

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ACTION OF SODIUM-POTASSIUM ALLOY ON PETROLEUM¹

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RECEIVED OCTOBER 31, 1927

PUBLISHED FEBRUARY 4, 1928

When a sample of crude Pennsylvania petroleum, diluted with anhydrous ether, is shaken with sodium-potassium alloy in an inert atmosphere an intense brown solution and precipitate result. The color is discharged by introducing moisture or dry carbon dioxide. In the latter case large amounts of the gas are absorbed and a white precipitate is formed. This precipitate is evidently the sodium (or potassium) salt of an organic acid since it readily dissolves in water, and on acidifying the aqueous solution a solid organic acid is precipitated.

The behavior of the highly colored reaction mixture obtained by the action of the alloy on petroleum clearly indicates that an organo-sodium (or potassium) compound is present. Such a compound might be formed either by the cleavage of a highly substituted ethane⁴ or by the addition of the metal to an unsaturated system.⁵ The preliminary results which are reported below point to the latter alternative.

We have found that samples of a variety of crude oils (Mid-Continent, California and Colombia, S. A.) and a sample of "cracking-coil residue" from a Mid-Continent gas oil behave in a similar fashion when treated with sodium-potassium alloy. On the other hand, there was no reaction with a sample of "cracking-coil distillate" from Mid-Continent gas oil. Twelve to twenty-four hours of vigorous shaking appeared to complete the reaction as further treatment of the recovered oil gave no metallic derivative. We hope in a later investigation to isolate the highly colored metallic derivative and from it obtain the corresponding saturated hydrocarbon by treatment with moisture. For the present we have confined ourselves to a preliminary study of the acids which are produced by the action of carbon dioxide on the reaction mixture.

¹ This paper contains preliminary results obtained in an investigation on "Isolation and Investigation of Thermo-Labile Hydrocarbons Present in Petroleum," listed as Project No. 16 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

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⁴ (a) Ziegler, *Ber.*, 56B, 1743 (1923); (b) Conant and Garvey, *THIS JOURNAL*, 49, 2599 (1927).

⁵ Schlenk, *Ber.*, 47, 473 (1914).

The Preparation of Acids from Petroleum by the Action of the Alloy and Carbon Dioxide

After the petroleum-ether mixture had been shaken with sodium-potassium alloy for twenty-four hours, dry carbon dioxide was admitted. The gas was absorbed as the mixture was gently agitated and the brown color disappeared. During the absorption of the gas considerable heat was evolved. The excess alloy was decomposed with moist ether and alcohol and the mixture extracted with water. The aqueous layer was then acidified with hydrochloric acid,⁶ which precipitated the organic acids as brown, amorphous powders. The details of a typical run are given in the experimental portion of this paper.

In order to determine how much, if any, "naphthenic acids"⁷ were extracted from the petroleum by our treatment, we carried out a blank determination. A sample of the petroleum was shaken with alloy in the usual way. Then, instead of admitting carbon dioxide, moist ether was added. This lightened the color at once, presumably due to the decomposition of the metallic derivative by the water thus added. The reaction mixture, after decomposition of the excess alloy with alcohol, was extracted with water in exactly the same way as in the runs in which the acids were prepared. The aqueous solution was then acidified. In the case of the Pennsylvania and Colombia oils only the barest perceptible trace of precipitate was formed. In the case of the Mid-Continent cracking-coil residue a considerable amount of material was present at this point in the blank determination. This material was filtered, dried and weighed. It amounted to 2.5 g. per liter of oil. This is about 11% of the weight of the acid which was obtained when the reaction mixture from the same oil was treated with carbon dioxide.

These experiments, in which the reaction mixture was decomposed with moisture instead of carbon dioxide, serve to prove that the acids which we have prepared from the Pennsylvania and Colombia oils are practically free from naphthenic acids. In the case of the acids from the Mid-Continent cracking-coil residue, however, they were contaminated with about 11% of naphthenic acids. As we have no assurance that our method of purification would eliminate the naphthenic acids, we shall confine our attention in this paper to the acids prepared from the Pennsylvania and Colombia oils.

The crude acids are brown, amorphous solids without sharp melting points and may be mixtures of several compounds. They can be partially

⁶ It is of some interest that with California and Colombia oils, which are known to contain considerable sulfur, hydrogen sulfide was evolved on acidification of the aqueous layer. Apparently the alloy had removed at least a portion of the sulfur as metallic sulfides. This reaction may be of use in the study of the sulfur compounds of crude oils.

⁷ We have used the term "naphthenic acids" to designate acidic material originally present in the oil and not formed by the action of alloy and carbon dioxide on the oil.

purified by solution in sodium carbonate, boiling the solution with decolorizing carbon and reprecipitation with hydrochloric acid. All attempts at further purification have so far failed. The acids could not be crystallized because in contact with organic solvents they formed thick oils. Distillation at 0.01 mm. was unsuccessful as the material decomposed before distilling. The substances contain no nitrogen, halogen or sulfur. (With the acids from the Colombia oil a faint sulfur test was obtained.) They are insoluble in boiling water and only slightly soluble in organic solvents. They dissolve in sodium hydroxide, sodium carbonate and sodium bicarbonate solutions. The samples for analysis were dried in a vacuum over phosphorus pentoxide.

TABLE I

Sample of oil	Condition of treatment	Yield, ^a g. per liter	Color	Melting point, °C.	Yield of "naphthenic acid" in blank run, g. per liter
Pennsylvania Crude ^b	Room temperature	10	Light tan	90-100, dec. at about 150	trace
Mid-Continent Crude ^c	Room temperature	5	Tan	120-130, dec. at about 170	1.2
Mid-Continent Cracking Coil Residue ^c	Room temperature	23	Dark brown	140-150, dec. at about 185	2.5
California Crude ^c	Room temperature	4.5	Light brown	125-130, dec. at about 150	.65
Colombia Crude ^c	Room temperature	17	Tan	110-120, dec. at about 140	trace

^a Treated at room temperature.

^b Kindly supplied by the Kendall Refining Company, Bradford, Pa. This oil is from the Bradford Field, near Bradford, Pa., and is obtained from a Devonian sand found at a depth of about 1500 feet.

^c Kindly supplied by the Standard Oil Company of New Jersey. The cracking coil distillate and residue are from an oil which is a mixture of various Mid-Continent oils. The Mid-Continent Crude is also a composite sample. The California Crude is a so-called Southern California oil of gravity 26.3. The Colombia Crude is a representative of the tank ship deliveries from Colombia, South America. It has the gravity 27.4.

Table I summarizes the yield of acids obtained from different oils and the amount of naphthenic acids obtained in the blank determinations.

Analyses and Combining Weight

The acid from the crude Pennsylvania oil was studied in most detail. A number of samples prepared in different experiments were analyzed for carbon and hydrogen. The values for carbon varied between 75 and 77%. An average sample taken from a great many different runs, purified as carefully as possible and dried to constant weight in a vacuum, gave the following analysis which we consider the most significant: C, 76.0; H, 7.3. The combining weight was determined by titration in 50% alcohol solution with sodium hydroxide using a hydrogen electrode; the addition of the alcohol made the "break" somewhat sharper. The acid was dissolved in a known excess of standard alkali, half the volume of alcohol added, and titrated back with hydrochloric acid using the "break" of the titration curve, as determined by the hydrogen electrode, as the end-point. The

combining weight thus found was 240 ± 10 . The simplest empirical formula for the Pennsylvania acid from the analysis is C_6H_7O ; this unit has the molecular weight of 95. Five times this unit would correspond to a dibasic acid with a molecular weight of 475 and a combining weight of 238. Thus the composition and combining weight correspond to an acid with the formula $(C_{28}H_{33}O)(COOH)_2$.

The composition of the Colombia acid was C, 75.8; H, = 8.0; its combining weight was 248. These numbers correspond to a unit $C_6.3H_8O$, with the molecular weight of 100. Five times this unit gives a dibasic acid $(C_{30}H_{38}O)(COOH)_2$, with the combining weight of 250.

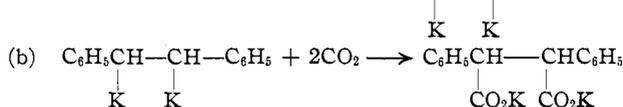
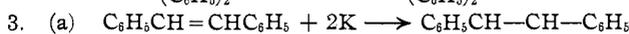
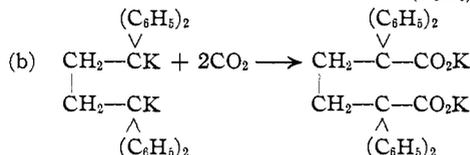
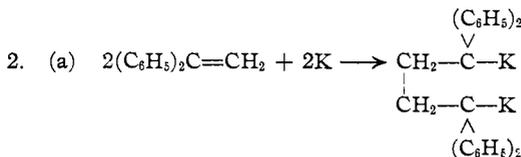
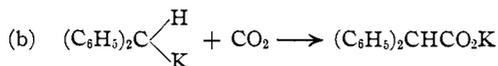
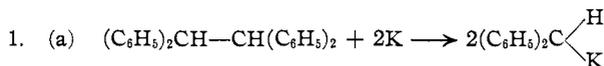
Because of the insolubility of the acids in the usual solvents we have no direct determinations of their molecular weights. Indeed, considering the tendency of acids to associate in solution, significant molecular weight determinations could only be performed with some derivatives. Attempts to obtain solid esters have so far failed. On treating the Pennsylvania acid with thionyl chloride and then ammonia an amide was obtained as an amorphous solid. It was separated from any unchanged acid by extraction with sodium hydroxide, in which it was insoluble. It was insoluble in all the solvents tried and could not be further purified. The analysis points to an imide of a dibasic acid, but the results are far from conclusive. (Calcd. for $(C_{28}H_{33}O)(CO)_2NH$, N, 3.07. Calcd. for $C_{14}H_{36}CONH_2$, N, 6.0. Found: N, 4.54.)

While one cannot attach much significance to analytical data obtained with substances which are probably mixtures, one or two points are perhaps worthy of discussion. The formulas derived above are at best representative of the mean composition of the mixture. If the acids are mixtures of several isomeric substances, this representation may be very near the ultimate truth in regard to the composition of the components. It is evident that the substances are not aliphatic acids. An acid $C_nH_{2n+1}COOH$ with a combining weight of 256 is $C_{16}H_{31}COOH$. This has the composition C, 75.0; H, 12.5. Both the Pennsylvania acid (H, 7.3) and the Colombia acid (H, 8.0) contain far less hydrogen than an aliphatic acid. If we assume that the fifth atom of oxygen in our acids is a ketonic oxygen then the parent acid is $(C_{28}H_{35})(COOH)_2$ in the case of the Pennsylvania product, and $(C_{30}H_{40})(COOH)_2$ in the case of the Colombia product. These formulas are of the type $C_nH_{2n-21}(COOH)_2$ and $C_nH_{2n-20}(COOH)_2$, respectively. A dibasic acid with two phenyl groups, for example, diphenylsuccinic acid $(C_6H_5CH_2)(COOH)_2$ is of the type $C_nH_{2n-16}(COOH)_2$; with four phenyl groups $[(C_6H_5)_2C]_2(COOH)_2$, the type is $C_nH_{2n-32}(COOH)_2$. It will be evident from this that our acids contain less hydrogen than corresponds to one phenyl group per carboxyl and more hydrogen than corresponds to two phenyl groups per carboxyl. If the assumption were made that the extra atom of oxygen in our acids

was linked as an ether, the type formulas would be for the Pennsylvania acid $C_nH_{2n-23}(COOH)_2$ and for the Colombia acid $C_nH_{2n-22}(COOH)_2$, and our tentative conclusion as to the degree of unsaturation of these acids would not be affected.

The inference that our acids contain at least one phenyl group per carboxyl group is substantiated by a consideration of the reactions in which organo-metallic derivatives, capable of yielding acids with carbon dioxide, are formed.⁸

These reactions are as follows



It will be noted that all of these reactions give rise to phenylated acids. Reactions 1 and 2 yield acids with two phenyl groups per carboxyl group, while Reaction 3 yields acids containing one phenyl group per carboxyl group. In some work with synthetic hydrocarbons of known structure,⁹ we have found that while Reaction 1 (cleavage) will not take place unless there are two phenyl groups on each carbon atom, Reaction 2 (dimolecular addition) will take place with compounds of the types $C_6H_5CH=CHR$ and $C_6H_5CH=CR_2$ ($R = \text{alkyl}$) and yields acids contain-

⁸ The possibility that the metallic derivatives were formed by the replacement of an active hydrogen atom by metal is removed by the fact that in none of our experiments was there any gas evolved. The amount of acid formed in a typical run of Pennsylvania oil would correspond to the liberation of about 50 cc. of hydrogen; in a typical run of Colombia oil to about 85 cc. of hydrogen. The gas volume in the reaction flask was about 100 cc. Consequently the increase in pressure due to the liberation of such volumes of hydrogen would be easily detected.

⁹ Conant and Blatt, *THIS JOURNAL*, 50, 551 (1928).

ing one phenyl group per carboxyl group. Therefore all of these possibilities must be reckoned with in the further study of this problem.

High Temperature Treatment of Pennsylvania Oil

The reaction with sodium-potassium alloy at low temperature in ether is complete in twelve hours, because further treatment failed to yield more material. Furthermore, at even 150° (in the absence of ether, of course) sodium-potassium alloy was without action on a sample of oil which had been put through the low temperature treatment.

Samples of the Pennsylvania oil which had been put through the low temperature treatment with sodium-potassium alloy were pumped free from ether and low-boiling constituents and treated with sodium-potassium alloy in the presence of carbon dioxide at 250°. At this temperature two materials are formed, a dark brown, neutral substance insoluble in water and all organic solvents, and the sodium or potassium salt of some acid. The latter material was dissolved in water and the acid precipitated and dried in the same way as the acid from the low temperature runs. The yield in three hours was 10 g. of neutral material per liter of original oil and 3 g. of the acid material. The loss in volatilization during the pumping between the low temperature run and the high temperature run was 25 to 30% of the original oil.

The acid from the high temperature runs was a very dark, amorphous solid with the same intractable properties as the low temperature acids. A carefully purified sample was analyzed and the following numbers were obtained: C, 71.0; H, 5.9. A titration with the hydrogen electrode as the indicator showed a combining weight of 190. The analyses correspond to a unit $C_{4.1}H_{4.1}O$ with the weight of 69. The neutral material was insoluble in all solvents, except acetylene tetrabromide, in which it was slightly soluble on boiling. A certain amount of coloring material could be removed by boiling with ether. The material thus "purified" and dried was analyzed. It contained 15.6% of ash. The carbon and hydrogen analyses after correction for the ash were as follows: C, 85.6; H, 6.9.

It is impossible at present to suggest the nature of the reaction between the oil and the alloy at 250°. Not only may the reactions previously outlined be involved, but in addition dehydrogenation of alicyclic and saturated systems may take place.

Experimental Part

Treatment of Oils with Sodium-Potassium Alloy at Room Temperature

The general directions given for the Pennsylvania crude oil were followed in all the other cases. Consequently details will be given only when there was some variation in the procedure. In every case a sample of 100 cc. of oil, diluted with ether, was shaken first with a solution of sodium carbonate, then with 20% sodium hydroxide, and the alkaline extracts thus obtained were acidified. In no case was there evidence of more than traces of acids or phenols.

Low Temperature Treatment of Pennsylvania Crude with Alloy.¹⁰—Crude Pennsylvania petroleum was kept at room temperature under a vacuum of 15 mm. until no more

¹⁰ The alloy is prepared by melting together under xylene five parts of potassium and two parts of sodium. It is liquid above -10°.

gas was evolved. One hundred cc. of the petroleum thus treated was placed in a 250cc. distilling flask, then 6 cc. of alloy and 50 cc. of dry ether were added. The flask was stoppered, then alternately evacuated and filled with dry, purified nitrogen, through the side arm, five times. After the last filling with nitrogen the side arm of the flask was stoppered and the flask placed on a shaking machine. In the course of the first few minutes of shaking the reaction began and an intense, dark brown precipitate was formed. After twelve hours of shaking, the flask was repeatedly evacuated and filled with pure, dry carbon dioxide until no more was absorbed. The absorption of carbon dioxide was very vigorous and the contents of the flask warmed up almost to the boiling point of ether.

Ordinary ether was now added and the contents of the flask were transferred to a large beaker. The unused alloy was removed, and alcohol and finally water were added. The mixture of oil, ether, alcohol and water separated into layers. The water layer was removed and the ether layer extracted once with a dilute solution of sodium carbonate. The combined aqueous layers were extracted once with ether,¹¹ heated on the steam-bath to remove ether and alcohol, then boiled down to a small volume.

The resulting dark-brown, aqueous solution of the alkali salts was cooled and extracted twice with alcohol-free ether. The ether was removed from the water layer by an air blast and then the solution was acidified with dilute hydrochloric acid. The crude low-temperature acid was thus obtained as a brown, amorphous solid. It was filtered and dried. One gram of crude acid was obtained.

The acid was purified by solution in dilute sodium carbonate and repeated boiling with bone black. It was finally precipitated with hydrochloric acid, dissolved in dilute sodium hydroxide, filtered, precipitated with hydrochloric acid, filtered, washed with water, then dried. The dry powder was ground to insure homogeneity and dried to constant weight for analysis.

Anal. I. Subs., 0.1137: CO₂, 0.3173; H₂O, 0.0750. II. Subs., 0.1246: CO₂, 0.3472; H₂O, 0.0814. Found: I. C, 76.1; H, 7.4. II. C, 76.0; H, 7.3. Combining weight by titration in 50% alcohol: I. Subs.: 0.2983 g. required 5.99 cc. of 0.2 *N* NaOH. II. Subs.: 0.2983 g. required 6.37 cc. of 0.2 *N* NaOH. Found: I, 248; II, 234.

The purified acid softens on heating to 70–80°, and melts at about 100°. It is slightly soluble in the common organic solvents. Qualitative tests show the absence of nitrogen, sulfur and halogen.

When the acid is heated with thionyl chloride and the resulting acid chloride poured into ammonia, an imide is formed. The imide is insoluble in all the solvents tried. For analysis it was purified by extraction with dilute sodium hydroxide, then washed with water and dried.

Anal. Subs., 0.2504: 10.4 cc. of N₂, 28°, 761 mm. Found: N, 4.54.

Blank Run to Determine the Amount of Napthenic Acids Obtained from Crude Pennsylvania Oil.—One hundred cc. of oil was placed in a 250cc. distilling flask, then 6 cc. of alloy and 50 cc. of ether were added. The flask was filled with nitrogen, stoppered and shaken exactly as in the runs to prepare acid. After the shaking was completed the contents of the flask were poured onto moist ether, which discharged the color of the metallic derivative. The succeeding decomposition of excess alloy and extraction of the alkali salts were carried out exactly as in the carbon dioxide runs. On acidifying the alkaline aqueous solution there was only the barest perceptible precipitate.

Mid-Continent Crude Oil.—The yield of crude, dried acids from this oil was 0.5

¹¹ The ether and the oil layers are combined and worked up to recover the oil. This process is described under the high temperature treatment.

g. per hundred cc. In the blank determination, decomposing with moist ether, the acid obtained from 100 cc. of oil amounted to 0.123 g.

The acids obtained by the carbon dioxide treatment were purified by solution in sodium carbonate, filtration to remove traces of non-acidic material and reprecipitation with hydrochloric acid. They were thus obtained as a brown, amorphous powder, free from nitrogen, halogen and sulfur, which, on heating, began to darken and shrivel at about 100°, melted at 120–130°, and decomposed with evolution of gas at about 170°.

Cracking Coil Distillate from Mid-Continent Oil.—This material gave practically no precipitate after shaking with alloy for twelve hours.

Cracking Coil Residue from Mid-Continent Oil.—This sample, a thick brown oil, gave the maximum yield of acids, 2.3 g. per 100 cc. of oil. In the blank determination 0.25 g. of naphthenic acids was obtained per 100 cc. of oil. The crude acids from the carbon dioxide runs were heated twice in carbonate solution with decolorizing carbon, the solution filtered, acidified and the precipitate filtered off and dried.

The purified acids thus obtained were chocolate brown in color and contained no sulfur, nitrogen or halogen. On heating they darkened at about 130°, melted at about 150° and some thirty degrees higher started to decompose with evolution of gas.

California Crude Oil.—On shaking with alloy the oil set to a stiff paste so that in each run it was necessary to use 100 cc. of ether for 100 cc. of oil. When the solution of the alkali salts of the acids was first acidified large amounts of hydrogen sulfide were evolved. The crude acids were purified by solution in alkali, filtration and precipitation with hydrochloric acid. The yield of crude, dry acid was 0.45 g. per 100 cc. of oil. In the blank run 0.065 g. of naphthenic acids per 100 cc. of oil was obtained.

Anal. Subs., 0.01326, 0.01411, 0.01498: CO₂, 0.03643, 0.03851, 0.04090; H₂O, 0.00826, 0.00871. Found: C, 74.95, 74.4, 74.5; H, 6.9, 6.7. Combining weight: Subs., 0.3100 g. required 6.89 cc. of 0.2 N NaOH. Found: 225.

The purified acids, light brown in color, contained neither nitrogen nor halogen. They gave a faint test for sulfur when fused with potassium and treated with sodium nitroprusside, but no color or precipitate with lead acetate. On heating to about 80° the acids began to shrivel and turn dark. At 125–130° they melted and at 140–150° decomposition with evolution of gas began.

Colombia Crude.—This oil, like the California crude, set to a paste on treatment with alloy so that it was necessary to use 100 cc. of ether with each 100 cc. of oil. On acidifying the alkaline solution of the acids for the first time there was much hydrogen sulfide evolved. The yield of crude acids in the carbon dioxide runs was 1.7 g. per 100 cc. of oil. In the blank determination, using the same volume of oil, only a bare trace of naphthenic acids was obtained. For purification the acids were treated in carbonate solution with decolorizing carbon, filtered, precipitated with hydrochloric acid, filtered and dried.

Anal. Subs., 0.1460, 0.1344, 0.1150: CO₂, 0.4068, 0.3730, 0.3175; H₂O, 0.0977, 0.0982, 0.0832. Found: C, 76.0, 75.9, 75.6; H, 7.5, 8.0, 8.0. Combining weight by titration in 50% alcohol: Subs., 0.2840 g. required 6.12 cc. of 0.2 N NaOH. Found: 232.

The acids contained neither nitrogen nor halogen. After fusion with potassium they gave a faint, positive test for sulfur with sodium nitroprusside, but no color or precipitate with lead acetate. They were light tan in color, amorphous and when heated began to shrivel and darken at about 75°. About 50° higher they melted, while at 140° decomposition, with evolution of gas, commenced.

High Temperature Treatment of Pennsylvania Oil with Alloy.—The mixture of oil, ether and alcohol recovered from the low temperature treatment was heated on the steam-bath, at ordinary pressure, then under a vacuum of 15 mm. to remove all low-

boiling material and to dry the oil. One hundred cc. of the oil thus prepared, which did not differ in appearance from the crude oil, was placed in a 500cc. flask fitted with an inlet for pure, dry carbon dioxide, a stirrer with mercury seal, and a reflux condenser. Preliminary experiments showed that there was no reaction when the oil was heated to 150° in a current of carbon dioxide, and that there was a reaction at 250° with formation of neutral and acidic products. At 200° there is formation of acidic products but not of neutral products. We have worked at 250°.

The oil, 100 cc. with 10 cc. of alloy, was heated for three hours at 250° in a current of carbon dioxide, cooled, then worked up in a fashion similar to the low temperature runs, save that in the present case the insoluble product was separated by filtration.

The high temperature acid obtained in this fashion was a dark, almost black, amorphous solid. It was purified for analysis by reprecipitation, then dried. The purified material was very dark brown in color.

Anal. I. Subs., 0.2048: CO₂, 0.5336; H₂O, 0.1084. II. Subs., 0.2402: CO₂, 0.6260; H₂O, 0.1284. Found: I. C, 71.0; H, 5.9. II. C, 71.0; H, 5.9.

The acid was moderately soluble in acetone and alcohol, and slightly soluble in ether and benzene. On heating it decomposed at about 200°. Qualitative tests showed the absence of nitrogen, sulfur and halogens.

The neutral product was also dark brown in color. It was insoluble in all solvents tried, except in acetylene tetrabromide in which it dissolved to a small extent and separated as an oil on cooling. For purification it was boiled repeatedly with ether and dried. This material contained a large portion of ash, but no nitrogen or sulfur.

Anal. Ash: 0.1668 gave 0.0260 of non-combustible residue, or 15.6%. Subs., 0.1408 (corrected for ash): CO₂, 0.4419; H₂O, 0.0863. Found: C, 85.6; H, 6.9.

Summary

1. Samples of various crude petroleums and a cracking coil residue were treated with sodium-potassium alloy in dry ether in an atmosphere of nitrogen. Highly-colored metallic derivatives were formed which on treatment with carbon dioxide yielded alkali salts of organic acids. On acidifying the water solution of these salts, complicated mixtures of acids were precipitated.

2. The analysis of the mixed acids from the Pennsylvania and Colombia oils indicated that they contained one aromatic group per carboxyl group. They were free from nitrogen, halogens and sulfur.

3. A sample of the Pennsylvania oil which had reacted completely with the alloy at room temperature yielded alkali salts of acids when heated with the alloy and carbon dioxide at 250°. A considerable amount of amorphous, neutral material was also formed.