Patented Sept. 19, 1950 2,522,678

UNITED STATES PATENT OFFICE

2,522,678

RECOVERY OF OXIDIZED PETROLEUM PRODUCTS

Alfred P. Kozacik and Alexander N. Sachanen, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

No Drawing. Application December 30, 1947, Serial No. 794,776

5 Claims. (Cl. 260—452)

1

This invention relates to the production of various oxygen-containing compounds from petroleum oils and waxes, and the separation of the mixtures of compounds so produced into usable increments. The principles of this invention are applicable to the production of oxygen-containing organic compounds from any type of hydrocarbon material and to the separation of oxygen-containing organic compounds from mixtures of such compounds, if the mixtures are of the type herein described, regardless of how those mixtures are originally produced.

As is well known, petroleum oils and waxes are comprised for the most part of hydrocarbons, the majority of which are usually straight and branched-chain aliphatics. A wide variety of methods have been proposed for introducing oxygen or other elements into these hydrocarbon compounds, thus changing the nature of the compounds and producing compounds useful for purposes for which the original hydrocarbons were not useful.

One method of altering the nature of the hydrocarbon compounds in petroleum oils and waxes, and in other hydrocarbon materials has been to treat these hydrocarbon materials with oxygen under conditions that cause the oxygen to combine with the hydrocarbon materials to yield oxygen-containing organic compounds. Of course, the oxidation must be controlled if useful compounds are to be produced in quantity. Obviously, if the oxidation of the hydrocarbon materials is carried to completion, the products will be carbon dioxide and water. However, by partial oxidation of these materials a whole series of oxygen-containing organic compounds can be produced. Furthermore, since petroleum oils and waxes, and many other sources of hydrocarbons, are mixtures of numerous hydrocarbons, the resultant partial oxidation products will be a mixture of various oxygen-containing organic compounds.

Generally, if a petroleum oil or wax is partially oxidized, a mixture will result which will contain varying proportions of the following types of compounds:

(1) Organic peroxides which are apparently primary oxidation products, from which other oxygen-containing compounds are formed as the process proceeds.

(2) Acids which are soluble in oils and insoluble in water. These acids are generally monobasic and usually contain comparatively large organic radicals which account for their oil-solubility and their insolubility in water.

2

(3) Acids which are insoluble in oils and soluble in water. These acids are usually either oxyacids or polybasic acids or monobasic acids containing comparatively small organic radicals.

(4) Saponifiable oxygen compounds such as esters, lactones and the like.

(5) Unsaponifiable oxygen compounds, such as ethers, alcohols, ketones and the like.

In addition to the types of compounds enumerated hereinbefore, there is almost invariably a residue of hydrocarbon material which has not been oxidized in the process, and if the conditions of oxidation are too severe and/or insufficiently controlled, asphaltic materials or resins may also result.

Prior patents and publications have mentioned methods of separating the various compounds produced by the partial oxidation of hydrocarbon material but have generally limited themselves to suggesting that the oxidation products be separated by treatment with alkaline solutions or treatment with solvents. Insofar as is known, no prior patent or publication has ever suggested a practical, efficient process for obtaining, in desirable form, the various components of the mixed products of the partial oxidation of hydrocarbons. It is an object of the present invention, therefore, to provide such a process.

The present invention is not concerned with the oxidation reaction itself except as it affects the separation of the resulting products. The partial oxidation of petroleum oils and waxes has been described in previous patents and in the literature. Insofar as this invention is concerned, the oxidation may be accomplished by any of the methods already known, providing only that the method of partial oxidation employed does not produce such excessive quantities of asphaltic materials or resins as to make the herein described process of separation impractical.

According to this invention, it has now been discovered that the products of the partial oxidation of petroleum oils and waxes, and other similar products, may be so treated as to derive therefrom several very useful components, each component comprised of a mixture of organic compounds of a particular type. Thus, in accordance with this invention, the organic peroxides in the original mixture are converted into other oxygen-containing organic compounds (oil-soluble acids, water-soluble acids, saponifiable oxygen-containing compounds, and unsaponifiable oxygen-containing compounds), the saponifiable compounds are saponified, and the resulting oil-soluble acids, water-soluble acids, and unsaponi-

fiable oxygen compounds are separated from each other and from the unoxidized hydrocarbons. Since each of these classes of compounds is usable for different purposes, and each class is often usable as a mixture instead of as a single pure compound, the resulting products of the process of this invention are highly desirable. In addition, the yields of organic acids are substantially increased at the expense of peroxides and saponifiable materials.

Briefly, the process of the present invention comprises the treatment of the partial oxidation products with an alkali or alkaline-earth hydroxide in aqueous solution at a temperature and for a period of time sufficient to convert the peroxides and esters into acids and other oxygen-containing organic compounds, falling within the other classifications. At the same time, all of the acids are converted into salts, usually sodium or potassium salts, which are water-soluble, and the saponifiable compounds are converted into salts of organic acids and other compounds, usually ethers, alcohols, ketones or the like, which are unsaponifiable.

The next step consists of separating the aqueous and oleaginous layers and washing the aqueous layer with naphtha or the like, if necessary, to remove any oil emulsified in the aqueous layer. The aqueous layer now contains the salts of the acids originally present, the salts of acids formed by the reaction of the alkaline solution on the peroxides, and the salts of acids formed by the action of the alkaline solution upon the saponifiable oxygen compounds. Practically all of the unsaponifiable oxygen compounds that were originally present, and practically all of the unsaponifiable oxygen compounds that were formed by the action of the alkaline solution will be found in the oleaginous layers.

The next step comprises treating the aqueous layer with dilute acid, usually hydrochloric acid, to liberate the acids from their salts. As the oil-soluble acids are liberated from their salts they become insoluble in the aqueous layer and may be separated therefrom. These oil-soluble acids may be further purified and/or separated from each other, or used as a mixture as a particular need may dictate. Thereafter, the aqueous layer with its remaining water-soluble acids may be neutralized and evaporated to produce dry salts. These salts can be extracted with alcohol or any other solvent which will dissolve the organic salts and not appreciably dissolve the inorganic salts formed in the process. For example, when the inorganic salt is sodium chloride, as it usually is, a mixture of methyl alcohol and ethyl alcohol containing approximately 90% by volume of ethyl alcohol, will dissolve the organic acid salts without appreciably dissolving the sodium chloride. The alcohol solution of the sodium salts of the organic acids may then be evaporated to recover the dry salt.

The oleaginous layer which contains the unreacted hydrocarbons and unsaponifiable oxygen compounds can be extracted with solvents such as liquid sulphur dioxide, phenol, acetonitrile, or the like, to separate the unsaponifiable oxygen compounds from the unreacted hydrocarbons.

As a result of the above-described process, there are obtained from the partial oxidation products of petroleum oils, waxes and the like, by a very efficient, easily conducted process, three valuable, stable, useful components: (1) water-soluble organic acids or salts, (2) oil-soluble organic acids or salts, and (3) unsaponifiable organic oxygen-containing compounds. In addition, the unreacted hydrocarbon materials are recovered for recycling to the oxidation process.

An advantage of the present invention lies in the possibility of using conditions that cause a high conversion of the petroleum oil charge stock in the oxidation stage. In accordance with the prior art, the oxidation was usually controlled to a limited extent in order to avoid the formation of a variety of oxygenated compounds. As indicated hereinafter, the degree of oxidation possible in accordance with the process of the present invention is above 70% of the original petroleum oil. The subsequent treatment converts all of the various classes of oxygen compounds formed into the three classes specified hereinbefore.

In the process of this invention it is preferred to use aqueous sodium hydroxide solution in a concentration of about 10% for the treatment of the partial oxidation products. Preferably a temperature of about 212° F. is used and the treatment is continued for about 4 to about 6 hours. It is to be understood, however, that aqueous potassium hydroxide, calcium, barium, or other alkaline earth hydroxide solutions may also be used in most instances. In some instances ammonium hydroxide or triethanolamine may be used. The concentration of sodium hydroxide or other base in the solution is not at all critical. Generally with a weaker base, a greater concentration will be used. With sodium hydroxide it will seldom be desirable to use less than 5% nor more than 25%. The temperature and time of treatment depend upon the concentration of base in the solution. Using 10% sodium hydroxide, temperatures between about 150° F. and about 250° F. and times between about 2 and about 10 hours can be considered to be a generally preferred range. We have found that under these conditions, all organic peroxides are decomposed to acids and other oxygen-containing organic compounds and all esters are saponified.

Further details and advantages of this invention will be apparent from the following specific example:

Example

A kerosene fraction, pretreated with sulfuric acid, specific gravity 0.8076, 60°/60° F., was oxidized by oxygen at 257° F. and thus converted into an oxidized product of specific gravity 0.956, 60°/60° F., a neutralization number 118.5, saponification number 253, active oxygen (peroxides) 48.6 mgm./100 cc.

Nine hundred grams of the oxidized oil was treated with 209 grams of sodium hydroxide (assay 97%) and 1890 grams of water.

The oxidized oil was placed in a 3-liter flask which was heated; as the oil was being heated the sodium hydroxide solution was added gradually. After the addition, the reaction mixture was heated for a total of 3⅓ hours; the entire temperature range was 79–216° F. By this treatment peroxides and esters were transformed as has been stated hereinbefore.

The reaction mixture consisting of sodium salts of acids, neutral oxygen compounds and unreacted hydrocarbons was placed in a separatory funnel, the lower alkaline layer was separated from the top layer consisting of unsaponifiable material; the lower layer was acidified with an 18% aqueous solution of hydrochloric acid and an oily layer, consisting for the major part of acids insoluble in water, separated. The water

layer contained sodium chloride and the water-soluble acids. The yields were as follows:

	Grams
Weight of unsaponified material	378
Weight of free acids (soluble in oil and insoluble in water)	382.5

The acids (382.5 grams), after drying by binary distillation of the water present with benzene, had a neutralization number of 195.5 and a specific gravity of 1.007 at 77° F.

The water layer, mentioned hereinbefore, amounting to 2881 grams was neutralized with sodium hydroxide. The resulting solution was evaporated to dryness and the solids were pulverized in a mill to a fine powder. The powder was then extracted with hot Formula 30 (methyl alcohol-ethyl alcohol) in order to recover the sodium salts of acids soluble in the water layer. The extraction was carried out in a three-liter flask equipped with a T stirrer; approximately 500 cc. of alcohol was added to the flask containing the pulverized solid. After stirring the heated solid-solvent for three-quarters of an hour, the alcohol solution was drained, then a fresh quantity of alcohol was added. The extraction process was repeated until the alcohol extractant was only lightly colored.

The alcohol extracts were combined, the alcohol removed by distillation, the solid remaining was pulverized and then dried by placing it in an oven. After drying, the solid amounted to 80 grams, corresponding to approximately 72 grams of acid. The material balance is:

	Grams
Unsaponifiable material	378.0
Acids insoluble in water	382.5
Acids soluble in water	72.0
Total	832.5

The loss, 900—832.5=67.5 grams, occurred in all separation operations described.

The unsaponifiable material (specific gravity 0.830 at 78.8° F.) amounting to 331 grams (400 cc.) was placed in a 2-liter separatory funnel, then 892 cc. of acetonitrile were added. The materials were shaken thoroughly for five minutes and after a settling period of forty minutes the lower layer, now referred to as the "raffinate," was withdrawn. The "raffinate" was re-extracted with 504 cc. (392 grams) of acetonitrile by shaking thoroughly for five minutes. After the layers had separated the acetonitrile "extract" solutions were combined, the acetonitrile was removed by distillation at atmospheric pressure and final traces removed under slight vacuum; there remained 140 grams of "extract." The "raffinate" portion was placed in a flask to remove any acetonitrile by distillation as mentioned for the "extract;" there remained 161 grams of "raffinate."

A tabulation of the yields and physical properties of the unsaponifiable material, "extract" and "raffinate" are:

	Quantity, Grams	Specific Gravity	Sapon. No.	Hydroxyl No.
Unsaponifiable Material.	331	0.830 at 78.8° F.	3.7	
"Extract"	140	0.866 at 78.8° F.	4.7	85
"Raffinate" (Hydrocarbon).	161	0.802 at 78.8° F.	2.9	15
Loss	30			

The properties of the "extract" and "raffinate" show clearly that the degree of separation was rather satisfactory. The extract contained a high percentage of oxygenated compounds (high specific gravity and high hydroxyl number) and the raffinate consisted of almost pure unreacted hydrocarbons.

This invention is particularly applicable to any oxidized liquid or solid petroleum product. The conditions of oxidation (temperature, pressure, light and the like) are immaterial provided the oxidation product consists in addition to unreacted hydrocarbons, of peroxides, acids and other oxygen compounds specified in the previous part of this application. If the conditions of oxidation are too severe and/or not sufficiently controlled, asphaltic compounds can be formed in addition to the above-mentioned oxygen compounds.

As will be readily apparent to those familiar with the art, the principles of this invention may be incorporated in either a batch, continuous, or semi-continuous process. Unreacted hydrocarbons may be recycled to the oxidation step and the various separating steps may be cascaded to improve their efficiency.

The products of this invention have numerous uses. They may be used among other things as ingredients in lubricating compositions, or as intermediates in the formation of a wide variety of chemical compositions. Many of the products, for example, may be sulphated or sulphonated and used as detergents. Many may also be used directly as lubricants, or added to already existing lubricants in minor proportions to change the characteristics of the lubricants.

What is claimed is:

1. In the process of producing valuable oxidation products from hydrocarbons, which includes partially oxidizing a hydrocarbon to produce an oxidized product; treating said oxidized product with an aqueous solution of a caustic material at a temperature and for a period of time sufficient to saponify and neutralize the saponifiable and neutralizable material present in said oxidized product, to produce an oleaginous layer containing unoxidized hydrocarbons and oxygen-containing unsaponifiable material and a primary aqueous layer containing salts of oil-soluble organic acids and of water-soluble organic acids; separating said oleaginous layer from said primary aqueous layer; adding an acidic material to said primary aqueous layer to convert said salts of the oil-soluble organic acids and of water-soluble organic acids into free organic acids to product a layer containing the oil-soluble organic acids and a secondary aqueous layer containing the water-soluble acids; and separating said layer containing the oil-soluble organic acids from said secondary aqueous layer; the improvement which comprises neutralizing said secondary aqueous layer with an aqueous solution of a caustic material to convert the water-soluble organic acids into salts thereof; evaporating the water from the thus neutralized secondary aqueous layer to obtain a solid material containing said salts of said water-soluble organic acids; extracting said solid material with an alcohol to produce an extract containing said salts of said water-soluble organic acids; extracting the oleaginous layer containing the unoxidized hydrocarbons and the oxygen-containing unsaponifiable material with a solvent selective for said oxygen-containing unsaponifiable material to produce an

extract; and removing said solvent from said extract.

2. The process defined in claim 1, wherein the caustic material used in neutralizing the secondary aqueous layer is an alkali-metal hydroxide.

3. The process defined in claim 2, wherein the alcohol used to extract the alkali-metal salts of the water-soluble organic acids from the solid material is an alcohol mixture containing about 10 per cent methanol and about 90 per cent ethanol by volume.

4. The process defined in claim 2, wherein the solvent selective for the oxygen-containing unsaponifiable material is acetonitrile.

5. The process defined in claim 3, wherein the alkali-metal hydroxide is sodium hydroxide and the solvent selective for the oxygen-containing unsaponifiable material is acetonitrile.

ALFRED P. KOZACIK.
ALEXANDER N. SACHANEN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,059,232	Harder	Nov. 3, 1936
2,230,582	Beller	Feb. 4, 1941
2,237,301	Burk et al.	Apr. 8, 1941
2,287,128	Pirkle	June 23, 1942
2,361,547	Jenkins	Oct. 31, 1944
2,391,236	Hirsch	Dec. 18, 1945

FOREIGN PATENTS

Number	Country	Date
174,099	Great Britain	Jan. 16, 1922