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NATIONAL BUREAU OF STANDARDS REPORT

2850

SELECTED BIBLIOGRAPHY ON THE CONSTITUTION OF ASPHALTS

by

Sidney H. Greenfeld



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SELECTED BIBLIOGRAPHY ON THE CONSTITUTION OF ASPHALTS

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SELECTED BIBLIOGRAPHY ON THE CONSTITUTION OF ASPHALTS

This bibliography is of selected references expected to be of assistance in studying the constitution of asphalts and the changes that occur when asphalts are exposed to the action of light, heat, and water. This listing is not meant to be complete, but is a working bibliography to which material will be added as work progresses. It is being circulated at the present time as a possible assistance to members of the Asphalt Roofing Industry Bureau who may have occasion to look further into the nature of the work being conducted on their Research Associate project at the National Bureau of Standards.

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I. General Treatments

"Asphalt-Prepared Roll Roofings and Shingles", H.R. Snoke, Building Materials and Structures Report BMS-70, National Bureau of Standards, April 10, 1941.
A review of materials and methods with 1939 specifications and statistics.

"Asphalts and Allied Substances", H. Abraham, D. Van Nostrand Co., Inc., New York, Fifth Edition, 1945.

"The Properties of Asphaltic Bitumen", J.P. Pfeiffer, Elsevier Publishing Co., 1950.
Summary of technical work on asphalt up to 1950.

II. Weathering Tests

"Light Action on Asphalts", V. Vojtech, J. Soc. Chem. Ind., page 654, 1906.
Glass coated with asphalt from a 4% benzene solution absorbed oxygen, but not carbon dioxide or nitrogen, rendering the asphalt insoluble in turpentine. Heat at 100°C has the same effect as light.

"Sensitiveness to Light of Asphalt", A. Rosinger, Chem. Ztg., Vol. 36, page 243, 1913.
CA 7, 1804 (1913). Sulfonated asphalt is sensitive to light directly as the thickness of the layer.

"Light Sensitiveness of Petroleum Asphalt", P. Goldrich, Chem. Ztg., Vol. 39, page 832, 1915.
Only paraffin-free asphalt was light sensitive when exposed in a thin film under a negative. Sulfering with S_2Cl_2 to 12% S destroyed the sensitivity as opposed to increasing it in natural asphalt.

"Light Sensitivity of Asphalts", J. Errera, Trans. Farad. Soc., page 314-17, 1923.
Ether insoluble with formula of $C_{32}H_{42}S_2$ is most light sensitive. Worked with Indian and Trinidad asphalts.

"Effects of Exposure Cycle Variation in a Weatherometer on the Weathering of Varnishes", H. A. Nelson and F. C. Schmutz, Proc. A.S.T.M., 24, page 920 (1924).

"The Characteristics of the Carbon Arc. How the Properties Vary With Voltage and Current", W. C. Kolb, Electrical Engineering, 53, 1173-9 (1934), 56, 319-24 (1937).

"A Modified Accelerated Weathering Test for Asphalts and Other Materials", O. G. Strieter and H. R. Snoke, J. Res. National Bureau of Standards, Vol. 16, page 481-5, 1936.

"The Action of Light Upon Bituminous Coatings", H. Walther, Asphalt Teer Straussenbautech, Vol. 36, page 1001-4, 1936.

Coatings of blown (I) and high-vacuum (II) Mexican asphalt bitumen and bituminous coal-tar pitch (III) in U-tubes were subjected to 420 hours of variable sunlight; under evacuation, in pure dry O, in H_2O-saturated O, and in H_2O-saturated air. Results are shown photographically, the changes being most extensive in the 3rd test with III least affected. Gains in weight were greatest with I in the last test, and least in all tests with III. Benzene-insoluble matter increased 6 times with I in the 2nd test. S content was little changed; II and III showed considerable acid-product formation.

"Microscopic Reactions in Translucent Asphaltic Films", J. R. Benson, Proc. Tech. Sessions, Assoc. Asphalt Paving Tech., Vol. 9, page 102-32, 1937.

A method for preparing translucent asphaltic films with an approximate thickness of 0.001 in. is described. The reaction of the films have been studied under 6 conditions of exposure: at 162.7 (325°F) and at 60° (140°F) in darkness with the film in contact with air; at 60 to 76.7° (170°F) exposed to mild ultraviolet infrared radiations, etc. The rapid reactions taking place, coagulation, flocculation, formation of waxey substances, checking and hardening are described.

"Laboratory Exposure and Simulated Service Tests of Slow-Curing Liquid Asphalts", R. H. Lewis and W. O'B. Hillman, Public Roads, Vol. 18, page 85-99, 1937.

An investigation of the weather resistant properties of slow-curing liquid asphalts was made to determine if the results of laboratory and exposure tests could be correlated.

"Effects of Weathering on the Properties of Asphalts and Road Tars", Erzo Nisikawa, Rept. Research Office Pub. Works, Dept. of Home Affairs, Japan, Vol. 37, 29-86, 1937.

Two straight asphalts, one blown, and four road tars in thin layers, were tested for changes in their properties by exposure for one year to the action of air in the laboratory, to natural weathering in open air, to water and to both acid and alkali solutions. The asphalts both hardened and increased in weight in air, sunlight and through natural weathering, showing that they absorbed O from the air. They increased in weight also in water and in chemical solution by absorbing water. They hardened somewhat during the long period of exposure, but it is not likely that they took any O from the liquids. Of the numerous elements, sunlight combined with air had the greatest effect on their properties.

"Accelerated Weathering Tests of Mineral-Surfaced Asphalt Shingles", H. R. Snoke & Braxton E. Gallup, J. Research, N.B.S., Vol. 18, 669-81, 1937.

All types of failure encountered in long outdoor exposures were produced in accelerated exposures of seven months or less. The type of asphalt used and the manufacturing process largely influenced the behavior to weathering. Samples which contained fine mineral filler withstood weathering best. Mechanical abrasion tests while of value in determining adhesion of granules at time of manufacture did not predict adherence on exposure.

"Constituents of Asphaltic Materials Versus Accelerated Weathering", R. R. Thurston, Proc. Am. Soc. Testing Materials, Vol. 37, page 569, 1937.

Several asphalts were separated into their components by Marcusson's method and reconstituted. The original asphalts always weathered better except in an instance when extra resins were used.

"A Study of Bituminous Materials - Weathering Tests", Joseph Zapata, Assoc. Paving Tech., Proc. Tech. Sessions, page 85-104, 1937.

Reasons are given for believing that a determination of unsaturated hard and soft asphalts, oily constituents and resins should serve as a measure of weathering resistance of bituminous products. Methods of determination and of tests are described and preliminary results graphed.

"The Properties of Road Tar - The Effect of Exposure", Mitchell, J. G., and Murdock, J. Soc. Chem. Ind. 57, 137, (1938).

"The Durability of Asphalt", Wilson, D. M., J. Soc. Chem. Ind. 57, 148-51, (1938).

The chief factor contributing to durability is the employment of as high a proportion of bitumen as is consistent with obtaining sufficient stability, together with the use of an aggregate of high bitumen carrying capacity. The manner in which the bitumen is employed to cement the grains of aggregate is so different for the different types that it is hardly likely that any single test will be found which is universally applicable and will be useful as a guide in determining the durability of them all.

"Weathering Tests on Filled Coating Asphalts", O. G. Strieter, J. Res. N.B.S., Research Paper RP1073, 20, 159-171 (1938).

Outdoor and accelerated weathering tests were in agreement. Stabilized asphalts were compared with pure asphalts at six outdoor stations around the country and in weatherometers at the Bureau.

"Influence of Weathering on Bitumen", H. Walther, Mitt. Dachpappen Ind., 135-52, (1938).

The effect of light, O_2 and O_3 on blown Mexican petroleum was determined. In dry air, light increases the content of asphaltenes, carbenes and complex oxidation products; in water, light does not have this effect, but the content of peroxides increases. The weathering of blown bituminous paint is accelerated by the formation of peroxides; it is reduced by the addition of antioxidants such as hydroquinone and B-naphthol.

"Accelerated Weathering of Bituminous Materials - Operating Variables", B. Weetman, Proc. A.S.T.M. 43, 1154-64, (1943).

A modified Atlas Weatherometer was used for conducting accelerated tests. The temperature of the test must be accurately controlled to assure reproducible results. A black-bulb panel temperature of 140°F is recommended to obtain values which will adequately differentiate between the weathering characteristics of different asphalts in the shortest practical time. Under normal conditions, amperage, refrigeration temperature, force of water-washing and surface cleanliness of the aluminum panels have no effect on the results.

"Current Procedures in Operating So-Called Accelerated Weathering Units", R. W. Matlack, A.S.T.M. Bulletin No. 131, December 1944.

"Official Digest of Federation Paint and Varnish Clubs", Cleveland Paint & Varnish Production Club, 250, 454, (1945), 262, 518, (1946).

A comparison of accelerated weathering with Florida weathering shows that the Atlas single arc is a little too mild, but comes close. If temperature is kept around 150°F and spray about 10-12 minutes/hr., this may be all right. EverReady machines are pretty good, but generally run too hot and too dry.

"Comparison of Outdoor and Accelerated Weathering", Cleveland Paint and Varnish Production Club, Am. Paint J. 32, No. 7-B, 8 (1947).

"Ten Years' Outdoor Exposure of Filled Asphalt Coatings on Saturated Felts", G. L. Oliensis, A.S.T.M. Bulletin No. 144, 32-48, January 1947.

Felt panels fastened to an old roof to get the effects of distortion in weathering. Tests seem too severe to warrant their use in predicting the relative merits of filled and unfilled asphalts.

"Correlating Laboratory and Outdoor Weathering Tests", D. M. Williams, A.S.T.M. Bulletin No. 144, 49-56, January 1947.

Machines are described for measuring film adhesion, elongation and hardness of paint films. Based on these measurements, accelerated tests with some types of machines correlated fairly well with Miami 4-month exposures.

"Laboratory Accelerated Weathering", J. Zapata, Proc. Assoc. Asph. Pav. Tech., 16, 154-73, 1948.

Zapata discusses various factors involved in preparing exposures, conducting tests, and end-point determination.

"Spectral Characteristics of Light Sources for Fading and Degradation Testing", B. S. Cooper and F. S. Hawkins, Symposium on Photochemistry in Relation to Textiles, Society of Dyers and Colourists, 32-34 Picadilly, Bradford, Yorkshire, England, pp. 1-10, 1949.

"Accelerated Weathering of Pitches and Asphalts", W. F. Fair, Jr., H. R. Beck, and B. K. McKee, (Koppers Co., Inc.), A.S.T.M. Spec. Tech. No. 94, 109-21, 1949.

The authors conclude that (1) their investigations confirm the studies of Strieter and Snoke concerning the formation of water-soluble products from asphalts by the action of ultraviolet light, heat and air, (2) water-soluble materials are extractable only to a small extent from pitches exposed to the above factors, (3) exposure of asphalts and pitches exhibit increases in softening point rise, (4) pitches show no change in rate of solubility in water during exposure; asphalts show considerable solubility for the first several five-week periods and show a decrease thereafter, (5) accelerated aging tests cannot duplicate long-time service performances.

"Mineral Stabilizers in Asphalt Roofing", L. Kirschbaum, R. H. Cubberly, and F. W. Yeager, A.S.T.M. Spec. Tech. No. 94, 122-36, 1949.

The authors conclude (1) accelerated durability tests of asphalt coatings, with and without stabilizers, on aluminum panels are a useful index of performance of such coatings on saturated-felt specimens, (2) mineral stabilizers delay the formation of cracks in coatings on aluminum panels and saturated felt specimens, (3) mineral stabilizers delay the formation of weathering cracks and ultimate loss of coatings in more advanced stages of weathering of both smooth- and granule-surfaced roofing and shingles, thereby materially increasing the service life of the product.

"Behavior of Bituminous Road Materials Under Accelerated Exposure Conditions and Laboratory Heat Tests", Richard H. Lewis, A.S.T.M. Spec. Tech. No. 94, 14-39, 1949.

The effects of accelerated weathering tests on road tars, liquid asphaltic materials, asphaltic cement, and bituminous mixtures. The behavior of materials under exposure was correlated with the changes that occur in laboratory heat tests. The thin-film oven test is proposed as a means of eliminating less durable asphalts, providing that 1) loss in weight is less than 1% for the 50-150 grade asphalts, 2) residues have a penetration of more than 50% of the original sample for the 50-150 grade asphalts, 3) the residue shall have a ductility at 77°F of not less than 40 cm for the 50-60 grades and not less than 100 cm for the 85-100, 100-120, and 120-150 grades.

"Test Methods for Performing Accelerated Durability Tests on Asphalts", T. E. Stanton and F. N. Hreem, A.S.T.M. Spec. Tech. No. 94, 84-99, 1949.

A test for noting changes in the abrasion resistance of asphaltic material is described. Specimens in the test are subjected to infrared light or heat under conditions permitting the loss of volatiles and oxidation of the asphalt. Factors to be considered in testing are (1) temperature-viscosity relationship of an asphalt, (2) apparatus should correspond closely to the destructive influences such as sun, wind and moisture, (3) test specimens should be prepared by mechanical means in order to provide uniformity of test specimens.

"The Effect of Fillers on the Durability of Asphalts", J. Zapata and R. S. Von Hazmburg, Proc. Assoc. Asphalt Pav. Tech., 18, 95-105, 1949.

The addition of fillers improves the performance of asphalt films exposed outdoors. Particle shape and size seem to be more important than gradation.

"20-30 Years' Weathering of Asphalt Shingles Made With Unfilled Coatings", G. L. Oliensis, A.S.T.M. Bulletin No. 165, 59-66, 1950.

Shingles made with straight asphalt weathered 20-30 years under certain conditions. The mineral matter found present was assumed to be dust.

"Fully Automatic Weathering Machine", V. Virtala, Paint Technology 1950, 15, 55-58, 1950.

Mercury lamps - 50% of energy in 2900-4800A (7 times the intensity of the summer sun in Washington), 2.5 times total solar intensity. Claim paints break down in 1/10 the time, lacquers 1/25, and roofing felts 1/12 of natural weathering.

"Study of the Evaluation of Bitumens", Louis Marcel, Comptus Rendus, 233, 84-6, 1951.

The $CHCl_3$ extract (and its asphaltic, oil, and resinous fractions) of a bitumen from Ocalet was subjected to ultraviolet light for about 1000 hours. The oily constituent yielded resins; the resins formed mainly asphaltics and carbenes; and the asphaltics formed mainly carbenes and carbenoids, with some oils and resins.

III. Inert Additives

"Effect of Mineral Fillers on the Serviceability of Coating Asphalts", O. G. Strieter, Proc. Am. Soc. for Testing Materials, Vol. 36, Part II, 486-93, 1936.

"Viscosities of Liquid-Solid Systems - Influence of Dispersed Particles", R. N. Traxler, H. E. Schweyer, and Moffatt, Ind. Eng. Chem. 29, 489, 1937.

A concentric cylinder viscosimeter for measuring viscosities of stabilized asphalts is described.

"Influence of the Shape of Sand Particles on the Plasticity of Asphalt Concrete", N. Ewers and F. Schiel, Bitumen, Vol. 10, 42-7, May 1940.

Thorough laboratory and road tests are reported showing the appreciable influence of the shape of sand particles on the plasticity of asphalt concrete. Results summarized in tables and graphs show that the depth of the groove produced in asphalt concrete containing 6% binder by 100 wheel passages in the same track at 50° was 5 mm when pit sand was used, and only 1 mm when broken sand was used in preparing the concrete mixture. To obtain pavements which would exhibit a 3 mm groove depth in the standard track test, 5.8% binder was required with pit sand compared with 6.5% when broken sand was used.

"The Influence of the Addition of Fillers on the Properties of Plastic Materials and the Explanation of This Influence", L. W. Nijboer, Polytech. Weekblad, 37, 219-21, 1943. Chem. Zentr. 1943, II, 2128.

Nijboer discusses systematically the system asphalt-filler, with respect to the effect of concentration of filler on the physical properties of the aggregation.

"Physics and Chemistry of Pigments", C. E. Barnett, Ind. Eng. Chem. 41, 272-279, 1949.

A review stressing the importance of light absorption, index of refraction, and particle size on the properties of pigments.

"Asphalt Compositions", V. R. Smith and C. G. Schmutz, U.S.P. 2,506,283, Feb. 14, 1950.
Ca & Mg & hydroxides up to 2% added after the blowing process inhibit scumming and hardening of asphalts in use.

"Fillers in Asphaltic Concrete", Carl A. Carpenter, Public Roads, 27, 101, December 1952.
Fly ash from New Jersey and Illinois were equally good with limestone dust in maintaining the compressive strength of asphaltic concrete after 4 days immersion in H_2O at 120°F.

"Coating Compositions and the Like", J. E. Fratis, U.S.P. 2,384,671.
20% loading of 100% -200 mesh mica is recommended for filling asphaltic roofing materials. Eveready machine used in testing mica and seven other fillers.

IV. Separations by Solvents and Adsorbents

(A). Separations

"Recovering Polynuclear Compounds from Hydrocarbon Oils Containing Asphalts", Ger. 629,241 (I. G. Farben.), Dec. 3, 1936.
Hydrocarbon oils containing asphalts, particularly high boiling fractions of petroleum or tar or of their destructive hydrogenation or cracking products, are treated in known manner to remove asphalts, preferably only the hard asphalts, and are then hydrogenated under pressure under conditions not conducive to cracking. Polynuclear compounds are then recovered from hydrogenation product by appropriate physical or chemical processes. The liquid residue may be dehydrogenated and further polynuclear compounds then recovered from the product. Processes are described in which different products are recovered.

"Water-White Hydrocarbons from Trinidad Asphalt", H. T. Gaetz, Refiner Natural Gasoline Mfr. 15, 313-17, 1936.
By petroleum-ether extraction, treatment with fuller's earth, fractionation, acid treatment in solvent, dilution, digestion over Na and redigestion, approximately 12% of water-white hydrocarbons were separated from Trinidad asphalt. Determination of density, refractive index, viscosity, optical activity, molecular weight, combustion analysis, molecular refraction, and molecular volume identified hydrocarbons of the series C_nH_{2n-2} to C_nH_{2n-8} and possibly C_nH_{2n-10}, all of a cyclic structure.

"The Adsorption of Bitumen by Certain Natural and Treated Earths", H. T. Lorne, J. Inst. Pet. Tech. 22, 541, 1936.

"Asphalts, Bitumens and Pitches", Martinenghi, G., Olii Min. 31, 1-7, 1937.
The composition and properties of these products are summarized, and 6 proposed methods of classification are outlined. That of Marcusson, Richardson and Hofer is considered the most serviceable.

"Critical Surface Tension of Asphaltic Bitumens and Tar Solutions", Nellensteyn, F. J., Chem. Weekblad 34, 646-9, 1937.
The colloidal nature of asphaltic bitumens and coal-tar pitches is discussed. (In German).

"The Recovery of Bitumen", L. J. Chalk, J. Soc. Chem. Ind. 56, 156-60, 1937.
A modification of Greutert's process for the recovery of asphaltic bitumen which may be used in routine testing is described. The CS_2 solvent is distilled off in a current of CO_2 at atmospheric pressure. To remove remaining solvent, the distillation flask is connected to a water pump to reduce the pressure to 1-2 cm Hg and the temperature raised to 100° above the established softening point of the recovered bitumen. Seventy g. of bitumen can be recovered from a sample of suitable size in 1.5 hours. Results obtained with the method are tabulated. The results are satisfactory except that the ductility of the recovered bitumen is usually high owing probably to traces of solvent, a defect of all known recovery methods.

"Asphalt", Heinrich Egli, Swiss 194,709, March 1, 1938.
A process for the continuous disintegration of asphalt by treating with a solvent and centrifuging the resulting suspension to separate the solution from the insoluble part is described. The malthenes are extracted by this means.

"Separating Asphalt from Oils Containing It", Ulric B. Braz and Claude Swift, U.S.P. 2,081,473, May 25, 1939.
An asphalt-bearing oil is co-mingled at a temperature of about 50° or higher with a liquified, normally gaseous hydrocarbon solvent, such as liquified C_3H_8 and the asphalt is separated from the oil and solvent at an elevated temperature. Various features of apparatus arrangement and operation are described.

"Separating Wax from Asphalt-Wax Mixtures", Ulric B. Braz, U.S.P. 2,081,733, May 25, 1939.

A liquified, normally gaseous hydrocarbon solvent containing a major proportion of C_3H_8 is used to dissolve the wax, leaving the asphalt as an undissolved residue. Various details of apparatus arrangements and operation are described.

"The Properties and Composition of Asphalts of the Slow Curing Type", Arnold J. Hoiberg, Olaf Hougen, and J. Zapata, Bull. Univ. of Wisconsin Eng. Exptl. Sta. 86, 116, 1939.

Five commercial asphalts, all meeting the requirements for the slow curing type yet of wide differences in origin, chemical nature and method of refining, were studied for the purpose of obtaining information which might serve as a basis for predicting durability and behavior under service conditions.

"Separation and Reblending of Constituents of Asphalt", Augustus H. Batchelder, U.S.P. 2,200,484, May 14, 1940.

Asphalt is separated into an oil fraction and an asphaltene fraction by use of a selective solvent for the oil fraction such as liquid propane. The oil fraction and asphaltenes are freed of the solvent; the asphaltenes are dried and a substantially undissolved non-colloidal dispersion of the substantially oil free asphaltenes is formed in the oil (this dispersion having a lower viscosity than the starting asphalt and remaining liquid until heated above atmospheric temperature).

"Practical Laboratory Method of Analyzing for the Constituents of Asphalt", Francis R. Grant and Arnold J. Hoiberg, Proc. Assoc. Asphalt Paving Tech. 12, 87-122, 1940.

After a discussion of the general methods used for the separation of the constituents of asphalt and the importance of the study of each fraction, Grant and Hoiberg suggest a procedure for the direct recovery of all the fractions in an unchanged form without the use of high pressure equipment. Various combinations of solvents and temperatures for separating a bitumen into fractions are also discussed, and data evaluating several wax precipitating solutions are also given.

"Separation of Asphalts and Crude Oils", O. G. Strieter, J. Research of the National Bureau of Standards, 26, 415-18, 1941, (Research Paper No. 1387).

Substitution of pentane for petroleum naphtha and ether for carbon disulfide in the analysis of asphalt yields more reproducible results. The sample (5 g) is extracted with pentane (225 cc), the solution being filtered and the residue (asphaltenes) dried and weighed. The filtrate is evaporated to dryness at room temperature, the residue being dissolved in pentane (25 cc), mixed with Fuller's earth and extracted (Soxhlet) with pentane. The extract is evaporated and the residue (oily constituents)weighed. Extraction of the Fuller's earth with ether and evaporation of the solution gives the weight of the asphaltic resins.

"Asphalt Treatment", Donald E. Carr, U.S. 2,276,155, March 10, 1942.

A product having air blown characteristics and improved weathering life is prepared by a process which involves separating an asphalt residuum into an asphaltene fraction, a resin fraction, and an oil fraction, and blending the oil fraction with the asphaltene fraction and subjecting the blend to oxidation, as by blowing with air.

"Oxidized Asphalt", Ulric B. Braz, U.S. 2,277,842, March 31, 1942.

An oil which will oxidize into asphalt is blended with an oil which has been extracted from an asphalt-containing oil by a solvent (such as propane or butane) capable of dissolving oil, but not substantial quantities of asphalt, and the blend of oils is subsequently oxidized at an elevated temperature with an oxygen-containing gas to produce an oxidized asphalt having a higher weatherometer test than can be produced by oxidation of the first mentioned oil in the absence of the extracted oil to substantially the same melting points.

"Relations Between the Chemical Composition of Asphalts and Bitumens and Their Physical Properties", R. Grader, Oel u. Kohle 38, 867-78, 1942. (In German.)

A method for separating asphalts and bitumens into groups of substances, i.e., into asphaltenes, resins, and oily substances, is described. Chromatographic adsorption analysis is used to establish the quantitative proportions of the different groups of substances.

F. J. Nellensteyn and F. J. & J. P. Keupers, Chem. Weekblad 39, 58-61, 1942. Chem. Zentr. 1942, I, 3060-1. (In German.)
The surface tension rule has shown itself to be a suitable means for explaining the precipitation and segregation method which can be used to separate the asphaltenes. A new high-vacuum distillation method has permitted the isolation of a compound with high oxygen content from various asphaltenes.

"Study of Asphalts by Fractional Solution", Arsene Celerier, Chimie & Industrie, 51, 95-101, 1944. (In French.)
A review of relatively recent investigations and of the conclusions drawn therefrom regarding the composition and structure of asphalts.

"Analytical Fractionation of Asphalts", A. J. Hoiberg and W. E. Garris, Jr., Ind. Eng. Chem., Anal. Ed., 16, 294-302, 1944.
A procedure is described for the solvent separation of asphalts into 5 fractions: hexane-insolubles, hard resins, soft resins, oils, and waxes.

"Luminescence Analysis of Petroleums and Lubricating Oils", V. S. Krasnova, C.A. 1946, 4197, 1946.
Chloroform extract has long filter-paper strips inserted into it for 6-12 hours and the various components rise to different heights. Under ultra-violet light, the highest zone (oils) is green; lower zone (resins) yellow; lowest zone (asphaltenes) brown.

"Study of Asphaltenes by Extraction by Selective Solvents", M. Bestougeff and R. Darmois, Compt. Rend., 224, 1365-7, 1947.
An oriental and a Venezuelan asphalt were studied. Tables of properties are given in the article.

"New Method for Determining the Composition of Bitumen and Petroleum", A. I. Lysikhina, Stoitel. Doraq., 10, 17-18, 1947.
A solvent method of separating asphalts into their constituents, using benzene, chloroform and acetone.

"Fractionation of Asphaltenes by Gradual Precipitation", M. Bestougeff and R. Darmois, Compt. Rend., 227, 129-31, 1948. (See also C.A. 41, 6699h).
Fractional precipitation of asphaltenes from benzene solution by non-solvent and heat. Well characterized groups are not found.

"Precipitation of Asphaltenes from Bitumen Solutions", E. Cianetti, Ann. Chim. Applicata, 38, 249-54, 1948.
Asphaltenes are precipitated from a carbon disulfide solution of asphalt by various organic solvents. No correlation exists with surface tension as stated by Nellensteyn.

"Determination of Asphaltenes, Oils & Resins in Asphalt", R. L. Hubbard and K. E. Stanfield, Anal. Chem. 20, 460-5, 1948.
Separates asphalt into constituent groups with pentane, alumina, methanol and benzene.

"The Surface Tension Rule for Asphaltic Bitumen", F. J. Nellensteyn & M. Baart, J. Inst. Pet. 35, 302-5, 1949.
Correlations of the precipitating power of solvents for the asphaltenes of one asphalt with surface tension are presented with theory.

"The Determination of Asphalt in Crude Oil and Crude Oil Products", J. Moos, Erdol u. Kohl 2, 345-57, 1949. (In German.)
Various methods of precipitation and adsorption are evaluated. Aluminum oxide is best adsorbent. Several solvents are criticized.

"Evaluating Petroleum Residua and Lube-Oil Distillates - Adsorption Method", N. W. Furby, Anal. Chem. 22, 876-81, 1950.
Asphalt is fractionated by precipitating asphaltenes, adsorbing resins on Fuller's earth, dewaxing oils with silica gel. Data on various fractions are given.

"Constitution of Natural Bitumen", E. Mariani, Bull. Sci. Faculta Chim. Ind. 8, 70-6, 1950.
Natural bitumen from Selenizza (I) is fractionated into asphaltenes (II), oils (III), and resins (IV) by differential solvent extraction. Five g of I is extracted for several days with 50 ml. of solvent at 25°C. After decantation, the residue is extracted again for 2 days with 25 ml. of pure solvent. The latter part of the experiment is repeated. The final residue is separated by centrifuging at 3500 r.p.m. and transferred to a fritted-glass filter on which it is weighed after solvent washings are colorless. The combined extracts and filter washings are evaporated. The extracted bitumen is fractionated by solution in benzene followed by precipitation of II by petroleum naphtha and adsorption of IV on alumina, followed by filtration and isolation of II by solvent evaporation.

"Determination of the Paraffin Content of Mineral-Oil Products Containing Asphalt", H. P. Mojen, Erdol u. Kohl 3, 167-71, 1950. (In German.)

Fuller's earth is used to separate asphalt from oil. Non-asphaltic constituents are extracted with benzine, and the asphalt with benzene. Paraffin is determined by method of Holde (C.A. 22, 4241).

"The Solvent Extraction of Asphaltic Residues", H. E. Schweyer and O. M. Brown, Pet. Processing 5, 151-6, 1950.

Ternary diagrams were used to correlate the solubility of asphalts in n-butane at 50, 100 and 200°F. Many anomalies exist.

"Analysis of Bitumen by Means of Selective Solvents", K. Krenkler, Bitumen, Teere, Asphalte, Peche 2, (3), 59-63, (4) 85-8, (5) 105-10, 1951. (In German.)

Separation with n-butanol, n-heptane, cyclohexane, and centrifuge. Asphaltenes vary in composition.

"Bitumen Fractionation with the Aid of Selective Solvents", K. Krenkler et al., J. Inst. Pet., 362A and 468A, 1951.

Critical evaluation of methods of separation. Bit., Teere, Asph., Peche 3, 59-63, (2), 105-10, (2)(1951).

"Corn-Sirup Analysis Involving Selective Adsorption", E. J. McDonald and R. E. Perry, J. NBS 47, 363, 1951.

Darco-celite adsorbents were used to separate mixtures of dextrose, maltose, and dextrin. About 95-97% recoveries were obtained.

"Separating Asphalt Into Its Chemical Constituents", Gordon O'Donnell, Anal. Chem. 23, 894-8, 1951.

Asphalt, treated with isopentane to remove asphaltenes, was fractionated in a 14-inch cyclic molecular still to give 10 fractions of increasing molecular weight. Each fraction was separated into its constituents (saturates, aromatics, and resins) by chromatography on a silica gel column. Treatment of the saturates with methyl isobutyl ketone gave an oil and a wax which was further resolved by urea into paraffins and napthenes. The oil was separated into the naphthenic and paraffinic fractions by thermal diffusion. The aromatics were treated with hydrogen peroxide. The mixture was resolved into mono- and dicyclic aromatics and sulfones (from oxidation of benzothiophenes) by chromatography on an alumina column.

"Anhydrous Alumina as Adsorbent in Constituent Analysis of Asphalt", R. L. Hubbard, K. E. Stanfield and W. G. Kommes, Anal. Chem., Vol. 24, page 1410, 1952.

% resins increased with proportion of γ - alumina present. Regeneration procedures do not produce reproducible aluminas.

(b) Properties of Components.

"The Constitution of Cracked and Uncracked Asphalt", E. S. Hillman and B. Barnett, Reference Natural Gasoline Mfr., Vol. 16, pages 362-6, 1937.

In the residues studied cracked maltenes are aromatic in nature, while straight-run maltenes are paraffinic or aromatic with paraffin side chains. This is thought to account for the greater degree of dispersion in cracked than in straight run asphalt. No free paraffins exist in the cracked residue, except as side chains of aromatic or naphthenic molecules. The components of cracked residues appear to be closely related and made up of units of simpler compounds. The cracked asphaltenes have lower molecular weights than the straight-run compounds. Possible structures of asphaltenes and resins are discussed.

"Asphaltenes", F. J. Nellensteyn and J. P. Kuipers, J. Inst. Petroleum, Vol. 26, pages 401-6, 1940.

The ether extract of most asphaltic bitumens is less than the light-petroleum extracts; e.g. 20-40% against 35-38%. The reasons for such differences are discussed. It is suggested that ether should be employed for asphaltene determinations and further, that the ether soluble but light-petroleum insoluble matter should be termed "difference asphaltenes". In natural asphalts, e.g. from Trinidad Lake, the oxygen compounds appear to be concentrated in the "difference asphaltenes", while the sulfur compounds are largely present in the ether asphaltenes. Does not involve fundamental separation of all constituents.

"The Chemistry and Composition of Asphalts", B. A. Murphy, J. Inst. Petroleum, Vol. 31, pages 475-85, 1945.

A structure proposed for asphaltenes must, on the evidence, meet with certain specifications. The article describes and illustrates the structural specifications for asphaltenes.

"The Formation of the Picene Fraction in Distillation of Asphalt Bitumen", F. J. Nellensteyn and G. M. A. Steffeloor, Chem. Weekblad, Vol. 43, pages 105-6, 1947.

The picene (wax tailings) fraction is formed during distillation, probably through a free-radical reaction. (In German)

"Nature and Properties of Asphaltenes", M. Bestougeff, Chem. et Ind., Vol. 60, pages 137-41, 1948. Also, J. Inst. Petroleum 34, 309A, 1948.

Asphaltenes seem to be heterocyclic compounds of several series.

"Connection Between the Character of the Asphaltenes and the Type of Petroleum", O. A. Radchenko and O. P. Bolostkaya, Doklady Akad Nauk, USSR, Vol. 68, pages 733-6, 1949.

Asphaltenes fractionally precipitated by pet. ether from benzene solution by 5, 10, 20, 30, 40 volumes of pet. ether. Curves range from flat to sharp rise.

V. Physical Properties-Tests.

(a) Adhesion.

"The Adhesion of Bituminous Binders to Stone", W. Riedel and H. Weber, Asphalt u. Teer Strassenbautech 33, 677, 693, 713, 729, 749, 793, 809, (1933).

"A Method of Determining the Adhesion of Asphalt to Metal", E. B. Wedmore, Proc. World Pet. Cong. 2, 593 (1934), and U.S.P. 2, 113, 725.

"Wetting Agents, etc.", I. G. Farben, Brit. 461, 972, Feb. 26, 1937.

Oxidation products that have wetting properties and emulsify substances such as asphalts and tars are obtained by subjecting aliphatic or cycloaliphatic hydrocarbons to a treatment with mineral acids and then to oxidation with oxygen containing nitrogen compounds. In examples a brown coal hydrogenated product is treated with: 1) HCl or H_2SO_4 and then with NH_4NO_3 and, 2) HCl and then with HNO_3.

"Adhesion of Asphalt to Aggregates in the Presence of Water", P. Hubbard, Proc. Highway Research Board, Vol. 181, pages 238-49, 1938.

The causes and prevention of asphalt stripping from aggregate surfaces in the presence of water are discussed.

"Treatment of Tars and Asphalts", R. Lichtenstern, Austrian 153, 506, 6/10/38.

Products of improved adhesive capacity and elasticity are obtained from tars or asphalts by heating them with a small proportion of a polymerization product obtained from the same or other bituminous material by heating it with a metal chloride; e.g. Al Cl_3 or Zn Cl_2. Examples are given.

"Report of the Committee on Interfacial Relations", Victor Nicholson, Proc. Assoc. Asphalt Paving Tech., Vol. 12, pages 3-13, 1940.

Nicholson discusses the use of wetting agents to increase the adhesion between the asphalt and mineral aggregates with particular emphasis on the cationic agents; 17 of these have been tried out by adding them to wet sand followed by a liquid road oil and all of them enabled the oil to displace the water from the sand grains. Lecithin was also found to give the same results. Nicholson also discusses solvent mixtures to remove the asphalt from mineral aggregates in the cold, using a centrifuge and the following recommended mixtures: 98cc of specially denatured alcohol formula 2b, 7cc H_2O, 250cc C_6H_6 and 650cc CS_2.

"Asphaltic Compositions", Brit. 533, 927, to Standard Oil Development Co., Feb. 24, 1941.

A small proportion of a salt of a multivalent metal containing in the mol. at least 1 organic acid having a molecular weight of not more than 120 and at least 1 organic acid radical derived from an organic acid having a molecular weight greater than 120 is incorporated in an asphalt. This increased the adhesivity.

"Asphalt Compositions", Alvin P. Anderson and Fred H. Stross, U. S. 2, 370, 386, Feb. 27, 1945.

The presence of water soluble alkali compounds or compounds forming water-soluble alkalies on hydrolysis in an asphalt reduces the effect or destroys cation-active bonding agents.

"Asphalt Wetting Agents", Elinore M. Hawkins, U. S. 2, 534, 713 to Standard Oil Development Co., Dec. 19, 1950.

Asphalt is mixed with 0.25-2.0% anti-stripping agent. The latter is a condensation product of a polyaklylene polyamine with a halogen derivative of a polycyclopentadiene and the salt product derived by treating the condensation products with acid. The adherence qualities of asphalt to various types of rock aggregates are improved.

"Hydrocarbon Additive Oils et al", Charles Hoffman and Thomas R. Schweitzer, U.S. 2, 540, 114, Feb. 6, 1951.

"Fatty Acid Alkyloamine Condensations and Products", Maurice J. Kelley, U. S. 2, 540, 678, Feb. 6, 1951.

Surface-active agents from the condensation of at least 2 mols. of an alkyloamine and 1 mol. of a monobasic acid are claimed to be improved textile softeners and are also useful as detergents, defoamers, synthetic waxes, asphalt anti-strippers and anti-static agents.

(b) Blistering.

"The Formation of Blisters in Asphalt Coatings", E. Kindscher and H. Wicht, Wiss Abhandl Deut Material Prufungsanstalt.

The occurrence, structure and growth of blisters are discussed. The cause is ascribed to air or vapors released from underlying concrete by heat of the sun. Among preventives are listed the employment of a dry concrete, a minimum of asphalt and maximum of stone, good anchoring of the asphalt by coating the concrete with a cold bitumen solution and by the introduction of separating materials.

"Formation of Bubbles and Faults in (Bituminous) Coverings", Riehm, Vol. 36, Pages 249-50, 1938.

Apparatus is described whereby gas in bubbles can be sampled to determine its origin.

(c) Molecular Weight.

"Scientific Glass Blowing and Laboratory Techniques", W. E. Barr and V. J. Anhorn, "Instruments", Vol. 20, page 342, 1947.
Complete description of the Modified Menzies - Wright Molecular Weight apparatus used for the determination of molecular weight.

"Mean Molecular Weights of Asphalts and Their Constituents", G. W. Eckert and B. Weetman, Ind. Eng. Chem., Vol. 39, pages 1512-16, 1947.
Molecular weight of oils and resins are determined cryoscopically to be 370-900. Molecular weights of asphaltenes, determined by viscosity are 700-1800; increase with blowing. Data needs confirmation because of complicating factors.

"The Modified Menzies - Wright Molecular Weight Apparatus", W. E. Barr and V. J. Anhorn, Scientific and Industrial Glass Blowing and Lab Techniques, Instruments Publishing Co., Pittsburgh 12, Pa., pages 284-291, Jan. 1949.
Essentially the same article as published in "Instruments", Vol. 20, page 342, 1947.

"Modified Molecular Weight Apparatus", R. Matteson, Anal. Chem., Vol. 22, page 172, 1950.
An apparatus for determining molecular weight in the range of 100 to 1000, using B.P. rise in chloroform. Calibrated with Naphthalene (128), Diphenyl Bismuthine (216), Tetrachlorobenzene (440), and Tristearin (891).

"Determination of Molecular Weights of Low Vapor Pressure Oils and Greases", G. Burrows and R. Jackson, Vol. 2, page 50, 1952.
Molecular weights were determined cryoscopically on apiezon, vacuum-pump oils and solicones.

(d) Physical Tests.

"Fourth Colloid Symposium Monograph", F. E. Bartell and H. J. Osterhofft, page 420, Chem. Cat. Co., New York, 1926.
A cell for measuring contact angle between a liquid and a finely divided solid.

"Determination of the Cloud Point of Dark Oil", W. R. Van Wijk, J. Inst. Petroleum Tech., Vol. 22, pages 754-60, 1936.
The cloud point of a dark oil can be recognized by the change in transmission of infra-red radiations. Apparatus and procedure are described for measuring the amount of radiation transmitted at a series of temperatures.

"The Mechanism of Film Formation in Tars", J. G. Mitchell, J. Soc. Chem. Ind., 56, 253T (1937).
Deals with the evaporation of constituents from asphalts.

"Composition of Asphaltic Bitumens", J. Oberbach, J. Inst. Petroleum Tech., Vol. 23, page 222A, 1937.

Many analytical data show change in characteristics of asphalt around penetration. 80-100.

"The Determination of the Drop Point, Softening Point, Melting Point, and Flow Point", A. R. Matthis, Cong. Chem. Ind., pages 575-84, 1938.

A discussion of the inconsistencies in the results obtained. For cylinder oils or mixtures of cylinder oils and resin, the time elapsed between filling of the cup and the determination of the drop point has considerable effect on the results; for petroleum or asphalt it has none. Matthis allows 14 hours between filling the cup and making the test in the first two cases. For the determination of the softening point, the U tube method is preferable to Ubbelohdes method.

"Classifying Asphalts by Means of a Penetration Index", J. P. Pfeiffer and P. M. VanDoormal, Natl. Petroleum News, Vol. 30, pages 80-2, 1938.

The penetration index is based on the relation between penetration and ball and ring softening point. A nomograph is developed by means of which the penetration index can be obtained. Asphalts are grouped roughly into "N" type, with indexes of "-1 to +1", comprising most normal road asphalts; type "Z" with an index below -1 (that is the coal-tar pitch type) having great susceptibility and a tendency toward brittleness; and the "R" type, with an index above 1, having low temperature susceptibility. The nomograph in the form of a slide rule is described.

"An Apparatus for Determining the Melting Point of Resins", C. Krauz and Antonin Majrich, Chem. Obzor, Vol. 15, pages 1-2, 1940.

Plugs of resins are placed in the end of a fine glass tube, 2 parallel copper wires are slipped into the glass tube so that the amalgamated tips touch the resin plug, and the plugged ends of the copper wires lie below the level of the mercury surface. When the resin melts the mercury forces the resin up the glass tube and establishes a contact between the 2 copper wires which complete a circuit lighting a bulb. At least 6 determinations can be made simultaneously. The apparatus functioned well for determining the points of softening of resins, asphalts, tars, paraffins, waxes, and glue.

"Physical Constants of Asphaltic Bitumens", R. N. J. Saal, W. Henkelom and P. C. Blokker, J. Inst. Petroleum, Vol. 26, pages 29-39, 1940.

"Physical Constants of Asphaltic Bitumens", R. N. J. Saal, K. Meinema and P. C. Blokker, Inst. Petroleum, Vol. 26, pages 246-55, 1940. Part II - Part I in Vol. 26, page 195, 1940.

The dielectric strength of a number of bitumens was determined with both plate and spherical electrodes. Dielectric losses, an important consideration in insulation technique, are due in part to "ohmic conduction" and in part to dielectric hysteresis. The first was measured as the tangent of the angle of dielectric loss; that is, the phase difference between the dielectric loss current and the current that would flow if the material were an ideal dielectric. The apparatus and procedure are described. Saal derived the relation between the viscosity and the penetration $n = c/pen^2$. This strictly applied only to bitumens that behave as purely viscous liquids.

"Surface Consistency Characteristics of Asphalts", E. C. Knowles, and F. C. McCoy, Ind. Eng. Chem., Vol. 35, pages 1118-22, 1943.

A method was developed for measuring the consistency of thin layers used in accelerated weathering tests on roofing asphalts. A modification of ASTM penetration method is described. Data are given on measurements of constant depth penetration and of surface hardening caused by various storage conditions.

"Current Colloid Theory of Asphalts" - Rheology, Solubility, Composition, Gel. Structure, Compatibility. H. J. Eilers, J. Phys. & Coll. Chem., Vol. 53, pages 1195-1210, 1949.

"Physical Testing of Asphalts and Similar Materials" E. Thelen, Franklin Institute, ACS Third meeting in miniature, Jan. 20, 1949 Methods of Test.

"Significance of Tests on Asphaltic Materials", Marshall Brown and Fred J. Benson, Texas, Eng. Expt. Station, Vol. 119, page 76, 1950.

The standard routine methods of analysis are described and the results of these tests are interpreted in relation to the performance of the asphalts on road surfaces. Two new test procedures are presented. The curing index test is used to indicate the comparative rates of curing of asphaltic materials. The vacuum distillation test identifies the various grades of asphalt which make up the semi-solid asphalts.

"Oil-exudation Property of Asphalts", E. C. Knowles, F. C. McCoy, H. E. Schweyer and C. E. Wilkinson, Ind. Eng. Chem., Vol. 42, pages 2340-3, 1950.

A complete description is given of the apparatus and procedures used to measure the number of layers of cigarette papers stained by the oil exuded from asphalt. This stain index is a function of the experimental conditions, such as the time, the temperature, and the pressure applied to the asphalt. A chart is presented which enables the estimation of the stain indices at conditions other than the observed ones. The source and the method of processing of the crude asphalts influence the oil-exudation properties of the asphalts.

"Determination of the Ring and Ball Softening of Asphaltic Bitumens With and Without Stirring", C. J. Krom, J. Inst. Petroleum, Vol. 36, pages 727-37, 1950.

In the determination of the softening point of asphaltic bitumen (ring and ball method) (I) according to Inst. Petroleum 58/44 mechanical stirring in the bath is prescribed, which is not the case in the normal ASTM method D36-26. The present investigation shows that stirring the bath reduces the (I) softening point for all bitumens by 1.6°, both in the water bath and in the glycerol bath and hence, if stirring were generally applied, all specifications with (I) limits would have to be altered. Statistical calculations have shown that reproducibility for one operator and one apparatus of the (I) determinations with stirring is not better than without stirring. There is no reason for stirring the bath during the determination of the (I) softening point.

"Bitumen Test Methods", K. P. Ledwoch, Erdol u. Kuhle, Vol. 4, pages 717-19, 1951. (Ref. J. Inst. Pet., Feb. 1952).

Survey of literature 1937-1951 on tests for viscosity, melting point, tensile, adhesion, etc.

"Investigations Concerning Composition of Asphaltic Materials", R. N. Traxler and H. F. Schweyer, Presented A.C.S. Cleveland Mtg., April 1951.
Refractive index determination of dark components and separation of asphalt into three groups.

"Research on Tar and Bitumen and Their Mixtures by Spreading Thin Films on Water". K. Letters, Bitumen-Teere-Asphalte-Peche, Vol. 3, pages 258-6, 1952. (In German).

(e) Rheology.

"Determination of Brittleness of Asphalt and Asphalt Mixtures", F. C. Van Heurn, Arch. Tech.Messen, Vol. 4, (T63), 1935.
A number of molded rods of the sample are mounted in an apparatus in which they are subjected to rising temperature and struck by weights; the temperature at which a rod breaks is a measure of its brittleness.

"Influence of Storage on the Viscosity of Diluted Asphalts", Celestino L. Ruiz, Bol. Informaciones Petrolera, Vol. 13 145, pages 57-60, 1936, Buenos Aires.
Discrepancies in the viscosity of "cut back" after transportation and storage caused Ruiz to investigate the cause. This behavior, attributed to flocculation of the organo-solution, was verified experimentally. Heating caused the viscosity to return to approximately the initial value, after a considerable increase on storage.

"Susceptibility of Asphalts to Temperature Change", J. Schweyer, C. E.Coombs, and R. N. Traxler, Proc. ASTM, Vol. 35, Part II, pages 531-43, 1936.

"Increase in Viscosity of Asphalts with Time", R. N. Traxler and H. E. Schweyer, Proc. ASTM, Vol. 36, Part II, pages 544-51, 1936.

"The Characteristic Plastic Properties of Asphalt and Pitch", E. I. Barg, Shornik, Vol. 2, pages 297-306, 1937.
The temperature interval of plasticity and the ductility are important characteristics of such materials. More stable colloidal structures like the pitches have smaller intervals of plasticity and greater ductility than the less homogeneous asphalts. The temperature interval for a change from the liquid viscous to the liquid state is about the same for most tars, but the interval from the liquid viscous to the solid state varies with the individual tar. Methods for measuring these properties are discussed.

"Rheological Properties of Asphalts", C. E. Coombs and R. N. Traxler, J. Applied Physics, Vol. 8, pages 291-6, 1937.
Elastic before and after effects were observed at low shearing stresses. Elastic return deformation was greater at high than at low temperatures. With increasing shearing force, many asphalts exhibited a "threshold" value above which viscosity decreased with time to a constant value, the shearing stress being held constant. Thixotropy was also shown by age hardening and by the observation that when shearing stress was suddenly reduced, the viscosity slowly increased even with continued washing. The viscosity values of viscous asphalts agreed well when taken with either the Bingham Stephans alternating stress or falling coaxial cylinder viscometer.

"Method for Measuring the Rheological Properties of Materials of Great Consistency, Such as Asphalts", E. Thelan, J. Applied Physics, Vol. 8 , pages 135-7, 1937.

An ASTM penetrometric needle was allowed to sink into various asphalts for a series of successive time intervals. The rate of flow varied linearly after the first penetrations. Results were nearly independent of shearing stress. The shape of the surface at the point of punch affected the mobility, but not the yield value. The negative log of mobility varied linearly with temperature. Yield values for particular crude stock asphalts varied directly as the asphaltene content. On aging, asphalts increased in yield value but decreased in mobility. In two particular stocks, it was found that the melting point could be predicted from mobility at 77°F.

"Penetration - Viscosity Relationship for Asphaltic Bitumens", R. N. Traxler and C. U. Pittman, J. Applied Physics, Vol. 8, pages 70-71, 1937.

The relation as given by $n = (5.13 \times 10^9) Lp^{-1.93}$ (cf Saal and Kolns, C.A. 27, 2795) is criticized on the grounds that, as it is stated to apply only to asphaltic bitumens which exhibit no elasticity, thrixotropy or anomalous flow properties, it is worthless from an industrial viewpoint since practically no asphalt used commercially lacks these properties.

"Viscosities of Liquid-Solid Systems....Influence of Dispersed Particles", R. N. Traxler, H. E. Schweyer and L. R. Moffatt, Ind. Eng. Chem., Vol. 29, pages 489-92, 1937.

Pulverized solids were dispersed in various asphalts and the viscosity was determined. Each pulverulent solid had a characteristic stability index, which is the percentage increase in viscosity with a 1% increase in volume of solid. It was found that the volume-concentration log-viscosity was linear and that the viscosity of the viscous-liquid pulverulent mixture with a certain power is inversely proportional to the average thickness of the liquid film separating the solid particle.

"Flow Properties of Asphalts Measured in Absolute Units", R. N. Traxler, Ind. Eng. Chem, ASTM, Symposium of Consistency, Vol. 30, pages 322-24, 1938.

The flow properties of asphalts are very important to the technologist and require measurements over a wide range of consistencies; Traxler describes the rheological methods useful in investigating these properties; empirical tests, although widely used, measure two or more simultaneously.

"The Measurements of the Flow Properties of Bitumens", D. C. Broome, J. Inst. Petroleum, Vol. 25, pages 509-30, 1939.

A review with fifty-two references.

"Asphalts of Low Susceptibility to Temperature Change", Charles Mack, U. S. 2,062,366, Dec. 1, 1939.

An asphalt-containing crude oil is reduced to a solid residue at ordinary temperatures and a portion of the reduced product is withdrawn and blown to a softening point of the order of about 185° and a resin content of not over about 20%; the distilling of the initial residue is continued to obtain a product having a softening point of about 38°, the heavy oil distillate is recovered, and the oxidized residue is then blended with a major proportion of the unblown residue to produce a final blended product which is of low resin content.

"The Flow Properties of Asphalt and Their Measurement by the Penetrometer", Charles Mack, J. Soc. Chem. Ind., Vol. 58, page 306-10, 1939.

After discussing the flow properties of asphaltic bitumens and their influence on the penetration determination Mack gives an equation based on experimental data which presents depth of penetration as a function of time.

"The Flow Properties of Bituminous Materials", A. R. Lee, J. B. Warren, and D. B. Waters, J. Inst. Petroleum, Vol. 26, pages 101-28, 1940.

The subject of the relations of rate of flow, stress and temperature was studied with the aid of a rotating conicylindrical viscometer, chosen as best fitted for applying constant stress at a series of temperatures. Ten asphaltic bitumens and asphalts were subjected to test.

"Rheological Properties of Asphaltic Bitumens", R. N. J. Saal, and J. W. A. Labout, J. Phys. Chem., Vol. 44, pages 149-65, 1940.

After an extensive study of the rheological properties of two quite different bitumens made by measuring the deformation under constant shearing stress and the elastic recovery, and different combinations of these by means of a conicylindrical viscometer, Saal and Labout conclude that asphaltic bitumens must be considered mixed gel-sol systems and that the degrees of structure exhibited can vary widely with composition. These conclusions were reached previously by Pfeiffer and Van Doormaal.

"Rheological Interpretation of Asphalt Tests", R. N. Traxler, H. E. Schweyer, and J. W. Romberg, Proc. ASTM, Vol. 40, pages 1182-1200, 1940.

After a brief review of the colloidal nature of asphalts as related to their flow properties, Traxler, Schweyer and Romberg present data showing that penetration test values at 25° (77°F) have no rheological significance, that the ductility test is too empirical to be helpful in evaluating the flow properties of asphalts and that other empirical tests such as float, fluidity factor and penetrations at high and low temperatures are also inadequate. An equation relating consistency, and ring and ball softening point for certain asphalts is given.

"Viscometer Suitable for Testing Asphalt", Harold P. Hayden and H. E. Schweyer, U. S. 2,182-082.

Various structural, mechanical and operative details.

"Rheology of Plastic Materials", D. C. Broome, L. Belmes, Nature, Vol. 147, pages 176-237, 1941.

(C.A. 7263, 1941). Theory and experiments involving extension and recovery of asphalt strips.

"Viscosity, Plasticity, Elasticity and Colloidal Structure of Bitumens", E. Hoeppler, Oel u Kohle, Vol. 37, pages 995-1009, 1941.

(Br CA 1942-B-I 219) Rheological properties of 13 steam reduced and blown asphalts.

"Measurement of the 'Firmness' of Asphaltic Bitumens", D. C. Broome, Petroleum (London), Vol. 5, pages 122-4, 1942.

The firmness of asphaltic bitumens as measured by twisting point determinations, penetrations tests, determination of the degree of plasticity and resistance to tensile stresses (all briefly described) is so largely affected by thixotropy, the thermal history of the sample, inherent variations in the test methods and personal factors as to result in values which are not always reproducible

"Rheology of Bituminous Mixtures Relative to the Properties of Asphalt", Charles Mack, Proc. Assoc. Asphalt Paving Tech, Vol. 13, pages 194-255, 1942.

After a discussion of the forces acting on pavements, of the physical properties of asphalt (viscous flow, plastic flow, thixotropy and elasticity), Mack described the tests necessary to determine the mechanical properties of bituminous mixtures by the following values; elastic flow in terms of percentage hardening, percentage of plastic flow, dissipation of stress and viscous flow. The asphalts used for the investigation consisted of a reduced asphalt "T" chosen for its readiness to form a thixotropic structure and three synthetic asphalts.

"Rheological Properties of Asphalt", R. N. Traxler, H. E. Schweyer and J. W. Romberg, Ind. Eng. Chem., Vol. 26, pages823-9, 1944.

Data are given that show that certain asphalts are simple liquids at atmospheric temperatures. Whereas others have the characteristics of complex liquids. The type of flow depends on the source, method, and degree of processing, and the temperature of the asphalt.

"Rheology of Asphalt", J. W. Romberg and R. N. Traxler, J. Colloid Sci., Vol. 2, pages 33-47, 1947.

Rheology of asphalts measured and reported in absolute units. Soft asphalts follow Nuttings equation, but blown ones don't. Nutting, J. Frank. Inst., 191, 679, (1921).

"A Review of the Rheology of Bituminous Materials", R. N. Traxler, J. Colloid Sci., Vol. 2, pages 49-68, 1947.

Seventy-five references. Review of the rheological measurements on asphalt.

"Studies in the Plasticity of Rubber (Asphalt Included)", J. Furukawa, and K. Tomihisa, J. Soc. Rubber Ind. Japan, Vol. 21, pages 17-21, 46-51, 97-101. 1948.

Equations for relating various rheological constants.

"Rheological Investigation of Asphaltic Bitumen in Connection with its Technical Application", R. N. J. Saal, J. Inst. Pet., Vol. 34, pages 69-79, 1948.

Investigation of viscosity of asphalt, filled asphalt and asphalt concrete concludes knowledge is too limited for lab studies, but penetration is good for road work.

"Plastic - Elastic Behavior of Matter", F. H. Muller, Kolloid - Z, Vol. 114, pages 2-14, 1949.

Elastic dispersion measurements yield an insight into the mechanical behavior of asphalt.

"Physical Tests of Asphalts and Similar Materials", E. Thelan, Proc. Assoc. Asph. Pav. Tech., Vol. 18, pages 154-84, 1949.

Correlations between working properties of asphalts and rheological properties. Methods of evaluating asphalts are described.

"Volume Flow of Asphalt", M. Reiner, P. J. Rigden and E. N. Thrower, J. Soc. Chem. Ind., Vol. 69, pages 257-60, 1950.

A mixture of bitumen and mineral filler under tension undergoes viscous flow and progressively increases in volume. The authors show that the shear and volume flow have a viscous (permanent) and elastic (recoverable) component. A method is given to calculate the viscosis and elastic shear deformation, and the ciscous and elastic volume deformation.

"Asphalts", R. N. Traxler, Colloid Chemistry, Vol. 7, Reinhold 1950.
A good review of some properties of low softening point asphalts.

"Some Correlations of Asphalt Compared with Physical Properties", E. C. Hughes, H. F. Hardman, Presented at Annual Meeting Assn. of Asphalt Pav. Tech., Feb. 1951.
Correlates deviation from Newtonian Flow (N) with composition by running viscosity of petroleum and figuring asphaltenes required to produce flow behavior.

(f) Solution Properties.

"Ultra-microscopical Researches on Asphalt", Nellensteyn and Van derBurgh, J. Inst. Pet. Tech., page 346, 1925.

"Heterogenity of Asphalt - a Quantitative Method", G. L. Oliensis, Proc. ASTM, Vol. 36, P. II, pages 494-519, 1936.

"The Oliensis Spot Test Improved", R. H. Lewis, and J. Y. Welborn, Public Roads, Vol. 18, pages 59-61, 1937.
The original qualitative test by Oliensis for determining heterogeneity in asphalts has been extended to a semi-quantitative basis by development of methods for determining gilsonite and xylene equivalents. Tests on 39 samples showed 23 were homogeneous and that 16 remained homogeneous after exposure for 15 weeks to winter weather. All of the homogeneous materials that became heterogeneous upon exposure had xylene equivalents of 16 or less. Under summer conditions all materials developed heterogenity by exposure within five weeks.

"Some Properties of Bitumen Solutions", E. Vellinger, G. Radulesco and H. Picot, Ann. Combustibles Liquids, Vol. B, pages 459-71, 1938.
The viscosity of dilute solutions of an asphaltic bitumen varies greatly with the 10 different solvents tested. Those of high solvent power such as CS_2 and C_6H_6 giving the lowest viscosity and cyclohexane the highest in the same order as the transparency of the solutions. Mixtures of these first two solvents give viscosities lower than calculated by addivity. The viscosity increases with age. No correlation between the surface tension and solvent power of the solvent, as claimed by Nellensteyn is found. The Conclusion - density relation is linear.

"Development of the Modified Quantitative Oliensis Spot Test", A. H. Benedict. Assoc. Asphalt Paving Tech., Proc. Technical Sessions, Vol. 11, pages 13-43, 1940.
Benedict reports that the quantitative Oliensis spot test failed when applied to California straight-run asphalts. After trying different test methods for the determinations of cracked products in asphalt, a modified Oliensis test was devised which replaced the "Oliensis solvent". (Shell - solve "S") by pure heptane with a boiling point of 98.58°. Data obtained by 5 different laboratories on 13 different California asphalts showed fairly consistent xylene equivalents. 11% of these asphalts were blended with Dubb's residuum and the results showed that as little as 4% of the highly cracked residuum added to straight-run asphalt could be detected. The procedure for the modified quantitative Oliensis spot test is given.

"Identification and Estimation of Bitumens in Asphaltic Materials", J. H. Martin, Petroleum, Vol. 4, pages 37-8 (48), 1941.

The reliability of test results in estimating and identifying the bituminous constituents of an asphaltic material is considered. The color of the bitumen, as determined by the panchrometer or preferably by the Loribond tintometer, is of positive help in identification, only if used in conjunction with a comprehensive examination of the material. The manner of testing asphalts is briefly outlined and colorimetric data on Trinidad Lake asphalt and residual bitumens are tabulated.

"Colloidal Stability of Asphalts. Spot Tests With Partial Solvents", H. F. Winterkorn and G. W. Eckert, Ind. Eng. Chem., Vol. 33, pages 1285-9, 1941.

Winterkorn and Eckert discuss the importance of the Oliensis spot test to determine the colloidal stability of bitumens. They have studied, besides the standard Oliensis procedure, the effect of variation of standing time and of ratio of naphtha to asphalt, the use of naphtha-xylene, naphtha-hexane and hexane-xylene mixtures; and the effect of heating bitumen solvent mixtures and the use of 19 different solvents in the Oliensis procedure.

"Electron Microscope Study of Asphalts", Preckshot, DeLisle, Gottrell, Katz, Trans. Inst. Min. & Met. Engrs., Vol. 151, page 188, 1943.

Since all photomicrographs were made on solutions, incorrect conclusions may have been drawn.

"Nature of Asphaltic Substances", D. L. Katz and K. E. Beu, Ind. Eng. Chem., Vol. 37, pages 195-200, 1945.

Thin films of asphalt and oil examined in the electron microscope show few or no asphaltene particles. The crude oils diluted with about 95-99% Benzene and petroleum ether always show particles in suspension. Asphaltene particles if present in undiluted oils and asphalts are less than 65 Angstroms in diameter.

"Dispersion of Extraneous Materials in Asphaltic Bitumen", F. J. Nellensteyn, Ingeniem (Utrect), Vol. 59, pages M89-91, 1947.

Ultra-microscopic examination of xylene solutions of asphalt shows particles of dispersed material. Nellensteyn calls them micelles of inorganic matter.

"Evaporation of Asphalt Cutbacks in Thin Films", Proc. Assoc. Asph. Pav. Tech., O. Holmes, Vol. 17, pages 311-22, 1948.

A comparison of the properties of the residual materials with those obtained by evaporation in thin films.

"The Preparation of Uniform Paint Films", S. Johanson, ASTM Bulletin, Dec. 1948.

Films of paint applied ±0.001" or better.

"Coagulation of Asphalt on Microscope Slides", J. R. Benson, Proc. Assoc. Asph. Pav. Tech., Vol. 9, page 63, 1937.

"Electron Microscopy - I Techniques", S. G. Ellis, Pet. Refiner, Vol. 27, pages 410-15, 1948.

Use of the electron microscope and electron diffraction to study asphalts.

"Dispersion in Media Other Than Water", J. L. Van du Minne, Verfkroniek, Vol. 21, pages 131-5, 1948.
Colloid Chemical discussion of dispersion in paints and asphalts.

(g) Spectroscopy.

"Spectra of Porphyrins in Petroleums and Bitumens", E. A. Glebovskaya, Mv. Vol'kinshtein, Zhur Obshchei Khim, Vol. 18, pages 1440-51, 1948.
Spectra of metals present in bitumens show Vanadium to be concentrated in the resin fraction as a porphyrin complex. It is acidic while the nickle complex is neutral. The complexes indicate an animal origin for petroleum.

"Developments of Spectroscopic Methods of Analysis of Petroleum Products", H. Luther, Erdol u Kohle, Vol. 4, pages 387-94, 1951.
(J. Inst. Pet. 505A, 1951) Raman and infra-red yield good results. U.V. for unsaturates and aromatics. Low concentrations for infra-red. Discusses analysis of mixtures of components up to C_{18}.

"Identification of Bitumens by Colorimetric Methods", D. C. Browne, and R. M. Edwards, J. Inst. Pet., pages 88-97, Feb. 1952.
C_6H_6 solutions of asphalts are examined with a Spekker absorptometer. Each has a characteristic light absorption pattern.

"A Study of Bitumen Solutions With a Phase Contrast Microscope", A. P. F. Kist, Overdurk vit het Weekblad de Ingeneur, Vol. 10, pages 1-7, 1953.
Solutions of bitumen in carbon disulfide show particles of about 1-5 microns by phase microscopy. Kist claims they confirm Nellensteyn's theory

(h) Structure, Physical.

"Nature and Properties of Asphaltenes", M. Bestougeff, Chimie & Industrie, Vol. 60, pages 137-41.
Nellensteyn's colloidal graphite hypothesis is contradicted. Asphaltenes are the heavy ends of the other petroleum fractions and can be fractionated further.

"Constitution of Cracked and Uncracked Asphalts", E. S. Hillman and B. Barnett, Proc. ASTM, Vol. 37, pages 558-66, 1937.
A theory of structure and some supporting data, with references to other work, are presented. This theory attempts to correlate apparent anomalies in physical and chemical properties of asphalts. A cracked and an uncracked asphalt are studied in terms of solubility in solvents (of varying internal pressure) molecular weight, sp. gr., specific refraction, H_2SO_4 reactivity and the degree of colloidal dispersion probably existing.

"Development of Internal Structure in Asphalts With Time", R. N. Traxler, C. E. Coombs, Vol. 37, pages 549-56, 1937.
Evidence is presented to show the development of internal structure. Consistency is measured by falling coaxial cyclinders and surface etchings by Et_2O and naphtha yield data, which are presented in tabular, graphic and photographic form.

"Extract Portion of the Lubricant Fraction From a Mid-Continent Petroleum. Chemical Constitution", Mair, Willingham & Strieff, Ind. Eng. Chem., Vol. 30, pages 1256-68, 1948.
Analytical work and proposed structure for asphaltic constituents.

"Structure in Asphalts Indicated by Solvent-Treated Surfaces", R. N. Traxler, C. E. Coombs, Ind. Eng. Chem, Vol. 30, pages 440-3, 1938.
A number of photographs are given which show surface patterns obtained when different asphalts were treated with 86° Bé naphtha or with ethyl either. The pattern varies with the solvent used but for a given solvent is characteristic of the particular asphalt of a definite age. With essentially viscous asphalts no patterns were obtained; such asphalts probably possess no interval structure.

"The Composition of the Micelle Nucleus of Asphalt, Bitumen and Coal Tar and Some Related Products", F. J. Nellensteyn, Chem. Weekblad, Vol. 36, pages 362-6, 1939.
The microscopic and untra-microscopic, the x-ray and the chem. modes of approach are reviewed. By means of apochromatic lenses a microscopic study of the coarse nuclei appearing in the form of black particles was possible. Some recent objections to the surface tension theory are due to erroneous observations or interpretations.

"Physical Chemistry of the Asphalts", John M. Swanson, J. Phys. Chem., Vol. 46, pages 141-50, 1942.
Studies were made of the dielectric constant and solution behavior of bituminous material commonly used in road construction. These road oils were separated by solubility fractionation into three fractions designated as asphaltenes, resins, and oily constituents. These constituents are believed to be combined as a colloidal system in the complete asphalt. The dielectric constant data were used to establish the macro molecular character of the asphaltenes and to develop a qualitative explanation of their solubility in various solvents.

"Colloids and Nellensteyn's Theory of the Colloidal Structure of Asphalt, Bitumen and Tar", A. O. Bohn, Dansk Vejtidsski, Vol. 22, pages 25-30, 1945.
No abstract in Chemical Abstracts.

"Chemistry and Constitution of Asphalts", B. A. Murphy, J. Inst. Pet., Vol. 31, pages 475-85, 1945.
Good discussion on the structure of asphalt constituents. A review article. No original contribution.

"The Colloidal Structure of Asphaltic Bitumens", R.N.J.Saal, P. W. Baas, W. Henkelorn, J. Chem. Phys., Vol. 43, pages 235-61, 1946.
Asphalts studied by rheological, electrical, molecular weight and separations. Conclusion is that they are asphaltenes (MW 2-30,000) dispersed in maltenes (MW 500); aromatics acting as dispersing agents.

"Study of Some Organographitic Substances by X-Ray Diffraction", H. A. Sack, J. J. Trillat, Comptus Rendus, Vol. 224, page 1502, 1947.
(Ref. J. Inst. Pet. 33, 314A, 1947)
X-ray diffraction of bitumens separated from Mexican petroleum by

electrophoresis in nitro-benzene gives a characteristic plateau, near 3.35Å° (graphite spacing). Also a diffuse at 4.35A° (similar to liquid patterns) and two spacings of 288 and 2.37Å°. Conclusion: not an organographite or graphite.

"The Colloidal Structure of Asphalts", H. Eilers, J. Phys. Colloidal Chem., Vol. 53, pages 1195-1211, 1949.
X-Ray diffraction and viscosity measurements were used in an effort to determine the structure of asphalts.

"Relationship Between Properties of Bitumens and Their Micelle Structure", K. Krenkler, Strassen u Tiefbau, Vol. 3 (10), pages 305-11, 1949.
(Hgwy. Res. Ab., May 1951) Flow properties, color, etc. are correlated with micelle structure. More asphaltenes; more micelles.

"Composition of Asphaltenes", C. Alexandrian and M. Louis, Compt. Rendus, Vol. 231, page 1233, 1950.
(Fuel Abst., Mar. 1952)Chemical composition and x-ray diffraction data are given for a number of asphaltenes and carbenes. Both are crystalline and some show chain orientation. Data are listed to show differences between these two materials and forms of carbon.

"Asphalt, A Colloidal Material", R. N, Traxler and J. W. Romberg, Ind. Eng. Chem. Vol. 44, pages 155-158, 1952.

(i) X-Ray Measurements.

"X-Ray Studies of Paving Asphalts", C. L. Williford, Bul. Agr. Mech. Col. Texas, Vol. 73, pages 7-70, 1943. Tex. Eng. Expt. Sta. Bul.
X-Ray diffraction patterns were obtained on samples of com. Texas and Arkansas asphalts. Comparison of intensity curves showed significant differences in the small angle scattering; this indicates differences in the amount of discrete particles present in the asphalt. Asphalts of known satisfactory performance in practice showed the most pronounced small-angle scattering.

"X-Ray Diffraction Patterns of Solid Aromatic Hydrocarbons", L.J.E. Hofer and W. C. Peebles, Anal. Chem., Vol. 23, pages 690-95, 1951.
Impurities enough to lower melting point by 15°C do not change pattern.

"Determination of Sulphur in Petroleum Fractions by X-ray Absorption", S. W. Levine and A. H. Okamoto, Anal. Chem., Vol. 23, pages 699-704, 1951.
Because the X-ray absorption of sulphur is greater than Hydrocarbons it can be estimated with an accuracy of ±0.02%.

VI. Chemical Tests, Properties & Reactions

(a) General.

"Chemistry of Asphalt", George W. Eckert, Oil Gas. J., Vol. 37, pages 60-62-64-66-68-70, 1939.

"Manufacture of Blown Asphalts. Their Physical and Chemical Variations", Alberto Rossi, Bol. Informacionis Petroleras (Buenos Aires), Vol. 19, No. 211, pages 37-47, 1942.

The action of air blowing on asphaltic residues of petroleum is discussed. Data are given on changes in various physical and chemical properties during blowing. Decrease in content of asphaltic acids as anhydrides and increases in asphaltenes at expense of asphaltic resins and oils after blowing were found. The role of oxygen during the process is that of a dehydrogenation and polymerization agent.

"Semimicro Quantitative Organic Analysis", E. P. Clark, Academic Press Inc., 1943, Book.

"Geochemical and Technical Study of Some French Asphalts", L. Marcel, Ann. Mines and Carburants, Vol. 135, pages 57-108, 1946.

French asphalts have carbon 71-84%, Hydrogen 9-12%, Sulphur 1-11%, Nitrogen 0.3-3%, Oxygen 0.5%-9%. Sulphur was concentrated in asphaltenes.

"Organic Quantitative Micro-Analysis", J. Niederl and V. Niederl, Pub. by Wiley. 2nd Ed., 1946.

"Recommended Specifications for Microanalysis", American Chem. Soc., Anal. Chem., Vol. 21, page 1555, 1949.

Latest recommended apparatus and procedures for the microdetermination of carbon-hydrogen, nitrogen, sulfur and halogens.

"Kinetics of Coal Hydrogenation. Conversion of Asphalt", Sol Weller, M. G. Pelipety, and Sam Friedman. Ind. Eng. Chem., Vol. 43, pages 1572-5, 1951.

The hydrogenation of asphalt was studied for a quantitative evaluation of the overall coal hydrogenation and for developing improved coal hydrogenation processes.

(b) Carbon-Hydrogen Ratio

"Determination of Carbon-Hydrogen by Combustion", D. D. Tunnicliff et al, Anal. Chem., Vol. 18, pages 710-19, 1946.

A dual apparatus for rapid, accurate carbon-hydrogen determinations.

"Determination of Carbon-Hydrogen Groups in High Molecular Weight Hydrocarbons", A. Evans and R. R. Hubbard, Anal. Chem., Vol. 23, pages 1604-10, 1951.

Absorption in the 1.1-2.5 micron range shows CH_3, CH_2, CH groups. Good in paraffins, poor in aromatic and naphthenic molecules.

"Carbon-Hydrogen Ratio Determination", G. L. Roger, H. K. Albee, L. T. Hallet et al., Ind. Chem. Anal. Ed., Vol. 13, page 574, 1941.

(c) Halogens and Sulfur.

"The Reaction of Chlorine with Butane Asphaltenes", F. J. Nellensteyn and J. Dorleyn, Chem. Weekblad, Vol. 43, pages 4-8, 1947.
Benzene and an oily substance are formed on chlorination at 200-550°C. Nellensteyn and Dorleyn claim it proves existence of free radicals.

"Researches on Asphaltenes - II Radical Reactions", F. J. Nellensteyn, J. Inst. Pet., Vol. 32, pages 582-6, 1946.
Asphalt from Dutch East Indies was chlorinated. Benzene was isolated. No reaction between chlorine and sulfur compounds.

"Determinations of Sulfur in Rubber", Sheen, Kahler and Cline, Ind. Eng. Chem., Anal. Ed., Vol. 9, page 69-1937.
Sulfur precipitated from solution as Barium Sulfate. Re-dissolved in potassium hydroxide and back-titrated with sodium sulfate in presence of tetra hydroquinine. Color changes from red to yellow.

"Effect of Sulfur on Some of the Properties of Asphalts", I. Bencowitz and E. S. Bol, ASTM Preprint, 9pp, 1938.
Bencowitz and Bol described a method of preparing mixtures of asphalt and sulfur at temperatures at which no chemical reaction resulting in the evolution of hydrogen sulfide occurs. Data shows that, on weathering, mixtures containing 25 and 40% sulfur, have a smaller increase in softening point but a higher decrease in penetration than the corresponding straight asphalt, and that mixtures made with aggregates have a much higher stability at 60° (140°F.) than mixtures made with asphalt without sulfur. Three tables and four figures are given.

"Determination of Total Sulfur in Asphalt", S. Pellerano, Ind. Eng. Chem., Anal. Ed., Vol. 11, pages 446-7, 1939.
After having investigated several methods for the determination of sulfur in asphalts, Pellerano devised a procedure utilizing a manganese dioxide - copper oxide catalyst with anhydrous sodium carbonate in a combustion tube through which the oxygen is passed. The results are concordant with those of the bomb method and simpler and less expensive equipment is required.

"Sulfur Determination in Rubber", Fed. Specification ZZR 601a, page 37, 1940.
Fusion and zinc-nitric acid methods for digesting organic material for sulfur analysis gravimetrically.

"Halogen and Sulfur Determination by Microcombustion", G. L. Royer, H. K. Liber et al, Ind. Eng. Chem., Anal Ed., Vol. 15, page 230, 1943.

"Microdetermination of Halogen and Sulfur", O. E. Sundberg and G. I. Royer, Anal. Chem., Vol. 18, pages 719-24, 1946.
A volumetric method of determining sulfur by titrating (SO_4) sulfate solution with ($BaCl_2$) Barium Chloride in the presence of potassium rhodizonate as an indicator.

"The Sulfurization of Unsaturated Compounds", H. E. Westlake, Jr., Chem. Reviews, Vol. 39, pages 219-39, 1946.
A review of the procedures and mechanixms of sulfurizing asphalts and other unsaturated organic materials.

"Constitution of Natural Bitumen. VI Extraction with Liquid Sulfur Dioxide", Eugenio Mariani and Renato Tunziani, Boll. Sci. Facolta Chem. Ind. Bolonga, Vol. 8, pages 98-100, 1950.

"Determination of Sulfur in the Presence of Halogens", R. R. Jay, Pet. Eng. Vol. 25, page c49, 1953.
Sulfur determination by the lamp method suffers from interference by halogens. After the acids are titrated with sodium hydroxide, the halogen is titrated with silver nitrate.

(d) Nitrogen.

"Nitrogen Determination. Micro-Combustion Method", G. L. Royer, H. K. Alber et al, Ind. Eng. Chem., Anal. Ed., Vol. 15, page 476, 1943.

"Spectrophotometric Determination of Total Nitrogen in Oils", C. H. Hall, M. W. Hale, W. H. Jones, Anal. Chem. Vol. 21, pages 1549-51, 1949.
A semi-micro Kjedahl method for determining nitrogen between 0.002 and 1.0 percent in organic materials. Accuracy ±10%.

"Distribution of Nitrogen in Petroleum According to Basicity", J. P. Richter, P. D. Ceasar, S. L. Meisel, Ind. Eng. Chem., Vol. 44, pages 2601-5, 1952.
The ratio of basic to total nitrogen, as determined by Perchloric acid titration varied from 0.25 to 0.34 for 14 crudes. Did not change with heating at 600°F.

(e) Oxygen.

"Oxygen Absorption Test on Asphalt Constituents", R. R. Thurston, E. C. Knowles, Ind. Eng. Chem., Vol. 28, page 88 (1936).

"A Laboratory Oxidation Test", F. L. Raschig, P. C. Doyle and K. H. Rudd. Assoc. Asphalt Paving Tech., pages 208-14, Dec. 1937.
An apparatus to oxidize asphalt in the laboratory at 204.4° (400°F) is described. Data are given on 11 samples.

"Chemical and Physical Properties of Asphalt", Jack Carlen, Mines Mag. (Colo. School of Mines), Vol. 29, pages 221-2, 1939.
A survey of methods of separating fractions of asphaltic constituents, and oxidation of asphalts. Research on chemical composition and oxidation of asphalts is important in their respective relationship to the physical properties of these products and may lead to the discovery of hydrocarbons stable to oxidation as well as to products of oxidation of industrial importance.

"Asphalt and Its Constituents - Oxidation at Service Temperatures", R. R. Thurston, E. C. Knowles, Ind. Eng. Chem., Vol. 33, pages 320-4, 1941.
Thurston and Knowles previously reported (C. A. 30 2739[5]) their results on the oxidation of asphalt and its constituents in the temperature range 400-500°F. In this paper they present the results they obtained on oxidizing three different types of asphalts and their 5 constituents (asphaltenes, resins, naphthene oil, paraffine oil, and wax) by exposing the samples in oxygen-filled sealed Pyrex tubes and Erlenmeyer flasks under a Mazda S-1 bulb at temperatures around 170°F. The data show that the three asphalts and their constituents absorb oxygen.

"Oxidation of Asphalt in Thin Films", Ebberts, Ind. Eng. Chem., Vol. 34, pages 1048-51, 1942.
Ebberts describes a new method for measuring the oxidation of asphalts in thin films; it is fast, precise, and requires no special apparatus.

"Measurement of Oxidation Stability of Road Asphalts", A. P. Anderson, F. H. Stross and H. Ellings, Ind. Eng. Chem., Anal. Ed., Vol. 14, page 45, 1942.

"Oxygen in Organic Compounds", V. A. Aluise, R. T. Hall, F. C. Staats, W. W. Becker, Anal. Chem. Vol. 19, pages 347-52, 1947.
Modified Unterzaucher method.

"Constitution of Natural Bitumen IV - Preliminary Oxidation Experiments", Eugenio Mariani, Frances Spinelli, Ann. Chim. (Rome) Vol. 40, pages 512-26.

"Direct Microdetermination of Oxygen in Organic Compounds", A. O. Maylott, J. B. Lewis, Anal. Chem., Vol. 22, pages 1051-55, 1950.
Comparison between Unterzaucher, Liebig and ter Meulen methods. Unterzaucher satisfactory in presence of inorganic carbonates and oxides. Liebig lumps all errors in with oxygen, and ter Meulen is not satisfactory in the presence of nitrogen compounds. Liquid nitrogen trap is needed on all methods in the presence of sulfur compounds.

"The Influence of Tars and Asphaltenes on the Oxidation of Lubricating Oil", P. P. Borisox, B. L. Zaltsman et al, Vestnik Moskov, Univ., Vol. 7, No. 5, 1952.
The oxidation of lubricating oils is inhibited best by the addition of 1% tars. Grozny asphaltenes have 70% Carbon, 7.3-7.5% Hydrogen, 9.5-9.6% Sulfur, 11.1-11.4% Oxygen, and 1.7-1.8% Nitrogen.

(f) Saponification and Titration.

American Society for Testing Materials, Volume II, D-663-42T - Acid No. of Petroleum Produced by Titration; D-664-42T, Acid No. of Petroleum Produced by Elec. Titration.

"Determination of the Saponification Value of Asphalts and Asphalt Oils. Use of an Improved Titration Flask", J. E. Fratis and D. H. Condit; Ind. Eng. Chem., Anal. Ed., Vol. 9, pages 576-7, 1937.
A procedure is described for determining the saponification value of asphalts and asphaltic oils. A new 250cc special Erlenmeyer titration flask is described. It is provided with a horizontal tube reaching one-third around the bottom of the flask. When the end point is approached the flask is tilted so that the side tube is downward. The last trace of pink in it should be taken as the end point. Data are given on the saponification values of natural and of petroleum asphalts, on the accuracy of the method as checked by electrometric titration using a glass electrode.

(g) Structure, Chemical.

"Improved Methods of Examining Mineral Oils. Especially the High Boiling Components", Vlugter, Waterman and VonWesten, J. Inst. Pet. Tech. Vol. 21, page 661, 1935.
Concentration of carbon in the molecule determined to be paraffins, aromatics and naphthenes by specific refraction measurements.

"The Constitution of Cracked and Uncracked Asphalts", E. S. Hillman, D. Barnett, Refiner Natural Gas Mfg., Vol. 16, pages 362-6, 1937.
In the residues studied, cracked maltenes are aromatic in nature while straight-run maltenes are paraffinic or aromatic with paraffinic side chains. This is thought to account for the greater degree of dispersion in cracked than in straight-run asphalts. Possible structures of asphaltenes and residues are discussed.

"Aromatics in Petroleum Fractions", M. R. Lipkin, et al, Anal. Chem., Vol. 20, pages 130-35, 1948.
Determination of compounds containing at least one aromatic ring (BP 200°C) to an accuracy of 1% by adsorption on silica gel.

"Determination of Unsaturation in Organic Compounds by Electrometric Titration", B. Braae, Anal. Chem., Vol. 21, pages 1461-66, 1949.

"Physical Chemistry of Asphalt", J. M. Swanson, J. Phys. Chem., Vol. 46, pages 141-50, 1942.
Dielectric measurements of asphalt components solutions show resins and asphaltenes are polar and oils are not. By suitable resins, asphaltene can be dispersed in oils.

"Determination of Organic Functionality by Molecular Spectroscopy", N. D. Coggeshall. Vol. 22, pages 381-95, 1950.
Review of spectroscopy. 64 References.

"Determination of Organic Functionality", P. J. Elving, Anal. Chem., Vol. 22, pages 376-8, 1950.
Introductory comments on a symposium on functionality.

"Determination of Organic Functionality by Electrical Measurements", I. Lykken, Anal. Chem., Vol. 22, pages 396-402, 1950.
57 references. Reviews. Potentiometric and Conductimetric titrations. Polarography, Magnetic susceptibility, High Frequency and amperometric titrations, etc.

"Determination of Organic Functional Groups by Chemical Means", S. Siggia, Anal. Chem., Vol. 22, pages 378-82, 1950.
Review of chemical type reactions.

"Analysis of Dielectric Dispersion Curves for Bituminous Materials", H. Walther, Kolloid - Z, Vol. 117, pages 75-96, 1950.
Dielectric dispersion curves at various temperatures give the structure of asphalts. Gausian curves are sol. type and non-Gausian, gel. type.

"Simple Method for Determining Double Bond Index of Pure Unsaturated Hydrocarbons", Y. M. Liu and N. F. Chu, Chinese Chem. Ind. Eng., Vol. 2, pages 12-27, 1951.
Empirical method of calculating D.B.I. from M.W., Refractive Index, and hydrogen present. See Lipkin and Martin (CA 40, 5232[2]) and (CA 42, 7010a).

"Molecular Structure and Properties of Lubricating-Oil Components", J. G. Hillard and R. E. Jones, Ind. Eng. Chem., Vol. 44, pages 2582-2586, 1952.
Wax-free oils were separated with silica gel and groups were characterized by carbon-hydrogen ratios, viscosity, ultraviolet absorptions and infrared spectra.

"Determination of Aromatic and Naphthene Rings in Aromatics from Petroleum" C. C. Martin and A. Sankiri, Anal. Chem., Vol. 25, pages 206-14, 1953.
A graph is presented for the determination of the average number of aromatic and naphthene rings per molecule from the density, specific dispersion and molecular weight. The molecular weight can be estimated from the viscosities at 100 and 210°F. or from the density and mid-boiling point.

"Recovery of Polycyclic Aromatic Compounds from Mixtures", G. B. Arnold and H. V. Hess (To Texaco), Brit. 680,271, 10/1/52.
Polycyclic aromatics are removed from mixtures with monocyclic aromatics, aliphatics, naphthenics and heterocyclic compounds by treatment with a tetrahalophthalic anyhydride at 350°F. Then the mixture is cooled to 150°F for precipitation; then it is filtered at 90°F. and washed with pentane. Steam distillation at 350°F. yields naphthalene. Caustic wash removes the tetrahalophthalate.

(h) Emulsions.

"The Breaking of Bituminous Compositions Upon Stones", G. H. Klinkman, Asphalt u Teer, Strassenbautech 33, pages 342, 373, 403, (1933).

"Study of Emulsions of Tar and Asphalt with Water, Preparation of the Emulsions", R. Veroni, C. Fostiropol, Bull. Chim. Soc. Romaine, Vol. 38, pages 91-135, 1935-36.
Scientific study of tar-water and asphalt-water emulsions. Alkali hydroxides used as emulsifiers were added in amounts of 0.05 to 10%. Study of 250 different combinations showed that (1) the type of emulsion depends on the order of introduction of phases, of percentage of phases, and the percentage of KOH in the emulsions. (2) the particle size of the dispersed phase varied within close limits, (3) color of emulsion depends on that of prime materials used, (4) the stability of the emulsions depend on type, percentage of tar, or mixture of tar and asphalt, and viscosity. The viscosity increases with an increase in added phase.

"Asphalt Emulsions", J. W. Smith, Refiner Natural Gasoline Mfr., Vol. 15, pages 306-8, 1936.
Asphalt emulsions facilitate applications of asphalt of high softening points. Emulsions are prepared by treating asphalt with resin, and Na OH soap solution in a mill. ASTM Tests for asphalt content, viscosity, demulsibility, settlement, miscibility, stone coating and sieve test are significant.

"Physiochemical Research on Bitumen Emulsions", Georges Nadulesco, Ann. Combustibles Liquides, Vol. 13, pages 659-730, 1938.
Results of an extensive experimental study show that the properties of

asphaltic bitumen emulsions are determined principally by the origin and composition of the asphalt, the particle size of the emulsion and its pH. The two asphalts studied, from Mexican and Colombian petroleum, have similar characteristics but give emulsions which differ in some properties, especially in stability.

"Frost Stability of Asphalt Emulsions and Their Testing", H. Roadenbusch, Bitumen., Vol. 9, pages 201-5, 1938.

Stability of asphalt emulsions and frost stability are discussed along with methods for determining the latter property.

"Apparatus for Preparing Emulsions of Petroleum Asphalt and Water or Other Materials", Daniel E. Thalman, U. S. 2,092,992, Sept. 14, 1939.

Various details of a mixing apparatus comprising a pocketed cyclinder through which a shaft extends, on which discs and blades are mounted.

"Effect of Nature and Concentration of the Emulsifier on the Stability of Aqueous Asphalt Emulsions", S. M. Avetikyan, D. O. Gol'dberg., Kolloid Zhur. Vol. 12, pages 401-7, 1950.

Petroleum asphalt (I) was agitated with an emulsifier solution (II). The stability of the resulting emulsion was greatest when the temperature of (I) was 130° (better than 140° and 160°), the temperature of (II) remained 80°, when the time of stirring was 20 minutes or more, when the concentration of (I) in the emulsion was 25% (25% - 50% was tested), when the stirrer made 1200 (rather than 950) revolutions per minute, and when (II) was made with distilled water. As emulsifier, 0.0035 N sodium oleate (III) was 45 efficient as 0.35N sodium stearate. The efficiency of sodium naphthenates increased with their molecular weight and exceeded that of (III) at M = 394. The efficiency of sodium benzoate had a maximum in 0.04 N solution. It was greater than that of sodium naphthenate, MW 193, but much less than that of (III). Sodium phthalate was even less efficient.

Willem Frederick Jense, U. S. 2,550,481 April 24, 1951.

A soap of polymerized hydroxyalkyl carboxylic acid is incorporated into a bituminous emulsion. The stability of the emulsion is improved. Asphalt emulsions of extremely fine particle size are created, and emulsion characteristics of asphalt having low acid numbers are improved.

"The Effect of the Nature of Bitumen on the Preparation of Stable Bitumen-Water Emulsions", S. M. Avetikyan, and D. O. Gol'dberg, Kolloid Zhur, Vol. 13, page 159-63, 1951.

Three petroleum asphalts were emulsified in aqueous solutions of sodium stearate, sodium oleate, a-sodium naphthenate (I) and sodium benzoate. The stability of the emulsions often was greater when asphalts rich in naphthenes were emulsified with (I), and the asphalt rich in aromatic hydrocarbons was emulsified with sodium benzoate. However, the amount of asphaltenes and tar in the asphalt and the concentration of the emulsifier also have effects making the above rule.

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