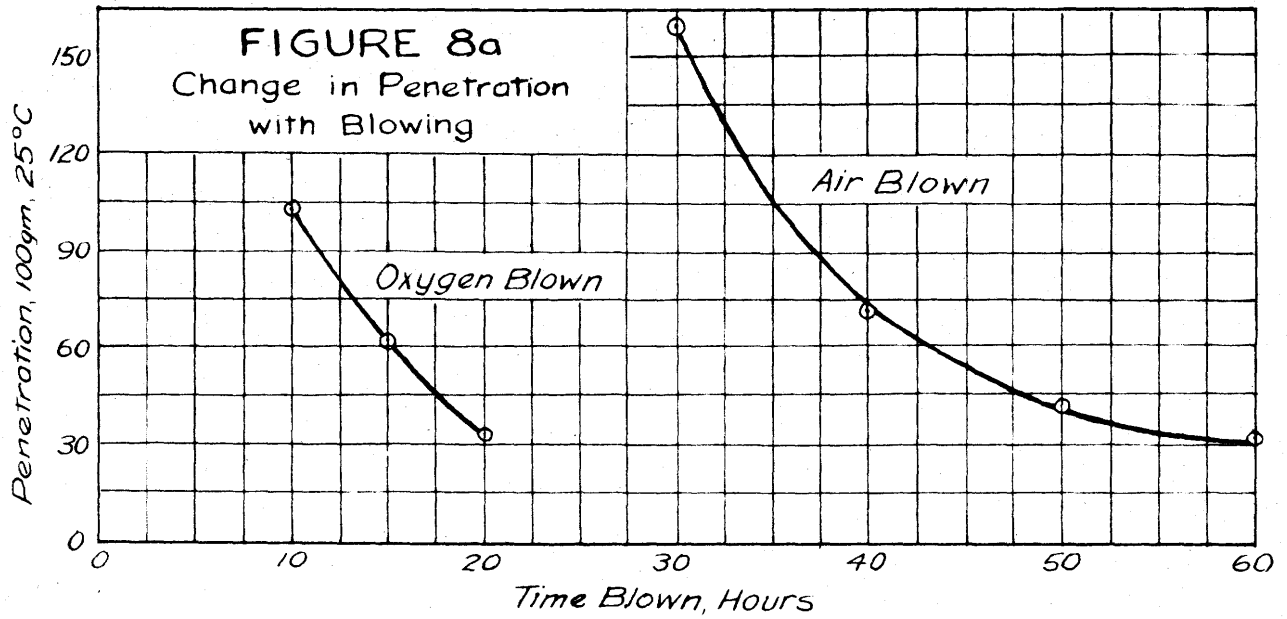
The penetration, softening point and ductility of the asphalt residues recovered are given in Table XI. These data have been plotted against time in Figures 8a and 8b, to show the relative changes in these properties. Nitrogen

TABLE XI
Physical Properties of Blown Asphalt Residues

Asphalt Residue	Penetration, 100 gm.		Softening Point, Ring & Ball, °F	Ductility, gm.
	@ 0°C	@ 25°C		
L-20-N ₂	-	-	Soft	-
L-60-N ₂	-	-	Soft	-
L-120-N ₂	85	-	82-83	-
L-10-A	182	-	Soft	-
L-20-A	95	-	87-88	-
L-30-A	-	160	111-112	110
L-40-A	-	72	134-134	44.8
L-50-A	-	43	154-155	8.6
L-60-A	-	31	172-174	5.5
L-10-O ₂	-	113	129-129	17.5
L-15-O ₂	-	62	160-162	6.3
L-20-O ₂	-	33	195-195	2.9

blowing for 120 hours was required to produce the same penetration as obtained with 20 hours air blowing. The former sample, however, lost 19 grams of oil per 100 grams of reduced crude, while the latter lost only 6.4 grams of oil. This serves to indicate the profound effect of oxidation upon the physical properties of the residue. The rapid initial decrease in penetration and the short ductilities are characteristic of air blown asphalts (1).

It should be noted that the physical properties of blown asphalts from a given crude depend on (a) the extent to which the crude is topped, (b) temperature of blowing, (c) rate of blowing and (d) time of blowing. Consequently, these data have importance only for comparing times of blowing and blowing agents used in these investigations.



2. Conversion Indicated by Fractionation

Eight of the recovered asphalt residues, as indicated in Table X, were fractionated, as well as the original reduced crude. The percentage of oils, resins and asphaltenes present in the recovered asphalt residues is given in Table XII. In order to compare the conversion indicated by these figures to the water and carbon dioxide produced, it is necessary to convert them to a common basis, i.e. to a basis of 100 grams of reduced crude as charged. The assumption is made in these calculations that the oil distilled is identical to the oils remaining in the flask, and these quantities have been added to give the total oil which would be present in the asphalt had no distillation taken place. The oil, resin and asphaltene content of the petroleum products on this basis is indicated in Table XIII.

While these figures account for the oil removed by distillation, they do not account for the hydrogen and carbon removed from the asphalt as water and carbon dioxide. For example, the hydrogen removed during the twenty hour oxygen blowing experiments amounts to 0.22 grams per 100 grams of reduced crude. However, the error in fractionation experiments is of the order of 0.7 grams per 100 grams of reduced crude, while the error in determination of the oils distilled is estimated at 0.3 grams; and the total error in the material balance is 0.8 grams per 100 grams of

TABLE XII

Oil, Resin and Asphaltene Content of
Recovered Blown Asphalts

Fractionation by U.S. Bureau of Mines Method (43)
Solvent: n-pentane, b.p. 33°-36°C; Extraction at 25°C;
Alcoa Activated Alumina, 100-200 mesh, activated at 700°C
for two hours, cooled in vacuum desiccator.

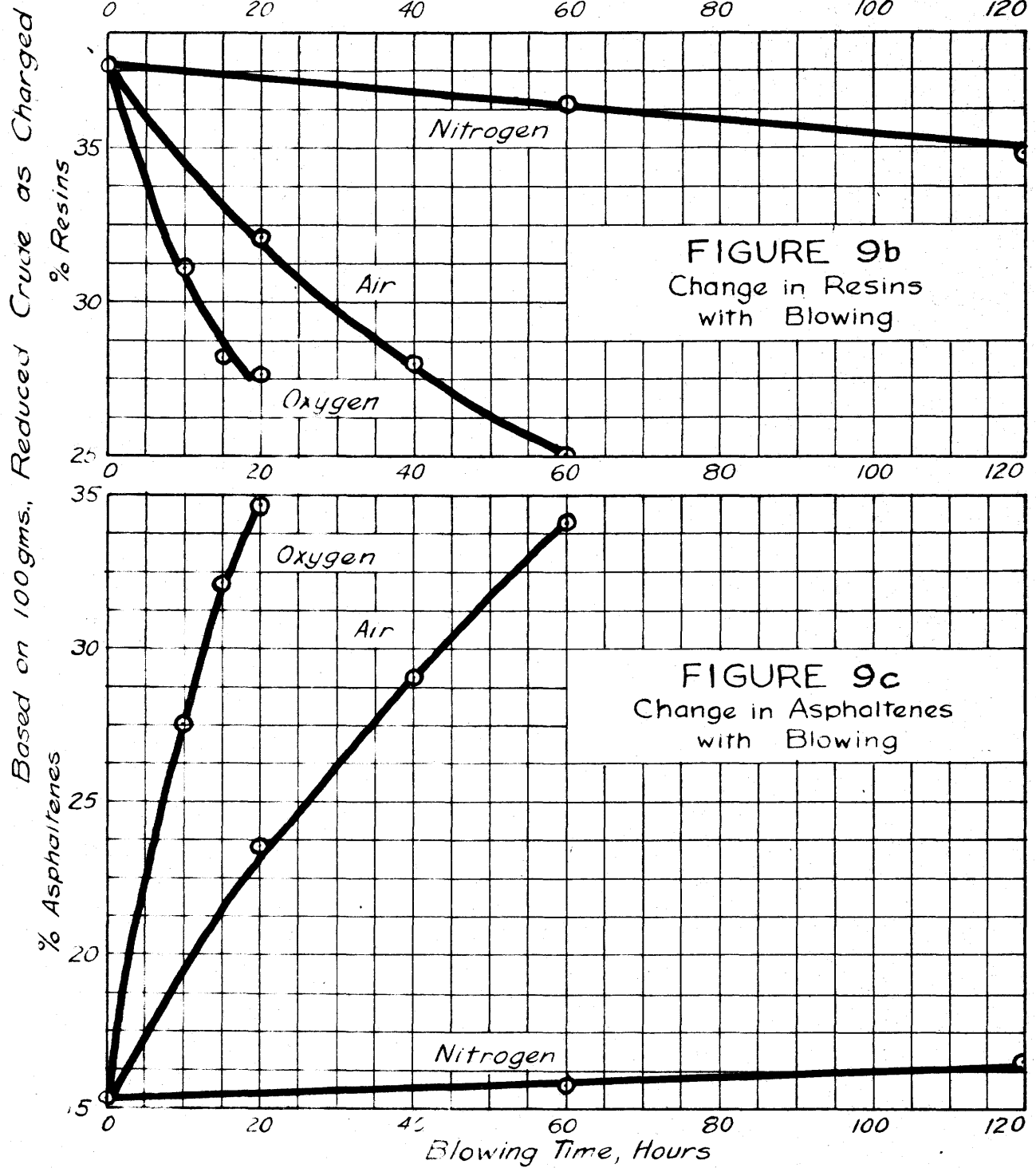
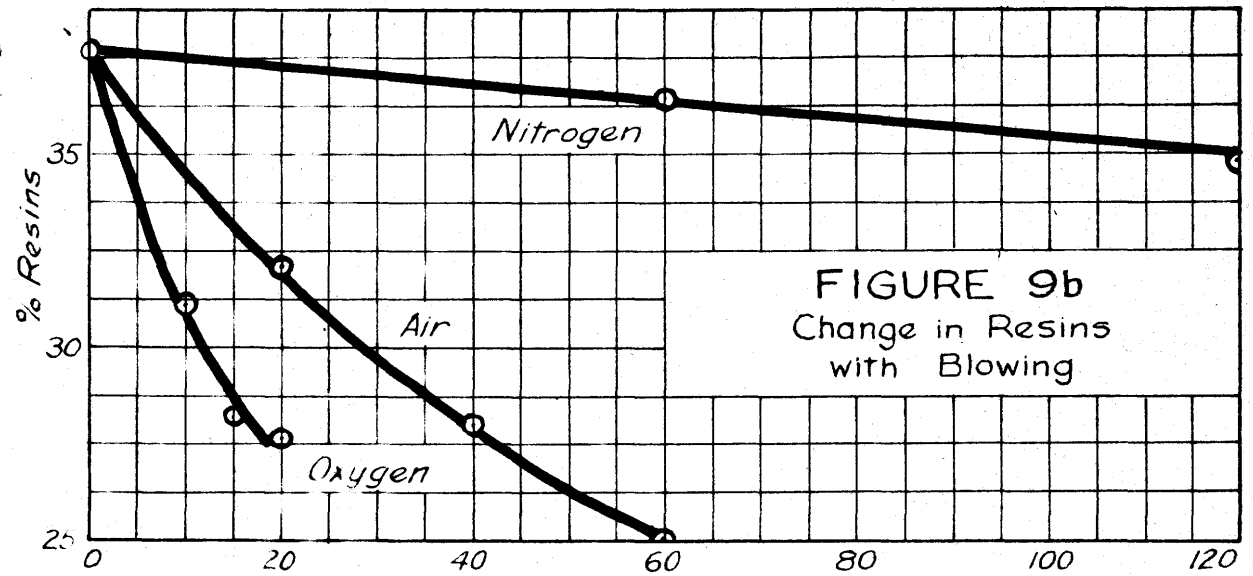
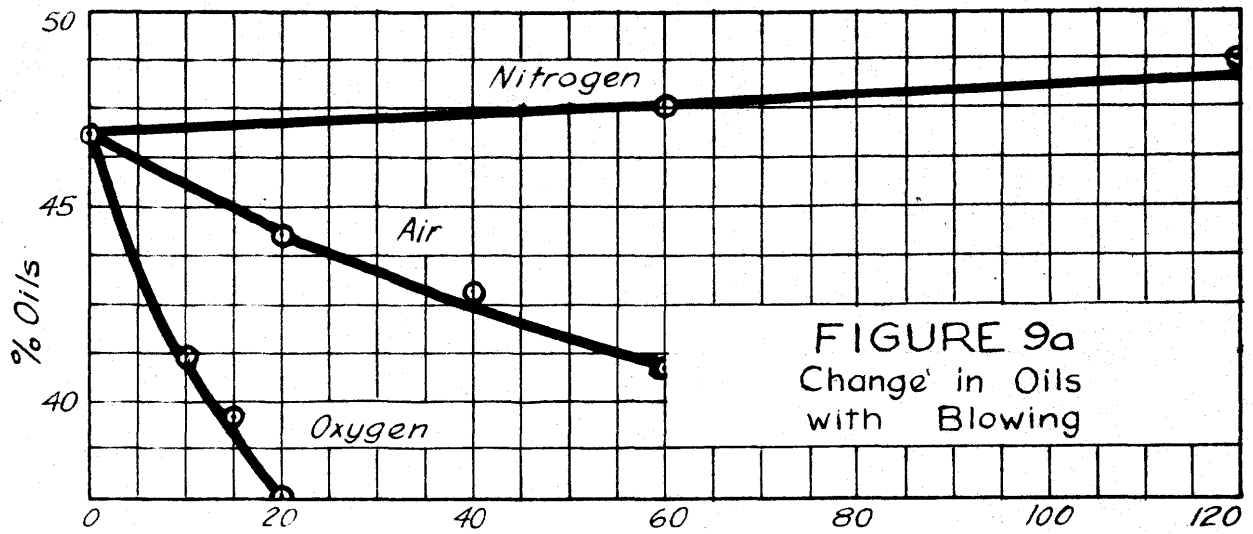
Asphalt Residue	% Oils	% Resins	% Asphaltenes	Recovery
Original	47.1	37.5	15.3	99.9
	46.6	38.4	15.4	100.4
	46.9	37.2	15.2	99.3
Av.	46.9	37.7	15.3	99.9
L-60-N ₂	40.7	40.5	17.9	99.1
	40.4	40.6	18.1	99.1
Av.	40.6	40.5	18.0	99.1
L-120-N ₂	36.6	43.2	20.3	100.1
	36.8	42.9	19.9	99.6
Av.	36.7	43.1	20.1	99.9
L-20-A	40.5	33.6	25.3	99.4
	39.9	34.4	25.2	99.5
	39.9	34.3	25.0	99.2
Av.	40.2	34.1	25.1	99.4
L-40-A	35.8	31.3	32.8	99.9
	34.9	32.1	32.9	99.9
Av.	35.3	31.7	32.9	99.9
L-60-A	32.2	28.3	39.2	99.7
	31.6	28.9	38.7	99.2
Av.	31.9	28.6	39.0	99.5
L-10-O ₂	37.0	33.8	29.0	99.8
	37.8	32.4	29.6	99.8
Av.	37.4	33.1	29.3	99.8
L-15-O ₂	35.6	29.4	34.3	99.3
	35.1	30.3	33.9	99.3
Av.	35.3	29.9	34.1	99.3
L-20-O ₂	33.4	28.6	37.7	99.7
	33.5	29.2	37.6	100.0
Av.	33.4	28.9	37.5	99.8

TABLE XIII
Oil, Resin and Asphaltene Content
 Based on 100 grams Reduced Crude as Charged

Blowing Run	Oils Distilled	Oils in Residue	(6) Total Oils Grams/100	(7) Resins grams	(8) Asphaltenes Reduced Crude
Original	-	46.9	46.9	37.7	15.3
L-60-N ₂	11.2	36.6	47.8	36.5	15.8
L-120-N ₂	19.0	29.7	48.7	34.9	16.3
L-20-A	6.4	37.8	44.2	32.1	23.6
L-40-A	11.5	30.8	42.3	27.6	28.7
L-60-A	13.1	27.9	41.0	25.0	34.1
L-10-O ₂	4.9	36.5	41.4	31.4	27.8
L-15-O ₂	6.1	33.1	39.2	28.0	32.0
L-20-O ₂	6.7	31.2	37.9	27.9	35.0

reduced crude. Consequently, the loss of hydrogen and carbon from the asphalt may be neglected in comparing the conversion obtained with various blowing times and blowing agents.

The values in columns 6, 7 and 8, Table XIII, have been plotted against the blowing time in Figures 9a, 9b and 9c, to indicate the relative change in these components with time. It will be seen from these curves that the change in these fractions with nitrogen blowing is negligible compared to the conversion on air and oxygen blowing. It is possible that the slight increase in oils on nitrogen blowing may be due to some thermal cracking, while the increase in asphaltenes may be due to polymerization of resin molecules.



On air and oxygen blowing, the asphaltenes increased at the expense of the oils and resins. The mechanism of conversion is not known, but if dehydrogenation and polymerization are responsible, it is logical to expect the oils to be converted to resins, and these in turn to asphaltenes. If this assumption is correct, it is evident that the resins are less stable than the oils, since they are converted to asphaltenes more quickly than they are formed from the oils.

By making the assumption that oils do not form appreciable amounts of asphaltenes directly but pass through the intermediate resin stage, it is possible to calculate the conversion which has taken place within the asphalt. This was calculated from columns 6 and 8, Table XIII, by summation of the decrease in oils and the increase in asphaltenes based on the reduced crude. The conversion is given in Table XIV.

TABLE XIV

Conversion of Asphalt Fractions
Based on 100 grams Reduced Crude as Charged

Blowing Run	(9) Decrease in Oils	(10) Increase in Asphaltenes	(11) Conversion gm.
L-20-A	2.6	8.3	10.9
L-40-A	4.6	13.4	18.0
L-60-A	5.9	18.8	24.7
L-10-O ₂	5.5	12.5	18.0
L-15-O ₂	7.7	16.7	24.4
L-20-O ₂	9.0	19.7	28.7

3. Oxygen Content

The results of the oxygen analysis are given in Table XV. For all fractions the oxygen content is low.

TABLE XV

Oxygen Content of Asphalt Fractions

Carbon Furnace: 1125-1130°C Time of Run: 35 Min.
 Burning Time: 10 Min. I₂O₅ Temp.: 118°C
 Normality Na₂S₂O₃: 0.02462

OILS

Asphalt Residue	Weight Sample, gm.	Blank ml.	Titre (Less Blank)	(12) % O
Original	0.1533	0.39	3.90	0.42
L-60-N ₂	0.1311	0.68	3.96	0.49
L-120-N ₂	0.1399	0.87	4.20	0.49
L-20-A	0.1571	0.13	3.32	0.35
L-40-A	0.1290	0.28	2.75	0.35
L-60-A	0.1361	0.45	2.65	0.32
L-10-O ₂	0.1387	0.77	3.75	0.44
L-15-O ₂	0.1312	0.58	2.82	0.35
L-20-O ₂	0.1435	0.30	3.21	0.37

RESINS

Original	0.08389	0.70	6.59	1.29
L-60-N ₂	0.1886	0.51	13.56	1.19
L-120-N ₂	0.1778	0.77	12.70	1.11
L-20-A	0.2189	0.75	18.39	1.38
L-40-A	0.1459	0.55	13.25	1.49
L-60-A	0.1677	0.48	15.37	1.50
	0.1643	0.61	15.25	1.52
L-10-O ₂	0.1603	0.65	14.81	1.52
L-15-O ₂	0.1762	0.63	16.83	1.57
L-20-O ₂	0.1800	0.53	20.41	1.86

TABLE XV (Continued)

ASPHALTENES

Asphalt Residue	Weight Sample, gm.	Blank ml.	Titre (Less Blank)	(12) % O
Original	0.05642	0.85	10.94	2.89
L-60-N ₂	-	-	-	2.72 [*]
L-120-N ₂	0.07182	0.96	12.33	2.75
L-20-A	0.08791	0.92	14.80	2.76
L-40-A	0.11516	0.63	18.19	2.59
L-60-A	0.1261	0.43	20.23	2.63
L-10-O ₂	0.1395	0.57	21.67	2.55
L-15-O ₂	0.1135	0.98	19.78	2.86
L-20-O ₂	0.1033	0.56	17.01	2.72

^{*} Estimated; average of oxygen contents of other asphaltenes

However, these determinations indicate that the asphaltenes contain more oxygen than the resins which in turn contain more oxygen than the oils. It will be seen that the oxygen content of the oils and asphaltenes remains essentially the same throughout the blowing experiments. For the oils, this indicates that oxidation of an oil molecule results in almost immediate conversion to either asphaltenes or resins. Similarly, the formation of asphaltenes must be effected by a mechanism which includes the same quantities of oxygen as were contained in the asphaltenes present in the reduced crude. It does not appear that oxidation of the asphaltenes themselves has been accompanied by inclusion of oxygen;

since the asphaltenes are regarded as occupying the central portion of the asphalt micelle it is not likely that they were attacked by oxygen in these experiments.

The analysis of the resin fractions indicates that the oxygen content of these bodies increases on blowing with oxygen and air, and decreases on nitrogen blowing. Very little can be deduced from these experimental facts, since there is no indication of the source of these oxygen-containing resins. The increase in oxygen content may be due to the presence of relatively unstable oxidized resin molecules, from either oil or resin fractions, representing a transient stage in the formation of asphaltenes. On the other hand, the oxygen-containing molecules may be stable products of the oxidation of oil molecules, and may be resistant to further oxidation. Finally, the increase in oxygen content may be due to the presence of relatively stable oxygen-containing compounds in the reduced crude which remain as resins while less stable resins are converted to asphaltenes. There may be some significance in the observed decrease in oxygen content of the nitrogen blown resins, since it was seen (see Figure 9c) that a slight increase in asphaltene content occurred on blowing with this inert agent. It would appear that heat has resulted in the conversion of oxygen-containing resins to asphaltenes.

To calculate the increase in oxygen content of the reduced crude on blowing, the assumption was made that the

distilled oils have the same oxygen content as those oils remaining in the asphalt. The oxygen content of the reduced crudes was obtained from the oxygen content of the three fractions (Column 12, Table XV) and the oil, resin and asphaltene content, based on 100 grams of reduced crude (Columns 6, 7 and 8, Table XIII). These results are tabulated in Table XVI.

TABLE XVI

Oxygen in Asphalt Fractions
Grams per 100 grams of Reduced Crude as Charged

Blowing Run	Oils	Resins	Asphalt- enes	(13) Asphalt (Total)	(14) Increase
Original	0.20	0.49	0.44	1.13	-
L-60-N ₂	0.23	0.47	0.43	1.13	-
L-120-N ₂	0.24	0.42	0.45	1.11	-
L-20-A	0.15	0.44	0.65	1.24	0.11
L-40-A	0.15	0.41	0.74	1.30	0.17
L-60-A	0.13	0.37	0.89	1.39	0.26
L-10-O ₂	0.18	0.48	0.71	1.37	0.24
L-15-O ₂	0.14	0.44	0.91	1.49	0.36
L-20-O ₂	0.14	0.52	0.95	1.61	0.48

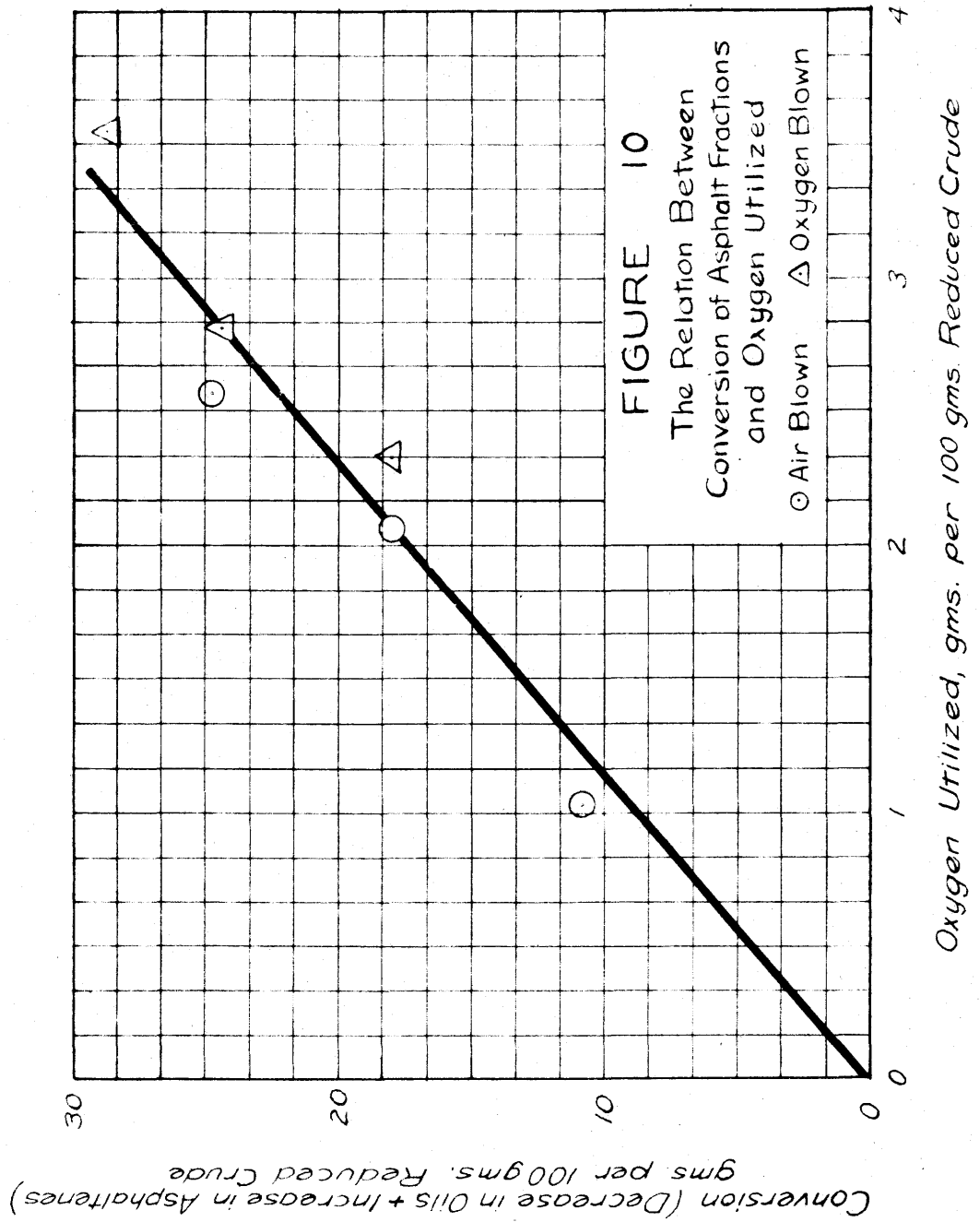
It is evident from these results that the oxygen content of the reduced crude remained constant on blowing with nitrogen but increased appreciably with air and oxygen blowing. This increase in oxygen content over the original reduced crude is indicated in Column 14, Table XVI. It is possible from these data and the results obtained during

the air blowing experiments (Table X) to calculate the oxygen utilized in formation of water, carbon dioxide, and oxidized products remaining in the asphalt residue. The figures for the oxygen so utilized are given in Table XVII.

TABLE XVII
Oxygen Utilized in Oxidation Reactions
Grams per 100 grams of Reduced Crude as Charged

	(15)	(16)	(17)	(18)	(11)
Blowing Run	As H ₂ O (From Column 2)	As CO ₂ (From Column 3)	As in- crease in O content of Asphalt (Table XVI)	Oxygen Used	Conver- sion (Table XIV)
L-20-A	0.87	0.05	0.11	1.03	10.9
L-40-A	1.68	0.11	0.17	2.06	18.0
L-60-A	2.18	0.13	0.26	2.57	24.7
L-10-O ₂	2.03	0.07	0.24	2.34	18.0
L-15-O ₂	2.35	0.10	0.36	2.81	24.4
L-20-O ₂	2.95	0.12	0.48	3.55	28.7

These data indicate that in all runs over 85% of the oxygen used was recovered as water; hence, the oxidation reaction is predominantly one of dehydrogenation. When the oxygen used is plotted against the conversion (Column 11, Table XIV, repeated in Table XVII), a straight line is obtained (Figure 10). It may be concluded that the conversion is directly proportional to the oxygen utilized, and that the reactions occurring on air and oxygen blowing are identical.



In studies of lubricating oils, Larsen et al (22,53,120) found that pure aromatic compounds on air oxidation yield a dark sludge while naphthenes remain homogeneous and light in color. Comparison of oxidation products of lubricating oils and pure compounds enabled Larsen to conclude that lube oils compare closely to alkyl naphthenes. Using Larsen's figures on the oxygen utilized as water, $O(H_2O)$, and the oxygen used in the formation of carbon dioxide $O(CO_2)$, in the oxidation of pure compounds, the following $O(H_2O)/O(CO_2)$ ratios for the different classes of compounds are obtained:

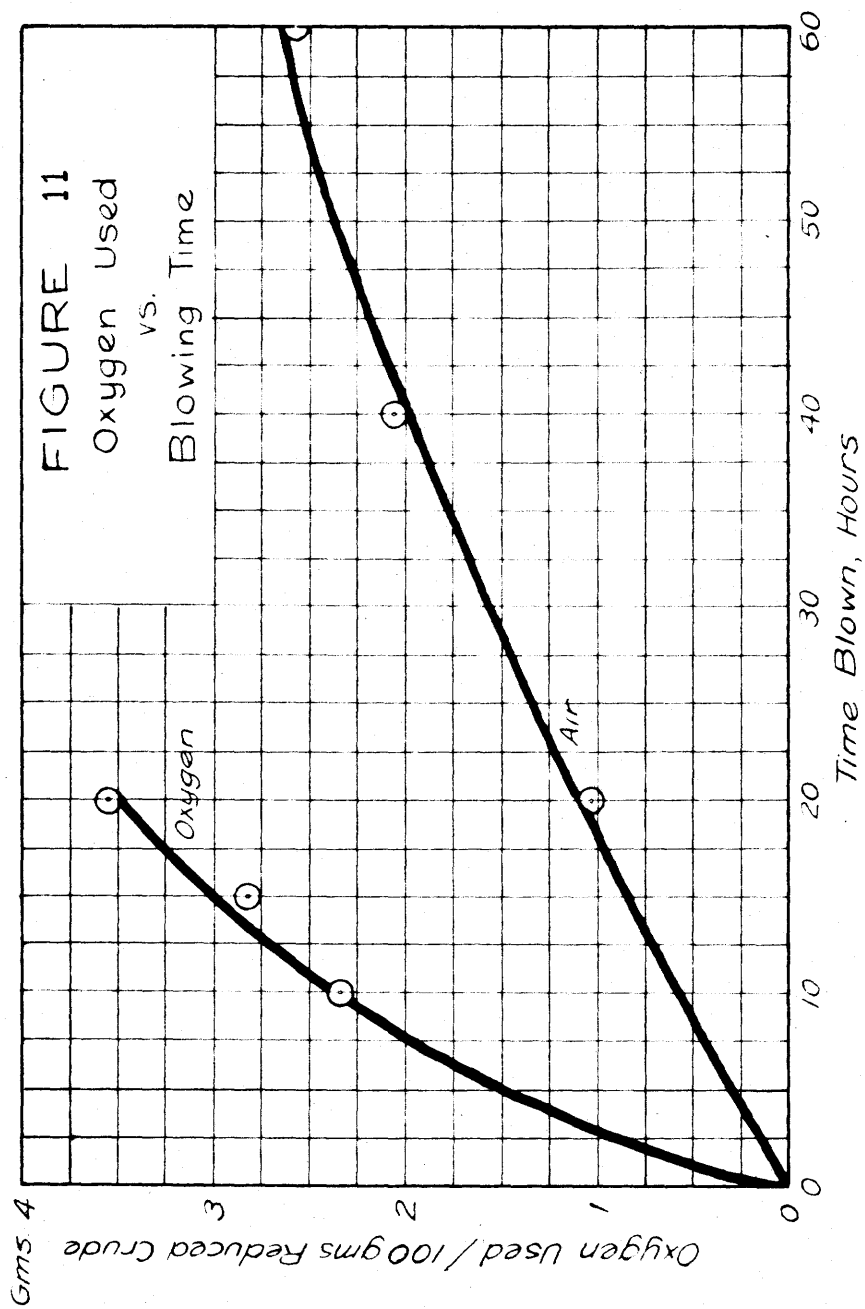
Class	$O(H_2O)/O(CO_2)$
Paraffins	9.2
Naphthenes and Alkyl naphthenes	5.8
Aromatic naphthenes	13.9
Alkyl benzenes	2.8
Naphthalene and Alkyl naphthalenes	6.6

The data in Columns 15 and 17 (Table XVII) give an average $O(H_2O)/O(CO_2)$ ratio of 19.5. This is considerably greater than any of the ratios listed in the above table; however, Larsen's oxidations were conducted at a temperature lower than $200^{\circ}C$. If it is assumed that these ratios increase with increasing temperature and remain in the same order,

this may indicate that the molecules in the asphalt being oxidized are aromatic naphthenes.

Further indication of the type of compounds being oxidized may be obtained by comparing the oxygen uptake in unit time with the oxygen uptake in unit time for pure compounds. This rate curve, dO/dt , for these investigations is illustrated in Figure 11. The curve indicates that the reaction is autoretardant in nature. Larsen (53) found that autoretardant oxidations are characteristic of partially hydrogenated anthracenes, alkyl naphthenes and polynuclear aromatics.

It may be concluded from these comparisons that in all probability the compounds in the asphalt undergoing oxidation are either polynuclear aromatic molecules or aromatic naphthenic molecules. This is in agreement with the proposed structures for the asphalt "building blocks". (See Figure 3.) However, this cannot be considered as strong evidence in support of these structures. von Fuchs (27) has shown that the rate curve is in some cases drastically altered in form with increase in temperature; Larsen's work was conducted at temperatures below 200°C, the temperature used in blowing these asphalt samples. In addition, von Fuchs has shown that preferential oxidation need not take place when compounds of unequal stability are mixed; consequently, it is possible that other classes of compounds



present in the reduced crude may also be undergoing oxidation.

4. Conclusions

From the results and discussion given above, the following conclusions may be made regarding the oxidation mechanism occurring when asphalt is blown with air or oxygen:

(1) The oxidation reactions occurring on air and on oxygen blowing are essentially the same.

(2) The oxidation reaction is accompanied by the evolution of water and small amounts of carbon dioxide, and by an increase in asphaltene content at the expense of the oils and resins. Whether the oils pass through an intermediate resin state before being converted to asphaltenes or are converted directly is not known. There is also the possibility that oils produce relatively stable resins.

(3) The resins are less stable to oxidation than the oils.

(4) The oxygen content of the asphalt increases on blowing with air and oxygen.

(5) The oil and asphaltene oxygen contents remain constant on blowing while the resin oxygen content increases. This indicates that:

- a. Oxidized oil molecules are not stable but quickly form resins and/or asphaltenes,
- b. Asphaltene molecules produced by oxidation contain the same amount of oxygen as the original asphaltenes.

(6) The predominance of water as an oxidation product over oxygen realized as carbon dioxide and oxygen incorporated in the asphalt molecules, indicates that at this temperature dehydrogenation is the primary oxidation reaction.

(7) Evidence indicating that the molecules undergoing oxidation are polynuclear aromatics or aromatic naphthenes may be drawn from comparison of the oxidation products with those of pure hydrocarbons if it is assumed that temperature has little effect on the shape of the rate curve for oxygen utilization.

(8) It has been shown that the fractionation procedure for asphalts, outlined by Hubbard and Stanfield (43), must be further defined with respect to the alumina used if the method is to be reproducible.

5. Suggestions for Further Investigations

Several investigations have been suggested during the above experiments and by consideration of the results obtained in these experiments; these are listed here as a proposed outline for future work.

(1) Average molecular weight determinations would indicate the extent of polymerization, if any, in the oil, resin and asphaltene fractions. It may be possible with such figures to correlate polymerization, conversion and oxygen uptake.

(2) The role of sulfur in the oxidation reaction could

be studied by the determination of the sulfur content of these fractions. It is suggested that methods using Raney Nickel would be most suitable for these investigations.

(3) The extent to which the asphaltene molecules are attacked on air blowing might be determined by investigating the carbene and/or carboid content of each blown residue. Presumably, these fractions are formed by oxidation of asphaltenes.

(4) It was observed that the resin oxygen content increases on blowing with air. The stability of these oxygen-containing compounds could be studied by subjecting the air or oxygen blown asphalts to elevated temperatures (e.g. 200°C) for considerable periods of time, followed by fractionation to determine if the asphaltene content has increased. If the asphaltene content is greater, these oxygen-containing resin molecules might be regarded as intermediate oxidation products.

(5) The assumption was made in the calculation of the oxygen content of asphalts that the distilled oils have the same oxygen content as the oils in the asphalt. It is suggested that this assumption be verified or disproved by determination of the oxygen content of these distilled oils.

(6) Qualitative analysis of the precipitate obtained in the barium hydroxide traps during oxidation should be conducted to determine the permanganate-reducing component.

(7) Oxidation of the oil fraction alone at 200°C by blowing (with oxygen to prevent undue distillation) would give information on the rate of resin formation and indicate whether a step-wise conversion to asphaltenes is followed. It is suggested that a suitable oil fraction might be obtained by vacuum or steam distillation of the reduced crude.

(8) Repetition of the blowing experiments at temperatures other than 200°C (e.g. 180° and 220°C, or 230° and 260°C) and fractionation of the resulting residues would indicate the effect of temperature on conversion.

(9) Similar investigations should be conducted on reduced crudes from other sources, preferably non-asphaltic base crudes, and on cracked stock to ascertain the similarity in the oxidation reactions for various petroleum residues.

It is the author's opinion that this method of investigation, if continued, will result in a greater appreciation of the oxidation reactions occurring on blowing asphalts, and will make a substantial contribution to the knowledge of the chemistry of asphalts.

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