

ular weights of the acids obtained are fairly close to the simple molecular weight as calculated from the combining numbers. With the possible exception noted, then, the method can be applied to routine determinations without the necessity of laboriously plotting curves showing the concentration effect for each oil used.

Owing to the great solubility in stearic acid of the various oils likely to be encountered, the method is widely applicable and, in fact, there will be but very few oils found that cannot be dissolved completely in the quantities required for a determination. The method is simple and easy to operate. No correction for loss of solvent by evaporation need be applied. The solvent is non-hygroscopic and the precautions which must be taken with nitrobenzol and, to some extent, with benzol, can therefore be omitted.

Some difficulties with the method have, of course, developed during its investigation in this laboratory; these in general, however, admit of satisfactory solution. For example, to obtain concordant results it is necessary to keep the bath in which the freezing point tube is immersed at approximately 40° C. Variation of more than one degree in the temperature of the bath will cause slight variation in the observed freezing point. If an automatically regulated thermostat is available that factor will cause no trouble. It is necessary to stir somewhat more vigorously than when benzol is used, in order to prevent undue supercooling. Under no circumstances are the observed freezing points sharper than one one-hundredth of a degree. On this account the accuracy of the method is not as great as the freezing point method in benzol but it compares very favorably with any of the boiling point methods.

The method as outlined clears up a number of difficulties which have been found with the determinations of molecular weights of oils and varnishes in the past and opens up the field for further investigations of this type. It has been found in this laboratory, for example, that determinations of molecular weights are of great importance in varnish control work and of even greater value in varnish analysis, for in many cases the treatment of an oil or varnish will be more accurately represented by its molecular weight than by any other of the common constants. For such application it is, of course, necessary to have at hand methods for determining the molecular weight of the various substances which make up the mixture of which the mean molecular weight has been determined by the methods indicated.

The process of determining such individual molecular weights in substances as simple as oils and polymerized oils is comparatively easy and will be outlined in full in a subsequent paper on polymerized linseed oil. Much greater difficulties arise when the molecular weight of the oil portion of a rosin-China wood oil varnish needs to be determined, but considerable progress has been made in the development of satisfactory methods. This will also be reported on later.

SUMMARY

The question of the determinations of molecular weights of oils, treated oils and varnishes has been outlined and the value of such investigations brought out.

The most usual solvents used in molecular weight determinations have been investigated and their inadaptability to the present problem pointed out.

A method for determinations of molecular weights of these products by use of stearic acid as a solvent has been outlined and the conditions surrounding its use developed.

Determinations by this method have been made on a large number of oil and varnish products.

The applicability and value of such a method have been indicated.

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GILSONITE AND GRAHAMITE: THE RESULT OF THE METAMORPHISM OF PETROLEUM UNDER A PARTICULAR ENVIRONMENT

By CLIFFORD RICHARDSON
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Gilsonite and grahamite are two forms of solid native bitumen which are not widely distributed in nature, gilsonite being the rarer, and are the result of metamorphism of petroleum under a particular environment. They are found in fissure veins which approach the vertical and afford conditions which are favorable for the metamorphosis of petroleum into those materials. This change has gone on, under a varying time factor, to an extent that has resulted in substances presenting various degrees of condensation, from one which flows slowly in the sun, as in the case of the softest gilsonite, to one of the hardness of the brittlest grahamite, which does not melt even at high temperatures. Between these extremes is to be found materials of varying consistency, both in the gilsonite and grahamite series, showing that these bitumens are the products of metamorphism, to a varying extent, under the environment to which they have been subjected, of some more or less liquid bitumen.

The indication of these changes or metamorphism is to be explained in the gradual decrease, as the metamorphism goes on, of the hydrocarbons and their derivatives which are soluble in naphtha, from the amount present in the softest gilsonite to that found in the hardest grahamite, with a corresponding increase in the residual coke which they yield on ignition. The following data for typical gilsonites and grahamites demonstrate this very plainly.

The gradual decrease from the softer to the harder form in the percentage of bitumen soluble in naphtha and increase in the yield of residual coke is striking. At the same time there is a corresponding increase, as the metamorphism increases in degree, in the melting point and in the specific gravity. These results

demonstrate very plainly the changes which go on in nature, under a certain environment, in particular types of petroleum. The environment is a governing condition. Under a different one true asphalt would be formed, such as is widely distributed in nature. The question arises as to what these conditions are, especially in view of the fact that both forms of solid bitumen must be looked upon as originating in petroleum and are sharply differentiated from each other. The asphalts consist, to a very considerable extent,

SOURCE	Flow ° F.	Specific Gravity	Per cent Soluble in Naphtha	Per cent Residual Coke
RESIDUAL:				
Texas Residual Petroleum.....		0.9524	88.0	6.5
GILSONITES:				
1 Utah (softest).....	285	1.011	55.5	10.0
2 Utah.....		1.037	46.9	12.3
3 Utah.....	260		47.2	12.8
4 Utah.....	345	1.037	46.1	13.9
5 Utah (hardest).....	Intumesces	1.057	24.5	16.7
GRAHAMITES:				
Cuba, Bahia.....	Intumesces	1.157	38.8	40.0
Trinidad.....	Intumesces	1.156	14.8	40.0
West Va.....	Intumesces	1.130	9.4	36.8
Colorado.....	Intumesces	1.160	0.8	47.4
Oklahoma.....	Intumesces	1.184	0.4	51.4

of hydrocarbons not acted upon by sulfuric acid; *i. e.*, of saturated hydrocarbons. Gilsonite, on the other hand, contains but a very small amount of such components. They may both have a common origin in petroleum but the environment to which this has been subjected has been so dissimilar in each case as to result in quite a different product. In the case of the gilsonite, the bitumen in which it has originated has been confined in relatively narrow veins. In that of the asphalts it has been spread out horizontally and subjected to quite different conditions, with a resulting product of entirely different character, the one consisting of more than 20 per cent of saturated hydrocarbons and the gilsonites and grahamites containing but a relatively small amount, as appears from the following data:

	Specific Gravity	Per cent Soluble in Naphtha	Per cent Saturated Hydrocarbons
Petroleum Flux (Texas).....	0.956	97.5	72.8
Residual Pitch.....	1.089	65.0	33.1
Bermudez Asphalt.....	1.082	62.2	24.4
Gilsonite (Utah).....	1.044	47.7	5.5
Grahamite (Okla.).....	1.171	0.4	0.3

These differences in character may be accounted for by the fact that gilsonite and grahamite originate in veins which are vertical or nearly so while the asphalts occur under entirely different conditions.

A material intermediate between an asphalt and gilsonite is found in shales of Tertiary age in the Central Valley of California at Asphalto, in vertical fissures, which confirms the idea that the character of a solid bitumen originating in petroleum is dependent on the environment to which it is exposed.

It is of interest to observe that the veins of gilsonite and grahamite end rather abruptly at certain depths and do not thin out gradually, and also that the material near the vein walls and also the surface consists of a harder form of bitumen than the mass of the deposit.

Grahamite is the result of metamorphic changes in gilsonite and gilsonite of similar changes in petroleum brought about by its environment. That they are of considerable geological age as to origin can be

seen from the fact that in one instance in the strata in which gilsonite occurs there is a fault extending a quarter of a mile without any disturbance of the enclosed bitumen, showing that the gilsonite must have been introduced into the vein before the displacement.

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THE GALACTAN OF *LARIX OCCIDENTALIS*

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The western larch (*Larix occidentalis*, Nuttall) is found in extensive stand in the Pacific Northwest. It is a magnificent tree sometimes reaching a height of 200 feet and a diameter of 5 to 8 ft. In the course of some experiments it was found that a considerable portion of the wood was soluble in water. Further investigations led to the interesting discovery that the soluble matter consisted almost entirely of a galactan ($C_6H_{10}O_5$)_n (specific rotation $[\alpha]_D^{20} + 12.11^\circ$) yielding only galactose on hydrolysis. The water-soluble content of the wood varied from 8 to 17 per cent in the individual trees examined.

A large number of galactans have been found in nature but only a few have been well characterized. Many of the galactans yield other sugars than galactose on hydrolysis so that the terms galacto-mannan, galacto-araban, etc., are applied, depending upon the sugars obtained. The galactan from western larch has been called ϵ -galactan. The δ -galactan isolated by Müntz¹ from the seeds of lucerne, by Maxwell² from beans, and by Lindet³ from barley has the rotative $a_j + 84.6^\circ$ and is precipitated from aqueous solution with lead acetate: ϵ -galactan has the rotation $[\alpha]_D^{20} + 12.11^\circ$ and it is not precipitated from aqueous solution with lead acetate.

The β -galactan of Winter⁴ and Prinsen-Geerligs⁵ has a yellow color and when dried is insoluble in water: ϵ -galactan is white and is readily soluble in water after drying.

The γ -galactan of Lippman⁶ and others is *originally* insoluble in cold water and is precipitated from concentrated solutions by lead acetate: γ -galactan differs also from ϵ -galactan in having a very high rotation, $[\alpha]_D = +238^\circ$. The δ -galactan of Payen⁷ and Bauer⁸ obtained from agar-agar and other sources is insoluble in cold water and when dissolved in 500 parts of boiling water a gelatinous mass is formed on cooling: ϵ -galactan shows no inclination to gelatinize.

The unusual occurrence of ϵ -galactan was of such interest as to warrant a careful examination of the literature with respect to the occurrence in woods of carbohydrates yielding galactose. It was found that Trimble⁹ had examined an *excrescence* of *Larix occidentalis* that contained 19.4 per cent of reducing sugar and

¹ *Compt. rend.*, **94**, 453.

² *Am. Chem. J.*, **12**, 26.

³ *Bull. de l'assoc. Chem.*, **20**, 1223.

⁴ *Deut. Zuckerind.*, **15**, 538.

⁵ *Chem.-Ztg.*, **21**, Rep. 150.

⁶ *Ber.*, **20** (1887), 1001; *Z. Ver. Zuckerind.*, **36**, 259; **37**, 468; **38**, 1252.

⁷ *Compt. rend.*, **49**, 521.

⁸ *Jour. prakt. Chem.*, **30**, II, 283.

⁹ *Am. J. Pharm.*, **70** (1898), 152.