ACIDIC CONSTITUENTS OF A WEST TEXAS
PRESSURE DISTILLATE

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INTRODUCTION

Introduction

Altho Texas produces a large portion of the world's supply of petroleum, little work of scientific worth has been done on the chemical composition of either Texas crude or of refinery products derived from it. Chemical literature is particularly dearth in information relating to the components or characteristics of the acidic fractions, altho numerous investigations have been carried out on the acidic constituents of other, especially the Russian, oils for the past several decades.

In view of the interest which these compounds hold from an academic, as well as from an economical aspect, it was deemed advisable to carry out an investigation on the nature of the acidic components of a typical refinery product from a Texas crude; hence the inception of this work.

Historical Interlude

Iebal¹, in an investigation of Galician petroleum in 1830, found a portion of the crude product to be soluble in concentrated sulfuric acid, and to come out of solution as an oil on addition of water to the acid.

This fraction he termed "Ihenylsäuren".

In 1874, Hell and Medinger², at the request of a practical refiner of a Roumanian crude, attempted to isolate the acidic compounds in an alkali-soluble fraction. After freezing the fraction from neutral oils, they converted the acids so obtained to their methyl esters and fractionated these. Fractionation of the esters rather than of the acids was undertaken because of the greater stability of the former to distillation. A 10° fraction boiling at 230°-240°C. gave an acid on saponification which boiled at 233°-251°C. under atmospheric pressure. Analysis indicated the formula $C_{11}H_{16}O_2$, tho their results were admittedly in bad agreement with theoretical values, and the acid was far from being pure. Since this formula contains two less H atoms than would that of the corresponding aliphatic acid, and since the acid did not give definite positive response to unsaturation tests, they concluded that they were dealing with either a new kind of carboxyl group on a saturated straight chain, or a cyclic acid. In a later paper³ they reported attempts to determine the constitution of the acid, but admitted that they were still in a quandary as to the structure of the acid and the nature of the functional group.

Markownikoff and Oglobin⁴ in 1881 found that acids were present in Baku petroleum; preliminary work seemed to indicate that they were aliphatic. Later work⁵ by the same investigators led to the isolation of the acids $C_{10}H_{19}COOH$ and $C_{11}H_{21}COOH$. The former was assumed to be identical with Mell and Medinger's acid. The presence of phenols in the mixture was also noted.

Krämer and Böttcher subscribed to Markownikoff's earlier views that the petroleum acids were aliphatic in nature. Markownikoff, however, in his later work argued that the acids were cyclic and were derived from cyclic hydrocarbons, or naphthenes; hence the term naphthenic acids was applied to these compounds. Engler⁷ examined the acidic compounds in a German oil and reported them as a mixture of phenols and aliphatic acids.

Zaloziecki⁸ isolated the compounds $C_{12}H_{22}O_2$, $C_{13}H_{24}O_2$, and $C_{14}H_{26}O_2$ from a distillate and assigned to them the structures of "secondary lacto-alcohols" --hypothetical structures which had no basis on experimental knowledge.

Acids of the formulas $C_7H_{12}O_2$, $C_8H_{14}O_2$, and $C_9H_{16}O_2$ were isolated by Aschan⁹ in an investigation of the naphthenic acids of a Baku distillate. To

these he assigned the structure of hexahydro-benzoic, -toluic, and -xylenic acids respectively.

Markownikoff¹⁰ prepared the latter acids synthetically and demonstrated conclusively that they were not identical with the naphthenic acids. He then advanced the theory that aliphatic acids are mixed with the cyclic compounds in the natural products, and that the substances under consideration in previous works were really mixtures of the two types, and not pure individuals¹¹.

The first published work on the "naphthenic acids" from a Texas crude appeared in 1911 when Albrecht¹², in an investigation of a Spindletop fraction, observed that his acids differed from those of the Russian oils in that they showed greater stability to heat, as evidenced by the fact that they could be distilled at atmospheric pressure with little decomposition, while the Russian products decomposed readily. Optical activity of certain fractions was also noted.

The acidic fractions of Japanese petroleum were subjected to intensive research by Tanaka and Lagai¹³, who ascertained the presence of naphthenic acids, alkyl sulfonic acids, phenols, and unknown sulfur compounds. The naphthenic acids isolated were $C_{12}H_{23}COOH$.

$C_{13}H_{25}COOH$, and $C_{14}H_{27}COOH$. The phenols present were identified by Tanaka and Kobayashi¹⁴ as o-cresol (15%), m-cresol (20%), p-cresol (50%), 1,3,4, m-xyleneol (4%), and 1,2,3, o-xyleneol. The presence of diethyl and triethyl phenols was also indicated but was not confirmed. The presence of straight chain aliphatic acids in a fraction of Ishikari (Hokkaido) petroleum was definitely proved by Tanaka and Kuwata¹⁵. Myristic, palmitic, stearic, and arachidic acids were isolated and identified by means of their methyl esters and lithium salts.

Holzmann and S. von Filat in an investigation of the acidic fraction of a Boryslaw crude confirmed the presence of the three cresols and in addition identified 1,3,5 xyleneol, 1,3,4 xyleneol, and (β-naphthol; 1,2,4 xyleneol and a mesitol were tentatively identified, tho no corroborative evidence was obtained. These workers found no diethyl or triethyl phenols. Here, as in the sample under investigation by Tanaka and Kuwata, no trace of phenol itself was found.

Tschitschibabin¹⁷, in 1930, in a comprehensive survey of work done both by himself and others over a period of some twenty years, pointed out that the lower-boiling "naphthenic acids" were undoubtedly aliphatic. The acid in Russian petroleum containing

seven C atoms and boiling at 215-18°C. was shown by analysis to be aliphatic, and a provisional identification was made as either ischeptylic or (β,β diethyl propionic acid. (This, it should be noted, is in all probability the acid which Aschan isolated, and to which he assigned the constitution of hexahydro-benzoic acid.) The acids up to the C₁₀ individuals were found to be mixtures of aliphatic and cyclic compounds, the cyclic acids alone constituting higher fractions. The presence of optically active acids was also noted. The methyl ester fraction boiling at 255-60°C. exhibited a strong dextro-rotatory effect. Parenthetically, it should be observed that the Tschitschibabin's paper represents a most significant advance in knowledge of the exact status of the "naphthenic acid" question, it contains only fragmentary bits of experimental evidence in support of the author's contentions.

In an extensive review of work done on naphthenic acids, von Braun¹⁸, giving data accumulated from previous researches¹⁹, advanced the view that acids below C₃ are aliphatic, those from C₃ to C₁₃ inclusive are mono-cyclic, and those above C₁₃ are bicyclic. His observations were based partly upon rather inconclusive analytical data and partly upon analogy to terpene com-

pounds.

von Braun's method of treatment of the problem of isolation of the members differed from the classical procedure of Hell and Medinger in that the acids --after esterification, preliminary fractionation of the esters, and saponification--were treated in concentrated sulfuric acid solution with hydrazoic acid to give amines (Schmidt's reaction--really a modified Curtius' reaction.) These amines were then purified by fractional distillation and fractional crystallization of solid derivatives. In regard to the isolation of the individual acids, it may be mentioned that Komura²⁰ has recommended formation of the acid chlorides and subsequent fractionation of these. This method, however, possesses the obvious disadvantage that moisture must be excluded thruout the operations.

The first solid naphthenic acid was isolated by Tanaka and Kuwata²¹ from a Hokkaido petroleum. Its empirical formula was not definitely ascertained.

The constitution of the petroleum acids is not generally amenable to solution by the method of superposition, since all of the acids corresponding to the empirical formulas of either the aliphatic or cyclic series are not known. Of the few members which have

been isolated or prepared synthetically, very few have been critically examined as to properties, or properties of derivatives obtained from them. The difficulties of this method of determination of structure are also augmented by the superimposition of doubt as to the series, i.e., aliphatic or cyclic, to which the members belong, upon the above mentioned uncertainties.

As has been mentioned, Aschan⁹ made the first serious attempt to determine the constitutions of the petroleum acids. His assignment of the saturated six-membered ring structure was based mainly upon von Baeyer's theory of strain in the ring, and tho this theory would favor the existence of a five-membered ring in preference to a six-membered ring (angle of deviation of valence angles from normal $0^{\circ} 44'$ for the former as compared to $-5^{\circ} 15'$ for the latter) he justified this selection by the apparent absence of isomers of the acid individuals. The absence of isomers indicated the hexahydro benzoic acid, for instance, rather than a penta-methylene derivative which would be expected to be coexistent with its several isomers.

With Markownikoff's elimination of the structure by utilization of the method of superposition and con-

sequent negative results, there came the realization that the problem of constitution could be solved only by the application of more vigorous methods.

Zelinsky²² attempted to secure direct experimental evidence of the presence or absence of the hexamethylene ring by dehydrogenation of the latter, if present, to the aromatic nucleus. His procedure consisted of reduction of the acids to the alcohols by way of the chlorides, then of reduction of the alcohols to the hydrocarbons by means of phosphorous and hydriodic acid. The hydrocarbons were then passed over heated platinum black, and the solubility of the resultant liquid determined in fuming sulfuric acid, which would sulfonate any aromatics present, but not pentamethylene rings. Since no apparent sulfonation took place, Zelinsky concluded that the acids are methyl pentamethylene carboxylic acids.

Kuwata²³ carried out essentially the same procedure on the cuts of a Japanese naphthenic acid fraction and obtained only a very small portion of the hydrocarbons which gave evidence of sulfonation.

von Braun²⁴ attempted to corroborate the existence of the five-membered ring by a unique and independent method. It is possible to distinguish between primary,

secondary, and tertiary groups adjacent to the carboxyl group by von Braun's "imide chloride method"²⁵. If the acid be converted to a mono-alkyl amide (the ethyl amide actually used) and this treated with phosphorous pentachloride and subsequently hydrolyzed, it is found that if the adjacent group is primary, two chlorine atoms have entered the α -positions. If the acid be secondary, only one chlorine atom has entered the α -position; if the acid be tertiary, no reaction takes place. In short, the method gives a measure of the number of α -H atoms in the acid.

No tertiary acids were found by von Braun and his coworkers, but both primary and secondary acids were present. In order to extend the method to determination of structure, it was necessary to degrade the acid to the point at which it became secondary or tertiary. Since in the lower members this would indicate that the carboxyl group is adjacent to the ring, if the acid then contained only six carbon atoms, the five membered ring postulate could be considered proved. Altho these conditions were never realized in practice, it was possible to degrade the acids to the seven and eight carbon atom stage, convert to ketones, and tentatively identify these by superposition as

belonging to the five-membered ring type.

Degradation of the acids was accomplished by either converting to amines by the Curtius reaction, splitting out the amino groups by Hoffman's method to give olefinic compounds and splitting at the double bond with ozone, or by forming the α -bromo derivatives of the acids by the Hell-Volhard-Zelinsky reaction, splitting out hydrobromic acid to give α - β -unsaturated compounds, and splitting with ozone to give acids.

In this way von Braun demonstrated that the acid $C_{10}H_{18}O_2$ in reality is a mixture of the three types of structure

Some doubt was cast on the validity of von Braun's assumptions by Skraup and Dinder²⁶, who showed that six-membered rings rearrange under suitable conditions to form methyl cyclo-pentanes. They also attempted to determine the constitution of certain naphthenic acids by splitting out carbon dioxide from the phenyl esters to give hydrocarbons, but were not successful.

The first synthesis of a naturally occurring

naphthenic acid was accomplished by von Braun, Lannes and Reuter²⁷ in 1933. By the degradation of an acid $C_{10}H_{18}COOH$ they obtained a ketone of the empirical formula $C_8H_{14}O$ which was demonstrated to be identical with a known compound of the constitution

This was allowed to react with bromo-acetic ester in the presence of zinc to give a β -hydroxy ester, water was eliminated from this, the ester was hydrolyzed, and the resulting acid was converted to the saturated acid by addition of hydrogen. Thus:

This was shown to be identical with the naturally occurring acid from which the ketone was prepared.

Since, with very few exceptions, the samples of acids used by investigators in the field were derived from refinery distillates rather than from the crude petroleum before being put thru refinery processes, it becomes pertinent to consider whether or not the acids were present in the original crude, and if so, to what extent they may have been altered by refining processes.

That distillation of the petroleum fractions at atmospheric pressure does not affect the content of acids has been shown by the work of Zelinski and Rjachina²⁸, Mazet²⁹, and Kolbe, all of whom have examined the acid content of the crude petroleum and its distillates. It may be mentioned in passing that the acidic fractions comprise some 0.1-1.5% of European oils.

Ipatjew and Petrov³¹ have examined the effect of high temperature and pressure on naphthenic acids. It was found that heating the acids to 450° Fahrenheit under pressure equal to the vapor pressure of water at that temperature did not appreciably affect them, even in the presence of aluminum oxide, which might

be expected to catalyze decomposition to some extent. At higher temperatures and pressures there was evidence of some decarboxylation.

The effect of sulfuric acid agitation of fractions containing acidic components on the nature of these components has been investigated by Tanaka and Nagai³². The carboxylic acids isolated from the fractions before agitation were found to be identical with those found in the acid-agitated oil. Phenols, however, were partially extracted by the acid treatment. Apparently no oxidation either of the acids or of hydrocarbons to form acids takes place during acid agitation or in the alkaline wash solution used to extract the acids from the oil.

No mention has been made as yet of acidic sulfur compounds in petroleum. Altho the presence of sulfides and disulfides has long been recognized in various crudes and in their distillates, little is known of the alkali-soluble sulfur compounds present. These might be expected to include mercaptans, sulfonic acids, and possibly thiophene carboxylic acids.

Iakusin³³ has demonstrated the presence of mercaptans in Russian petroleum distillates. Birch and Norris³⁴, in an investigation of light oil distillates

from Persian crudes identified ethyl, isopropyl, and isobutyl mercaptans. It should be noted that an equilibrium may obtain between the acidic mercaptans and their neutral oxidation products, the disulfides. Identification of a given disulfide, then, connotes the presence, or at least the occurrence previous to an oxidation, of the corresponding mercaptans.

Altho thiophene and its homologs have been reported in petroleum distillates by McKittrick³⁵, Challenger³³, and Le Clerc³⁷, the corresponding carboxylic acids have apparently not been identified.

Introduction Continued —

In common refining practice in this country the acidic fractions obtained from both the alkali agitation of distillates and the alkali-fixed residues from the stills are termed "naphthenic acids". The former, by virtue of the distillation procedure which they have undergone, are in general more volatile because of their lower molecular weights, and contain more or less phenolic constituents, depending on whether distillation was carried out at greater than atmospheric pressure, or at normal pressure. The

latter acids, designated more specifically by the term "still-bottom acids", are in general viscous tarry oils containing high molecular weight compounds which are not amenable to a convenient separation from neutral compounds, or to the isolation of the individual acidic members.

Altho an acidic fraction from a straight run distillate may be tacitly accepted as a representative sample of the acidic constituents present in the parent petroleum, most of the commercial acid fractions produced in refineries are obtained by acidification of the alkali wash of cracked, or partially cracked, distillate; as has been mentioned, some doubt may be attached to the hypothesis that the alkali-soluble components of a cracked distillate were present as such in the original crude. It is certain, however, that the character of the original compounds has not been entirely changed by pressure distillations as ordinarily carried out in refinery practice.

Low molecular weight carboxylic acids present in the original crude would not be expected to be as susceptible to rupture of the molecule as would those of

high molecular weight, extremely high molecular weight acids, however, are excluded from most petroleum distillates by virtue of their high boiling points.

A portion of the phenols present in a cracked distillate apparently has its genesis in the pressure distillation, tho the mechanism of this process is not known.

The object of the work described in the following pages was the determination of the type of true carboxylic acids present in a typical Texas "naphthenic acid" fraction; identification of the individual members of the series; identification of phenols, mercaptans, and any other alkali-soluble compounds present; and, if possible, a semi-quantitative estimation of the amounts of the constituents in the mixture.

A sample of commercial "naphthenic acids" from the alkali wash of a Dubbs pressure distillate was furnished for the investigation by a local refinery. The change to the pressure still was the gas oil fraction of a West Texas crude.

EXPERIMENTAL

Since the sample contained neutral oil which was insoluble in alkali, and phenolic constituents, as evidenced by the odor, preliminary experiments were made to determine a satisfactory method of separation of the acids from these compounds. An attempt was first made to utilize the solubility of carboxylic acids in saturated sodium bicarbonate solution and the corresponding insolubility of phenols in the same reagent.

100 cc. of acids were shaken with 500 cc. of saturated bicarbonate solution; evolution of small amounts of carbon dioxide obtained. After standing, the oil layer (lighter than the aqueous phase) was separated off-volume, ca. 80 cc.; the solution was acidified, and after standing, ca. 3 cc. of an oily liquid separated out. A modification of the same procedure was then tried--; 50 cc. of the sample were dissolved in 100 cc. of 3N NaOH and the solution subjected to steam distillation. About 3 cc. of a neutral oil came over in the distillate. The alkaline solution was then extracted with ligroin to free it from tarry neutral compounds, and CO_2 was passed in slowly. Then the solution was saturated with respect

to CO_2 , ca 43 cc. of oil had separated out. This was removed and acid added to the solution; less than 2 cc. of acids separated.

Because of the nauseating odor of the sample, the presence of sulfur compounds, particularly mercaptans, was suspected -- an attempt was made to remove these, or a portion of these by oxidation to the insoluble disulfides. About 35 cc. of the sample were dissolved in 50 cc. dilute NaOH (containing 20 cc. 3M NaOH) and 2-3 cc. perhydrol was added. Even after standing no precipitate was evident.

Since separation by the bicarbonate method was incomplete, besides calling for the handling of rather cumbersome volumes of liquid, the classical procedure of Hell and Medinger (formation of methyl esters) was followed in "working up" the sample.

Two liters of the sample were dissolved in three liters of NaOH solution containing 450 gms. of the solid, and the resultant liquid subjected to steam distillation. About 200 cc. of a light yellow oil (less dense than water) distilled over with some 1.5 liters of water. This oil had a pronounced odor of mercaptans. The alkaline solution was cooled and

acidified with 375 cc. of concentrated H_2SO_4 in 750 cc. of H_2O . The resultant acid layer was steam distilled; after 4 liters of distillate had come over, 350 cc. of a heavier-than-water oil was collected.

In order to isolate the sulfur compounds in the oil distilling over from the alkaline solution of the sample, the liquid was dissolved in an equal amount of 95% ethyl alcohol and a saturated alcoholic solution of mercuric chloride added in excess. A voluminous white precipitate of mercaptan addition product was thrown down. This was filtered off, washed with alcohol and ligroin and suspended in dry ether. A slow stream of H_2S was then passed thru the ethereal suspension, with liberation of the original sulfur compounds and precipitation of mercuric sulfide. After this was filtered off, the ethereal solution was distilled on the water bath. Both the ether and any dissolved constituents distilled over below 50°C . Subsequent fractionation demonstrated that the mixture boiled from 35° to 57°C . The boiling point of ether is 34.6°C .; because of the strong mercaptan odor, however, there was no doubt that such a compound was distilling over with the ether. The ethereal solution was then extracted with NaOH , whereupon all odor dis-

appeared, suggesting that neutral sulfur compounds (sulfides and disulfides) were not present. The alkaline solution was acidified, extracted with ether, and the dried ethereal solution again distilled -- b.pt. 25° - 37° . Ethyl mercaptan has the b.pt. 35 - 37° ; this was obviously the only mercaptan which could be present.

An alcoholic solution of mercuric cyanide was added to a portion of the ethereal solution in excess; the resultant mercuric salt of the mercaptan was filtered off, and without further recrystallization, a melting point was taken -- m.pt. 73 - 73°C . (Mercuric salt of ethyl mercaptan, m.pt. 75 - 77°C .)

The silver salt of the mercaptan was prepared by addition of alcoholic silver nitrate to the ethereal solution. This was filtered off, washed with water, alcohol, and acetone, and dried in air. Microanalysis gave the Ag in this salt as 33.77 (average of three runs). The theoretical value for ethyl mercaptan is 33.84.

The oil which steam distilled over from the acids, after removal of neutral oils and the mercaptan, was subjected to examination. It decolorized KMnO_4 solution, reacted with Br_2 in CCl_4 with evolution of HBr , and gave a dirty greenish color with dilute FeCl_3 solu-

tion. (Characteristic reactions of phenols.) Since it reacted with sodium bicarbonate with evolution of CO_2 , it evidently contained some carboxylic acids. To separate these, 510 cc. of the oil were dissolved in 510 cc. of anhydrous methyl alcohol and 100 cc. concentrated H_2SO_4 added. The mixture was gently refluxed for several hours, then was poured into several liters of dilute NaOH solution. The small amount of esters separating was dried over CaCl_2 and distilled. Due to the small amount, however, no individuals could be isolated. The phenols recovered from the alkaline wash solution were combined with the ethereal extract of the water separated off from steam distillation of the original acids, and the mixture dried over anhydrous H_2SO_4 . The ether was distilled off on the water bath and the residual oil fractionated in a small Vigreux flask. The over point was at 175°C .; practically all had distilled over at 220°C .

The fraction boiling at $175-200^\circ$ had a most offensive cheese-like odor. This cut was shaken with saturated sodium bicarbonate solution, with evolution of much CO_2 . The residual oily layer was separated off and the solution extracted with ether and acidified. A small amount of an acid with a stupefying odor sepa-

rated. Fractionation gave a small cut (ca 0.5 cc.) which boiled at 172-75°C. A small amount of the acid was utilized for formation of the silver salt, which on micro-analysis gave 52.2% Ag. (Theoretical value for valeric acids 51.7%, for butyric acids 54.7%).

Since the odor and equivalent weight as determined by the silver salt analysis suggested that the compound was a valeric acid, the amide was prepared for confirmation. Approximately 0.2 cc. of thionyl chloride was added to 0.1 cc. of the acid and the mixture refluxed gently for a few minutes. The cooled solution was then poured into a small amount of cooled concentrated ammonium hydroxide. The resulting solution was evaporated to dryness and taken up in absolute alcohol. Evaporation of this gave a crystalline mass which melted at 125-30°. The acid is apparently isovaleric, which boils at 173.7°C., amide, m.pt. 123-28°C.

Fractional distillation of the phenols was continued until four fractions had been obtained. These had boiling points of 133-85°, 190-92°, 201-203° and 212-213°.

The cut boiling at 190-92° could not be fractionated further, so recourse was had to separation by a

"partial solution" procedure. The oil was shaken up with a relatively large volume of distilled water and allowed to stand until the emulsified particles had settled out. The aqueous solution was then treated with bromine until a distinct reddish color was obtained, a voluminous precipitate being thrown down. Sodium bisulfite was added and the mixture heated to 50°C. for a short while. The resultant white precipitate was filtered off and recrystallized twice from a 40% solution of alcohol in water. The crystals melted at 81-90°C. Recrystallization of the crystalline mass some six more times gave a product melting at 92-93° (tribromophenol, m.pt. 92-93°; dibromo o-cresol, m.pt. 57°; dibromo p-cresol m.pt. 48°; tribromo m-cresol, m.pt. 84°). The compound was evidently the tribromo derivative of phenol. Confirmation was obtained by preparing the tribromo-derivative of a sample of pure phenol by a similar procedure, determining the melting point (m.pt. 92-93°) and taking the mixed melting point (mixed m.pt. 92-93°).

As has been noted, both Japanese and Russian petroleum, as investigated by Tanaka and Kobayashi¹⁴, and Holzman and S. von Tilat¹⁵, respectively, contained no phenol. While the amount in the sample

under consideration was undeniably very small, the evidence of its presence cited above may be considered as fairly conclusive.

Density determination of the phenol fraction boiling at $199-210^{\circ}$ gave $d_{25}^{20} = 1.052$; o-cresol has b.pt. 191.8° , $d_{15}^{15} = 1.051$. The aryl oxyacetic acid was prepared as a derivative, and after three recrystallizations, gave m.pt. $150-52^{\circ}$ (o-cresyl oxyacetic acid, m.pt. $151-52^{\circ}$).

The fraction of phenols boiling at $201-25^{\circ}$ gave a greenish color with FeCl_3 . The boiling point of this cut corresponded to that of both m- and p-cresols (both b.pt. 202.0°). The identification of the isomer was made by the melting point of the aryl oxyacetic acid derivative. This was prepared and recrystallized eighteen times to give a melting point of $125-27^{\circ}$ (p-cresyl oxyacetic acid, 123° ; m-cresyl oxyacetic acid m.pt. 102°). While this sufficed to identify the p-cresol, the m-isomer which was present obviously could not be characterized by its aryl oxyacetic acid.

Use was made of the characteristic trinitro-derivative of the m-cresol for its identification. 2.5 cc. of the mixture boiling at $201-25^{\circ}$ were heated with 5cc. of concentrated H_2SO_4 for an hour at 100° ; 25 cc.

of concentrated HNO_3 were added, and the mixture allowed to stand for an hour. 25 cc. of H_2O were added, precipitating a gummy mass which was filtered off and recrystallized from 40% alcohol-water. Long standing produced a mass of orange colored crystals which, without further recrystallization, melted at $102-105^\circ$; (trinitro-m-cresol, m.pt. 103° ; nitro o- and p-cresols m.pt. 55.8°).

The fraction of phenols boiling at $212-18^\circ$ evidently consisted of one or more xylenols. Since the boiling points of the six isomeric xylenols range from $212-225^\circ$ and coincide for several isomers, it is practically impossible to effect a clean-cut separation by distillation. The aryl oxyacetic acid of the entire cut was therefore prepared in the hope that one individual would predominate and that its solid derivative could be isolated by repeated recrystallization. Eight or more recrystallizations gave an apparently pure product of m.pt. $63-63^\circ$. As may be seen from the following table (Leyer: "Nachweis der Organischen Verbindungen"), this corresponds to the melting point of the 1,3,5 xylene derivative.

Compound	b.pt.	m.pt. xylenyl oxyacetic acid
1,2,4 xylenol	225	132.5
1,3,2 xylenol	212	193.5
1,3,5 xylenol	219.5	63.
1,3,4 xylenol	211.5	141.5
1,4,3 xylenol	211.5	113
1,2,3 xylenol	218	--

The presence of 1,3,5 xylenol in this sample conforms with the work of Tanaka and Kobayashi¹⁴, and of Holzman and S. von Filat¹⁵, who have identified this compound in Japanese and Russian oils, respectively.

The residue (0.5 cc.) left in the distilling flask after fractionation of the phenols was dissolved in NaOH solution and the solution boiled with Lignite to clarify it slightly. The solution was acidified and the tar separating out extracted with carbon tetrachloride. The residue was shaken up with water, and dilute FeCl₃ solution added. A weak green color appeared, then a faint white precipitate (flocks) formed. This may be construed as an indication of the presence of β-naphthol, tho no corroborative evidence was obtained. No positive test for α-naphthol, which should have been extracted from the residue by the carbon tetrachloride, if present, was forthcoming.

The main body of carboxylic acids and phenols from which the neutral oil and a portion of the phenols

had been removed by steam distillation was esterified by the addition of 1.5 liters of previously dried methyl alcohol to the mixture, then over a period of four hours 750 cc. of concentrated H_2SO_4 were added. After this had been allowed to stand over night, it was poured into 6 liters of water. The oil separating was washed with dilute $NaOH$ solution, a sufficient amount of the solid being added to make the wash solution strongly alkaline. After a final washing with water, the esters (with some phenols which were not extracted by the alkaline solution) were shaken with anhydrous $CaCl_2$ and allowed to stand for a week or so.

The esters were then distilled in vacuo in a flask with a "non-foaming" stillhead. Distillation was carried out at 15 mm.; the temperature rose from 90° to approximately 170° , when some 450 cc. of distillate had come over. The residue was a black tar, quite solid at room temperature.

Fractionation of the distillate in a Clark column at a pressure of 2 mm. was attempted, but due to the excessive heat loss incurred in this type of column, "blowing" occurred, and distillation was not continued.

For further work use was made of a column con-

Fig. 1
 Fractionation of
 catene —
 Press — 1.2 mm

structed after the design of Teters and Baker. The distilling tube was of 14 mm. inner diameter with a length of approximately 1.5 meters. An electrically heated jacket thru which preheated air flowed extended from the flask up to a point about a meter above the lower end of the distilling tube. Above this a deflegmator tube allowed complete control of the reflux. Small copper Raschig rings were packed into the lower end of the tube for a distance of ca 75 cm.

Distillation was carried out in this apparatus at a pressure of 1.2 mm. $\pm$ 0.2 mm. The distillation curve for the esters is shown in Fig. 1. The boiling range was from 48° to 99.3°. Cuts were taken as shown.

Since the various fractions all possessed a typical phenol odor, each fraction was washed thoroughly with 6% NaOH, then with distilled water, and finally dried over anhydrous CaCl_2 .

A test for sulfur (sodium fusion) was run on each of the fractions. Legative results were obtained in all cases, altho the phenolic oils recovered from the alkali agitation of each ester fraction contained relatively large amounts of sulfur. Oxidation of the alkaline solutions of these fractions by iodine and hydrogen peroxide failed to produce any insoluble materials.

which would have been the case if the sulfur had been present in the form of mercaptans or thiophenols. Since the compounds were soluble in base and insoluble in water, the possibility of their being sulfonic acids was excluded. They were never isolated from the accompanying phenols. In all probability they represented thiophene carboxylic acids.

The ester fractions were tested for the presence of phenols by the Liebermann reaction and by coupling with diazotized sulfanilic acid. Each fraction gave definitely positive tests, so washing of the cuts with dilute NaOH was repeated, after which the esters were washed with water and dried over CaCl_2 .

Each of the fractions was examined in a polarimeter for possible optical activity, with negative results in all cases.

The first fraction of esters was refractionated several times in a small Vigreux flask, and a small fraction boiling at $45.2-46.0^\circ$ under 1.2 mm. was obtained. This was hydrolyzed by boiling with alcoholic KOH under reflux, distilling off the alcohol, and acidifying. The acid which separated out was taken up in ether, dried over anhydrous Na_2CO_3 and fractionated in a small flask under 2 mm. pressure. The first

fraction (b.pt. 55-55°) was mainly o-cresol. A fraction boiling at 80.0-83.5° was obtained which was free from phenols, as shown by failure to discolor bromine water. Micro-analysis of the silver salt of this acid gave 45.27% and 44.62% Ag, corresponding to a molecular weight of 132.

Subsequent refractionation of this acid gave a small fraction (0.5 cc.) which boiled from 83 to 84.2° under slightly less than 2 mm. pressure. This acid showed no reaction with bromine in carbon tetrachloride solution, or with dilute KMnO_4 . Micro-silver salt analysis gave 45.33 and 45.60% Ag (mean 45.43%) which is equivalent to a molecular weight of 130.5.

Micro combustion of the acid gave the following values:

	Run I	Run II		
Weight of sample	6.271 mg.	6.469 mg.		
Weight of H_2O	5.836	6.000		
Weight of CO_2	14.683	15.290		
			Mean	
%C	64.00	64.40	64.20	
%H	10.41	10.33	10.39	
%O	25.59	25.24	25.33	
	Mol. wt.	%C	%H	%O
Calc. for $\text{C}_7\text{H}_{14}\text{O}_2$	130.1	64.53	10.34	24.53
Calc. for $\text{C}_7\text{H}_{12}\text{O}_2$	128.1	65.57	9.45	24.93

From the above results the acid evidently has the empirical formula $\text{C}_7\text{H}_{14}\text{O}_2$; it is an aliphatic, rather

than a cyclic acid.

The boiling point at 770 mm. was determined by heating a small amount to boiling in a narrow test tube in an oil bath; the thermometer, bathed in the vapor directly above the boiling liquid, being read when equilibrium obtained. The boiling point was found to be 220.5° . Density determination in a micro pipette gave the value $d_{20}^{23.5} = 0.9259$.

n-Heptylic (oenanthic) acid has b.pt. $221-2^{\circ}$, $d_{20}^{23} 0.918$.

In order to determine whether or not the acid isolated was identical with the normal acid, the p-bromophenacyl ester was prepared from both the acid isolated and a sample of known n-heptylic acid (Schuchert and Co.). The m.pt. of the known derivative was $70.5-71.5^{\circ}$. The m.pt. as given by Moses and Reid³³ is 72.0° . The derivative of the unknown acid melted at $63-70^{\circ}$. The mixed m.pt. of this with the known compound was $70-71^{\circ}$. From this, the acid is n-heptylic acid.

This acid may well be identical with that described by Tschitschibabin¹⁷. His acid boiled at $215-218^{\circ}$ and gave on combustion an identical empirical formula. The structure provisionally assigned to it,

that of either isohexyloxy or 3,6-diethyl propanoic acid, was based on the apparent presence of a secondary or tertiary carbon atom in the molecule. As has been noted, however, lack of data does not permit confirmation or refutation of the identity of his acid with the normal compound.

The second ester fraction, boiling from 55-59° at 1.2 mm. was refractionated several times. A cut boiling at 52-55° was combined with a fraction of similar boiling range from the next higher ester fraction. After fractionation of this to give a constant boiling liquid with a range of ca 2°, the ester was extracted with 15% NaOH solution, then was hydrolyzed by refluxing with alcoholic KOH and acidifying. The acid which separated was fractionated in a small Vigreux flask under 2 mm. pressure. The distillate did not discolor bromine in carbon tetrachloride solution and did not react with dilute KMnO_4 .

After three fractionations a cut (less than 1 cc) was obtained which boiled at 87.0-87.5° under 1.3 mm.

The silver salt of this acid was prepared and micro-cumbustion of the salt carried out.

Values obtained were

Weight of sample	8.933 mg.
Weight of H_2O	4.892
Weight of CO_2	12.624
Weight of Ag	3.843

	Found	Calc. for $C_8H_{15}O_2Ag$
% C	33.33	33.24
H	6.04	6.02
Ag	42.83	43.00
O	12.74	12.74
mol.wt.	144.8	144.1

This acid is evidently an aliphatic (octylic) acid.

The boiling point, as determined by the "test tube method", using an Anschütz thermometer, was 235.5° (770 mm.)

Density determination in a micro pycnometer gave the value $d_{27.0}^{27.0}$ 0.923.

n-Octylic acid (caprylic acid) boils at 237.5° ;
 d_4^{20} 0.910

The p-bromo phenacyl ester was prepared for characterization. Derivatives of both the unknown acid and known n-octylic acid (Schuchert) were prepared. The known compound melted at $67.0-67.5^{\circ}$ (Moses and Reid³⁷ give m.pt. 67.4°). The ester of the acid isolated melted at $63-65^{\circ}$. Mixed melting point of the known and unknown compounds was $65-66^{\circ}$.

From this the acid is n-octylic.

The third cut of esters from fractionation in the Peters-Eaker column, boiling from 59.8-62.6° at 1.2 mm. was subjected to several refractionations in a short "low temperature type" column after a design by the same workers. A cut boiling at 61-65° (1.0 mm.) was combined with a fraction boiling thru the same range from the next higher cut of the main body of esters. This in turn was refractionated to a constant boiling fraction, washed with 15% NaOH and saponified by boiling with alcoholic KOH. The impure acid isolated was then fractionated in a small Vigreux flask some five times until an apparently pure fraction, boiling at 95.5-97.5° at 2 mm. was obtained. This was free from phenols as shown by the absence of reaction with bromine in CCl₄ solution, or with dilute KMnO₄. It was found that this acid could be further fractionated, however, giving n-octylic acid and a higher acid, as shown by silver salt analysis.

In order to obtain more material, the cut of esters taken from fractionation in the Peters-Eaker column boiling above 64.5° (1.2 mm.) was fractionated to give esters boiling from 61-65° (1.2 mm.). These were washed with dilute alkali, saponified, and the acid

obtained fractionated at 2 mm. pressure. Corresponding cuts of this acid and the impure acid boiling from 95.5-97.5° were combined. Repeated distillation led to the isolation of an acid boiling at 101-103° (2 mm.) which could not be fractionated further. This compound exhibited a faint reaction with bromine. Silver salt analysis gave 40.51% Ag, corresponding to an equivalent weight of 159.3.

The thoroughly dried silver salt was subjected to micro-combustion; the values obtained were:

	Weight of sample	10.023 mg.
	Weight of H ₂ O	5.621
	Weight of CO ₂	15.100
	Weight of Ag	4.058
	Found	Calc. for C ₉ H ₁₇ O ₂ Ag
% C	41.03	40.73
H	6.27	6.47
Ag	40.51	40.70
O	12.14	12.07
Mol.wt.	159.3	159.1

The acid has the empirical formula C₉H₁₇O₂.

The boiling point of this compound at 770 mm., as determined in a test tube, was 251.5°. Density determination gave the value $d_4^{27} = 0.929$.

n-Nonylic acid (relargonic acid) boils at 252-53°; $d_4^{20} = 0.935$. Despite the difference in densities, which may have been due to the presence of a small amount of phenols in the unknown acid, it seemed likely

that the acid isolated was the normal compound.

Confirmation was obtained by use of the p-bromophenacyl ester as a derivative. A sample of known pelargonic acid gave a derivative of m.pt. 34-37° (Moses and Reid³⁷ give m.pt. 63.5°). M.pt. of p-bromophenacyl ester of acid isolated, 62-64°; mixed m.pt. 63-65°.

Higher ester fractions than those containing methyl pelargonate were hydrolyzed in the hope of isolating higher acid members, but none of these were obtained in a pure enough state to warrant analysis.

The presence of the three aliphatic acids isolated tends to support Tschitschibabin's argument that the aliphatic members predominate in the low molecular-weight compounds of the petroleum acids, if it be granted that the sample under consideration here is comparable to the straight-run samples of other investigators. It is entirely likely, as von Braun points out, that most of the supposedly pure naphthenic acids isolated by previous workers have been in reality mixtures of cyclic and aliphatic acids.

The abnormally high densities found for the acids isolated may have been due to small amounts of phenolic

constituents present, which would tend to increase the actual values.

Phenolic components are also a disturbing factor in the determination of empirical formula by combustion. The presence of a small amount suffices to increase the carbon value and decrease the hydrogen value materially. Separation of the phenols from the acids, or even from their esters, is particularly difficult. In the former case, if the sodium bicarbonate method is used, separation is not quantitative; in the latter case, if alkali extraction is attempted, troublesome emulsions are formed and some extraction of the phenols from the aqueous phase takes place by the esters. The resistance which the phenolic compounds offer to complete separation from the acids suggests that many of the earlier investigations were in error as regards both empirical formulae and physical properties.

In order to ascertain the approximate amounts of the individuals present in their original mixture, a sample of this was subjected to a rough semi-quantitative examination.

A 1750 sample of the mixture was dissolved in excess alkali and steam distilled until the distillate contained no oil. The neutral oil and mercaptan phase

was separated from the water and the mercaptan isolated as the mercuric chloride addition product; volume of oil, 200 cc.; wt. of solid addition product, ca. 25 gms. Altho the mercaptan addition product is of variable composition, it is safe to say that approximately 5-10 gms. of ethyl mercaptan was in the original sample.

Slightly less than 1500 cc. of alkali soluble oil were recovered from the residue from steam distillation. This was allowed to settle, in order to separate off as much water as possible, then was dissolved in 1200 cc. of methyl alcohol. 500cc. of concentrated H_2SO_4 were added slowly, and the mixture allowed to stand for 24 hours. It was then poured into 12 liters of water. The oil separating was washed with water, then with cold 20% NaOH solution containing 600 gms. of the solid. This was decanted off, and the residual oil again agitated with a smaller amount of the alkali. The esters were finally washed with water, then with dilute H_2SO_4 . The volume of esters so obtained was slightly over 250 cc. and was practically free of phenols.

The alkaline extracts were combined and made distinctly acid with dilute H_2SO_4 . The oil which sepa-

Fig 2
Fractionation of
phenols —
Press — 770 mm

rated from the acid solution was washed with water and dried over anhydrous Na_2SO_4 . Volume, ca 1050 cc. The total loss in handling was approximately 150 cc.

The ester fraction was distilled in a Claissen flask at a pressure of 1 mm. The initial temperature was ca 50° ; the temperature rose to ca 180° , when approximately three-fourths of the esters had distilled over. If the acids be considered as aliphatic, from the boiling point, the mixture would correspond at the upper limit to the esters of palmitic, stearic, and possibly higher acids.

The phenols were distilled at atmospheric pressure to free them from tarry substances. The initial temperature was slightly less than 190° . A cut was taken at 230° , at which temperature ca 500 cc. had distilled over. Distillation was then continued to a temperature of 235° , giving an additional 75 cc. of distillate. The residue from this was a black almost solid tar.

The phenol fraction boiling from 190° to 230° was fractionated in the Peters-Baker column previously described at a pressure of 770 mm. The distillation curve is shown in Figure 2.

As may be seen from the curve, the volume of the

fraction corresponding to o-cresol was ca 145 cc; of the mixture of m- and p-cresols, ca 135 cc; of the total "xylenol" fraction ca 180 cc.

The fraction boiling at 207° was evidently not a xylene individual, and since azeotropic mixtures are rather uncommon in the phenol series, this possibility is unlikely. It is probable that this fraction may be o-ethyl phenol (phloral), which boils at $206.5-207.5$. The m- and p-isomers boil at 214° and 219° respectively; from the boiling point curve there is no indication of the presence of the former. The latter, if present, would be indicated by the curve as boiling with the two xylene isomers (2,3 dimethyl phenol b.pt. 213° , and 3,5 dimethyl phenol, b.pt. 219.5°) which were probably present.

The occurrence of the latter compound in the mixture has been already demonstrated (q.v.). Since the melting point of the oxycetic acid of the former is not tabulated in the literature, and since no other easily prepared derivatives are characteristic for this compound, no confirmation of its presence in the mixture could be obtained.

Similarly, no characteristic derivatives for the ethyl phenols are described in the literature. Here

again no definite proof of their presence was obtained, other than the evidence of the distillation curve.

The fraction boiling at 225° was redistilled to give a cut boiling from $223-225^{\circ}$, and 3 cc. of this converted to the aryl oxyacetic acid. The 1,2,4 xylenol, b.pt. 225° , should give an aryl oxyacetic acid melting at 132.5° . Some twenty recrystallizations of the solid gave a product which melted only slightly above 100° , so the attempt to isolate a derivative of this isomer was discontinued.

Refractionation of the cut taken at $210-212^{\circ}$ gave some 5 cc. of a constant boiling liquid, b.pt. ca $211-12^{\circ}$. This was converted to the aryl oxyacetic acid and the product recrystallized fifteen times until no change in melting point was evident upon further recrystallization. The melting point so obtained was $116-118^{\circ}$. 1,2,4 xylenol, b.pt. 211.5° , gives a derivative of m.pt. 118° . It is evident, then, that the compound under consideration is this isomer.

The phenols boiling above 230° were not investigated further, except that an alkaline solution of a fraction boiling at $235-40^{\circ}$ was subjected to steam-distillation and the absence of an oil phase in the distillate noted. Carvacol and thymol, if present in

the fraction, should have responded to this procedure by distilling over from alkaline solution.

The approximate amounts of each of the components isolated from the original sample are best shown in the "flow-sheet", Figure 3, accompanying. As shown, the amounts of phenolic constituents isolated are multiplied by a factor of 1.2 in estimating the percentage composition of the total sample. This factor is introduced to allow for loss in handling the sample, particularly in the separation of the phenols and esters of the carboxylic acids.

Fig 3

* This, and succeeding phenol volumes multiplied by 1.2 to allow for loss in handling —

SUMMARY

1. Commercial "naphthenic acids" from a West Texas pressure distillate were shown to consist for the most part of phenolic constituents.

2. The following compounds have been isolated from the sample: ethyl mercaptan, phenol, o-cresol, m-cresol, p-cresol, 1,3,5 xyleneol, 1,4,2 xyleneol, iso-valeric acid, n-heptylic acid, n-octylic acid, and n-nonylic acid.

3. The finding of aliphatic acids and of no cyclic acids tends to throw doubt on the claims of earlier investigators who reported the cyclic compounds exclusively.

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