and one-half grades for all rosins above WW and from one to two and one-half grades for all rosins from I to WG. Distilled gum rosins, in general, showed the greatest loss in grade. Extra light-colored American gum rosins (grade 8A) appeared to be no more sensitive to heat when in solution in turpentine than the ordinary commercial grades, WW and X. The darker the original rosins were below WG, the less was the loss in grade, which was to be expected and was no doubt due to the greater amount of color required to change the grades. The commercial samples of French rosin of grades N and I when heated showed the same drop in grade as American commercial gum rosins of the same grades.

Identification of Products of Oxidation of Gas Oil by Penniman Process[1]

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In the aqueous part of a distillate resulting from an air oxidation of a Pennsylvania gas oil at 750° F. (398.9° C.) and under a pressure of 300 pounds per square inch (21.09 kg. per sq. cm.), the following compounds were identified: acetaldehyde, acetone, methanol, methyl acetate, dimethyl acetal, ethyl alcohol, ethyl acetate, allyl alcohol, and acetic acid.

RESEARCH in the oxidation of petroleum has interested many investigators over a long period of time on account of the possibilities that petroleum offers as raw material for the synthesis of industrially useful products, particularly organic oxygen compounds of the aliphatic series. The studies in this field have been carried out with a large variety of pure aliphatic hydrocarbons, or mixtures, as starting materials. Both liquid- and vapor-phase oxidations have been tried with and without catalysts. It is evident that an entirely successful method for manufacturing organic chemicals from petroleum by oxidation has not been found, since aliphatic organic chemicals of industrial importance are, in general, manufactured from other raw materials. In the cases where petroluem fractions are used, the products are obtained by means other than oxidation.

The work described in this paper is the identification of products resulting from a liquid-phase oxidation of a gas oil which was carried out by Penniman (*4*). The process has operated successfully on a semiplant scale, using paraffin-base oils.

Description of Process

The Penniman process consists in passing air into hydrocarbons held in a still at about 750° F. (398.9° C.) under a pressure of 300 pounds per square inch (21.09 kg. per sq. cm.) and condensing the products which are evolved from the stillhead.

The particular apparatus used for the work described in this paper consisted of an upright cylindrical still 26 feet (7.9 meters) high and 4 feet (1.2 meters) in diameter, whose working capacity was about 20 barrels [1000 gallons (3790 liters)] of oil. The still was equipped with heat exchangers for preheating the oil as it entered the main body of the still, and two water coils for controlling the reflux. The still was connected by a vapor line through a condenser to a receiver.

It was found that when air was blown into the hot oil at the bottom of the still at a rate of approximately 400 cubic feet (11.3 cubic meters) per minute, partial oxidation took place and the temperature of the oil rose, owing to heat of reaction, from an initial temperature of 500° to 750° F. (260° to 398.9° C.), and a liquid consisting of aqueous and oil layers distilled over into the receiver. The process could be made continuous, and the operating conditions maintained within narrow limits by feeding fresh oil into the still at the proper rate, no external heating being necessary as the heat of reaction was sufficient.

The issuing gases contained about 1.5 per cent carbon dioxide, no oxygen, 0.5 per cent of combustibles, the rest being nitrogen. It was found necessary to draw off a certain amount of sludge from the bottom of the still from time to time.

The gas oil used to provide material for the work described in this paper was a Midcontinent distillate of the following specifications:

Specific gravity at 60° F. (15.6° C.) = 38.3° Bé.

Distillation	Oil		Vapor	
	° *F.*	(° *C.*)	° *F.*	(° *C.*)
Initial boiling point	552	(288.9)	432	(222.2)
Temp. 10% distilling	582	(305.6)	525	(273.9)
Temp. 20% distilling	600	(315.6)	558	(292.2)
Temp. 30% distilling	615	(323.9)	575	(301.7)
Temp. 40% distilling	631	(332.8)	592	(311.1)
Temp. 50% distilling	645	(340.6)	608	(320.0)
Temp. 60% distilling	661	(349.4)	624	(328.9)
Temp. 70% distilling	671	(355.0)	642	(338.9)
Temp. 80% distilling	701	(371.7)	666	(352.2)

The aqueous layer was the only part of the distillate investigated.

Concentration of Compounds in Aqueous Layer

In this run thirty-seven barrels of the gas oil were used. Sixteen barrels of oil and eight of aqueous layer were collected as distillate, but these proportions do not represent the results of continuous operation.

The oil layer was washed with 135 gallons (511.7 liters) of water which was added to the aqueous layer, making a total of 535 gallons (2027.7 liters) of an aqueous solution of organic compounds.

This solution was distilled by the U. S. Industrial Chemical Company. A precise fractional distillation was not attempted, the distillate being cut in 7-gallon (26.5-liter) fractions for convenience in storing. At the beginning of the distillation the condenser was cooled with brine to 17° C. The first two 7-gallon (26.5-liter) fractions were collected under these conditions. The thermometer at the top of the column registered room temperature. At this point the brine was replaced by water, and ten more fractions were collected until the thermometer at the top of the column registered 100° C., at which point the distillation was discontinued.

In all, 84 gallons (318.4 liters) of concentrated organic material were obtained, which was about 15 per cent by volume of the total aqueous layer. Samples from each of the fractions and of the still residue were taken as material to be identified.

Identification of Compounds of Aqueous Layer

The first step in the investigation of the water distillate was the determination of the boiling-point ranges and other properties of the fractions of concentrated organic material from the water distillate. The results are shown in Tables I and II.

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[1] Received July 2, 1931.

Table I—Boiling-Point Range of 100 cc. of Each Fraction

Fraction	1	2[a]	3	4	5	6	7	8	9	10	11	12	13
Cc.	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*
Initial	24.2	39.3	32.2	35.0	47.8	55.2	67.7	71.0	75.9	80.0	81.2	83.5	99.0
10	31.5	49.0	39.3	40.9	51.2	59.2	68.5	73.6	78.8	83.0	83.5	86.0	99.5
20	31.9	52.7	45.2	42.5	53.1	60.2	69.2	74.9	80.6	85.0	85.5	88.5	99.5
30	31.8	54.8	48.3	45.0	55.2	60.5	70.2	77.0	82.0	86.9	88.0	91.0	99.5
40	29.3	58.0	49.0	47.0	56.8	61.9	71.5	78.2	83.9	89.0	90.2	94.0	99.5
50	34.6	61.9	51.4	49.0	58.5	64.1	72.5	79.7	85.7	92.0	93.5	96.5	99.5
60	36.8	65.0	54.3	53.2	60.2	65.0	74.5	81.1	88.3	96.5	97.0	99.5	99.5
70	40.1	70.2	60.0	56.0	63.0	67.7	76.3	83.0	92.8	101.8	99.0	100.5	101.0
80	46.9	76.5	67.5	61.1	65.7	69.0	80.0	85.4	98.2	106.0	101.0	100.5	102.5
82.5	63.5	..	..	..	..	..	..	..	..	..	..	..	..
90	..	78.5	76.0	69.0	70.8	72.6	89.0	89.6	107.8	108.0	102.5	101.5	104.5
92.5	..	82.5	80.0	..	..	..	..	..	..	..	..	..	..
93.5	..	..	..	80.0	..	..	..	..	..	..	..	..	..
95	..	..	..	..	82.0	..	..	..	110.2	..	..	..	..
98	..	..	..	..	..	83.0	98.0	98.0	..	135.0	123.0	130.0	122.5

[a] Fraction 2 had evidently been misnumbered as it should come between 4 and 5.

Table II—General Properties of Distillate

Fraction	Sp. Gr., 25°/25° Bé.	Carbon	Approx. Acid per 1000 Grams	Approx. Aldehyde and Ketone per 1000 Grams
		%	*Mole*	*Moles*
1	0.753[a]	35.01	0.0312	17.8
2	0.849	50.80	0.0478	10.31
3	0.815	52.23	0.0273	12.69
4	0.820	51.77	0.0286	11.64
5	0.840	49.43	0.0570	7.99
6	0.840	41.98	0.0545	6.40
7	0.840	12.87	0.0091	3.51
8	0.868	15.26	0.0223	2.00
9	0.910	13.29	0.0838	1.11
10	0.943	8.68	0.1252	....
11	0.950	8.73	0.1751	....
12	0.962	6.70	0.1762	....
13	1.014	6.30	0.4975	....

[a] 0°/0° Bé.

The first fraction which consists mainly of acetaldehyde lost 17.5 per cent of its original volume and left no residue. A brown solid residue, insoluble in water, remained behind after the distillation of all of the other fractions. Braces placed around the temperature figures in Table I indicate that during that part of the distillation the distillate came over in two layers. The carbon content of each fraction was determined by the wet-combustion method of Franz and Lutze (*1*), using potassium persulfate as the oxidizing agent. It was found later that the values obtained for fractions 7 to 12 were inaccurate, owing to the presence of unsaturated material. The acidity was determined by titration with sodium hydroxide. The aldehyde was determined by the neutral sodium sulfite method of Seyewetz and Bardin as given by Kingscott and Knight (*3*). This determination was high on account of the presence of acetone and other ketones.

Identification of Individual Compounds

Acetaldehyde was identified first in fraction 1 by making the aldehyde-ammonia compound and combining this with semicarbazide hydrochloride according to the method of Thiele and Bailey (*7*). The semicarbazone thus prepared melted at 162° C. A mixed melting point with pure acetaldehyde semicarbazone (m. p. 162° C.) melted at the same temperature, giving a positive identification.

In order to identify the ketones in the fractions, it was necessary to remove the aldehyde. This was done by preparing the Schiff's bases with aniline. The compounds were formed very readily when aniline was added to each particular distillate up to fraction 6. It was found impossible to prepare Schiff's bases from fraction 7 up. This showed that the first six fractions differed in composition from the last six. Other evidence of the difference in general composition of the higher and lower parts of the distillate will be shown later.

Fraction 4 was chosen for the ketone investigation. After the aldehyde had been removed from a sample of this fraction by aniline, the remaining liquid was distilled away from the Schiff's base and free aniline, and a sample added to a solution of *p*-nitrophenyl hydrazine hydrochloride in water. The *p*-nitrophenyl hydrazone crystallized out immediately. Its melting point, after three recrystallizations from 50 per cent alcohol, was found to be 145–146° C. The mixed melting point taken with pure acetone *p*-nitrophenyl hydrazone (m. p. 145–146° C.) was found to be the same. This fact positively determined the presence of acetone.

Having found acetone and acetaldehyde in different fractions, each fraction of the distillate was tested for aldehydes and ketones. The method of identification for aldehydes was oxidation to acids by means of freshly prepared silver oxide. This mild oxidation left the ketone untouched. The acid thus obtained after filtering off the residue was neutralized with sodium hydroxide, and the sodium salt allowed to react with *p*-bromphenacyl bromide according to the method of Judefind and Reid (*2*) to give the corresponding ester. The acid was then identified by the melting point of this ester. It was found that acetaldehyde was presented in fractions 1 to 6, because in each case the *p*-bromphenacyl ester melted at 85° C., after one or two recrystallizations, which is the melting point of pure *p*-bromphenacyl acetate. Fractions 7 to 10 yielded an ester melting at 116–117° C. when treated in like manner. The ketones were tested with *p*-nitrophenyl hydrazine hydrochloride and only acetone was found up to fraction 6. No *p*-nitrophenyl hydrazone could be prepared from fraction 7 on account of the presence of unsaturated compounds which removed the hydrochloric acid from the *p*-nitrophenyl hydrazine, thus causing it to precipitate out.

The total amount of aldehyde and acetone was found to be about 73 per cent in a composite sample of fractions 1 to 6 by titration of the free sulfuric acid liberated when the weighed sample was added to a neutral hydroxylamine sulfate solution. This left 27 per cent to be identified. The sample was tested with sodium to detect alcohols, and no reaction occurred. It was concluded, therefore, that mixed compounds, such as esters, acetals, or both, were present.

In order to test for esters, fraction 6 was refluxed with a strong caustic soda solution which would polymerize the aldehyde and saponify the ester. After refluxing, the two layers were separated. The upper one was dried with potassium carbonate and treated again with sodium. This time the reaction was vigorous, showing the presence of alcohols which had been in combination as esters. The lower layer was evaporated down until a solid separated out, which was shown to be sodium acetate by its melting point. The esters, therefore, were evidently acetates. The alcohols were not identified.

To test for acetals, a part of the organic layer, after the removal of aldehydes by sodium hydroxide, was distilled with dilute sulfuric acid. The first distillate came over at about 30° C. and was unmistakably acetaldehyde from the odor. However, to determine this fact beyond question, the *p*-nitrophenyl hydrazone was prepared. It melted at 128° C., which is the melting point given in the literature for the acetaldehyde derivative. This showed the presence of acetals.

Therefore, the first half of the total distillate was found to contain acetaldehyde, acetone, acetates, and acetals. The acid content was negligible.

The next operation was the study of the second half of the distillate, which was shown to be different in general composition from the first. By its behavior it could be seen that this half of the distillate was made up of unsaturated compounds, aldehydes, and acids, with possibilities of other compounds.

It has been mentioned before that a *p*-bromphenacyl ester melting at 116–117° C. was obtained from the oxidation product of the aldehyde to acid in fractions 7 to 10. It was shown also that this aldehyde was saturated because the oxidation product could be prepared regardless of whether the unsaturated compounds had been removed or not. This product was not definitely identified.

In order to test for alcohols, fraction 9 was dried with potassium carbonate and treated with phthalic anhydride according to the method of Reid (*6*). The viscous oil obtained was neutralized with caustic soda and refluxed with *p*-nitrobenzyl bromide. After four recrystallizations, the resulting ester melted at 100° C. The mixed melting point with pure methyl *p*-nitrobenzyl phthalate was 105° C., showing the two compounds to be identical. This identified methanol.

Since it was known that unsaturated compounds existed in fractions 7 to 12, fraction 12 was treated with bromine to remove them. A dibromide formed easily with great evolution of heat and was separated off. During this separation the odor of allyl alcohol was detected, so a sample of fraction 12 was dried with potassium carbonate and treated with phthalic anhydride to prepare the monoallyl phthalate. This compound was treated with caustic soda and refluxed with *p*-nitrobenzyl bromide as before. The resulting *p*-nitrobenzyl ester melted between 58° and 61° C. after three recrystallizations. A mixed melting point with pure allyl *p*-nitrobenzyl phthalate (m. p. 61° C.) melted over the same range, positively identifying allyl alcohol.

On account of the fact that the acid content of the still residue was considerable, it was chosen for acid identification. No aldehyde was found in this when tested with fuchsin. The acid was found to be acetic by the melting points of the *p*-nitrobenzyl and *p*-bromphenacyl acetates which melted at 75° C. and 84.7° C., respectively, after three recrystallizations. The *p*-nitrobenzyl esters were prepared according to the procedure of Reid (*5*).

A rough quantitative analysis of alcohols in fractions 7 to 12 was made by weighing the residue left after drying 100 grams of a composite sample with potassium carbonate and removing the alcohols with phthalic anhydride. It was found that the organic material amounted to 50 per cent and the alcohols 17 per cent. Therefore, fractions 7 to 12 consisted of 17 per cent alcohols and the rest aldehydes, ketones, and water, and the still residue contained 3 per cent acetic acid.

Use of High-Precision Fractionating Still

At this stage of the investigation it was realized that further progress could not be made by chemical means alone. A Peters and Baker high-precision fractionating column was therefore set up, and a distillation curve run on a composite sample of 200 cc. taken from a mixture of 100 cc. of each original fraction. The curve indicated the presence of compounds or constant boiling-point mixtures at the following temperatures: 21° C., 54° C., 63° C., 78° C., and 86° C.

Quite obviously the 21° C. fraction consisted entirely of acetaldehyde. This was shown to be true, however, by hydroxylamine sulfate analysis.

The 54° C. fraction smelled strongly of acetone. It was positively identified by the melting point of dibenzal acetone. It is very probable that the methanol was present in this acetone fraction, although its presence was not determined.

A qualitative test for esters was carried out next, and it was found that a sample of the 54° C. fraction reacted with a caustic soda solution, indicating the presence of an ester. After the alcohol had been removed from a sample by treatment with phthalic anhydride, the residue was refluxed with caustic soda solution. The alcohol liberated was methanol, which was identified as the *p*-nitrobenzyl phthalate. The acid residue was identified by the melting point of the sodium salt as acetic acid. Therefore, the ester in the 54° C. fraction was methyl acetate.

The 63° C. fraction was examined next and gave a positive test for aldehydes when treated with fuchsin sulfurous acid. Even after refluxing with caustic soda, the fraction continued to give a color with fuchsin. Consequently, the presence of acetal was suspected. Any methanol or methyl acetate was removed by boiling with caustic soda, distilling, and treating with phthalic anhydride. The remaining liquid was distilled with dilute hydrochloric acid. The odor of acetaldehyde was noticed immediately. This was identified as the *p*-nitrophenyl hydrazone. Methanol was identified in the residue as the *p*-nitrobenzyl phthalate after neutralizing and drying over calcium oxide, showing that the acetal present was dimethyl acetal.

The 78° C. fraction, after drying with potassium carbonate, was tested for alcohols with sodium, giving a positive result. The *p*-nitrobenzyl phthalate appeared as an oil. Therefore, the 3, 5-dinitrobenzoate was prepared. This melted at 85° C. A mixed melting point with ethyl 3,5-dinitrobenzoate (m. p. 93° C.) was found to be 87–88° C., which identified ethyl alcohol. Ethyl acetate was also identified in this fraction in the same manner as methyl acetate. This fraction had a distinct odor of allyl alcohol and was lacrimatory. This would account for the lowering of the melting point of the ethyl 3,5-dinitrobenzoate.

The 86° C. fraction, which was extremely lacrimatory, yielded a heavy insoluble oil when treated with bromine. When dried with potassium carbonate, it gave a positive test for alcohols with sodium. It is very probable that allyl alcohol was present in large quantity in this fraction.

A rough estimate of the quantities was made. With change of operating conditions for the oxidation, the amounts and nature of the resulting constituents would probably vary. The figure for acetaldehyde represents only a fraction of that actually produced, as much was lost in handling and storage. The same remark applies also to the other more volatile constituents. The results are shown in Table III.

Table III—Organic Materials in Water Layer of Distillate[a]

	Pounds	*Kg.*		*Pounds*	*Kg.*
Acetaldehyde	5.5	2.50	Ethyl alcohol Ethyl acetate, etc.	2	0.91
Acetone Methanol Methyl acetate Dimethyl acetal	19	8.62	Allyl alcohol, etc.	3.5	1.59
			Acetic acid	7	3.18

[a] Per 1000 pounds (453.6 kg.) gas oil.

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