[CONTRIBUTION FROM THE CASE SCHOOL OF APPLIED SCIENCE]

"SATURATION" OF THE PETROLEUM LUBRICANT HYDROCARBONS AS SHOWN BY THEIR REACTION WITH BROMINE

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For some time I have observed the explosive action of bromine on the petroleum hydrocarbons, and recently I have taken up the study of this reaction with solvent fractions and with distillates. This paper briefly describes the method as now applied and it is here presented, for considerable time may elapse before the results now in prospect are completed.

In brief, the oil is dissolved in carbon tetrachloride and the calculated amount of bromine slowly dropped from a graduated buret into a flask containing it, with a side tube dipping into another flask containing water. The bromine readily reacts in the cold, and the change is completed by heating gradually in hot water to 50–60°. The hydrogen bromide evolved is washed out of both flasks, made up to a definite volume (after removing the small amount of the bromine that escapes the reaction) and titrated. Direct sunlight does not seem to assist the reaction. The brominated solution is evaporated on the water-bath, the residue dissolved in ether, a little alkali added to remove any possible bromine remaining, washed, dried with calcium chloride, the ether evaporated and the oil finally dried in a vacuum over sulfuric acid. The bromine-substituted oils are apparently stable under these conditions, but are decomposed in the air-bath at 100–120°, with the elimination of hydrogen bromide.

As an example of the operation of this method, the following data were obtained with a solvent fraction that distilled at 280–282° 30 mm., from an Illinois oil, and with another that distilled at 275–280° 30 mm., from a Pennsylvania oil.

TABLE I

ACTION OF BROMINE ON PETROLEUM LUBRICANT HYDROCARBONS

	D, found		Bromine, %		Mol. wt.			
					Oil		Bromide	
	Oil	Bromide	Calcd.	Found	Calcd.	Found	Calcd.	Found
Pa. oil	0.8662	1.005	16.16	15.87	416	408	491	496
Ill. oil	.9047	1.138	18.22	18.16	360	359	439	437

	Formulas		G. HBr from 10 g. of oil	
	Oil	Bromide	Calcd.	Found
Pa. oil	$C_{30}H_{55}$	$C_{30}H_{55}Br$	1.9	1.9
Ill. oil	$C_{26}H_{48}$	$C_{26}H_{47}Br$	2.3	2.3

The series C_nH_{2n-4} is assumed for these hydrocarbons from knowledge gained by previous analysis of the proportions of carbon and hydrogen in similar oils. The bromine derivatives react readily with alcoholic potassium cyanide and dilution with water precipitates the alkyl cyanide.

On boiling the cyanides with aqueous sodium hydroxide and acidifying this solution dense, oily acids are precipitated with the peculiar odor and other properties of the naphthenic acids contained in many varieties of petroleum. While it cannot be assumed that the fractional separation alluded to above has been carried far enough from the crude oils to insure pure individuals, since from general examination of other similar oils it appears that they are composed of hydrocarbons with boiling points 10° to 20° apart, those here presented should approach a definite composition.

This reaction seems to be general for the wide variety of oils that have been examined, even including what may be regarded as typical asphaltic oils that yield lubricants, such as the Russian (Baku) and Texas Sour Lake oils. Bromine seems to react less readily on these and the hydrocarbons from the Appalachian crudes than on the constituents of the Mid-Continent oils.

Since all the data in the table are based on determined molecular weights of the oils submitted to the action of bromine and molecular weights of the bromides formed and are supported by analytical determinations of specific gravity, bromine and hydrobromic acid, it seems difficult to escape the conclusion that one atom of bromine is absorbed by the oil in place of one atom of hydrogen to form one molecule of hydrogen bromide or, in other words, that there is no unsaturation in these oils.

Based on what seems to be a rather superficial study of Russian oils it has been assumed that they are unsaturated, and by inference American oils have been assigned to the same class. In fact, on the basis of his formolite reaction, Nastjukoff stated that "all Russian and American oils consist mainly of unsaturated hydrocarbons" (Holde).

Summary

A brief statement is given of the behavior of petroleum lubricant hydrocarbons with bromine. It appears that one atom of bromine replaces one atom of hydrogen, forming one molecule of hydrogen bromide and a bromine substitution product of the hydrocarbon.

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