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METHOD FOR REFINING ORGANIC ACIDS OBTAINED FROM OXIDIZED HYDROCARBONS

Arthur L. Blount, Palos Verdes Estates, Calif., assignor to Union Oil Company of California, Los Angeles, Calif., a corporation of California

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The present invention relates to the oxidation of hydrocarbons and more particularly pertains to the production of new and useful products resulting from the liquid phase oxidation of petroleum hydrocarbons with oxygen or oxygen-containing gases, such as air.

It is well known that the liquid phase oxidation of hydrocarbons gives rise to a wide variety of products embracing unsubstituted carboxylic acids, hydroxy acids, keto acids, aldehyde acids, alcohols, ethers, esters, ketones, resinous or resin-forming materials, and a number of other more or less oxygenated products, as well as unreacted or uncombined hydrocarbons. It is also known that the liquid phase oxidation of naphthenic or asphalt base petroleum fractions or distillates results in the formation of most of the aforementioned and other more or less oxygenated types of products. It is therefore the main object of the present invention to provide a method for treating said products of oxidation to isolate one or more new and valuable products or fractions having distinctive characteristics and utilities. A further object of the invention is to treat the products of the liquid phase oxidation of naphthenic or asphalt base petroleum fractions to produce and/or isolate therefrom the aforementioned new and useful products.

As previously stated, the oxidation of a naphthenic or asphaltic petroleum distillate produces a mixture containing some unreacted hydrocarbons and a mixture of products which are oxidized to a greater or less extent. These products vary in their solubility in the hydrocarbon fraction and in each other to such an extent that two phases are formed when the oxidation is sufficiently prolonged. In general, the more highly oxidized products are the least soluble, and their gradual formation during the progress of the oxidation is accompanied by the appearance and growth of the heavier second phase comprising them. This heavy phase which contains only minor amounts of unreacted hydrocarbons is hereinafter referred to as the "oil-insoluble fraction." Therefore, it is a still further object of the present invention to treat the oil-insoluble fraction obtained in the above liquid phase oxidation to isolate therefrom certain types of new and useful products having certain distinctive characteristics and utilities which will be more fully described hereinbelow.

It has now been discovered that the above and other objects may be obtained by the use of certain steps described hereinbelow, some of these steps being old per se, others being in the form of substitutions for known steps of operation, while still others constitute or comprise additional steps to be incorporated into the known methods of oxidation and treatment of petroleum fractions and particularly of fractions or distillates derived from naphthenic or asphalt base crude oils. These various steps will be pointed out hereinbelow with a typical description of a preferred form of realization of the treating operations constituting one of the objects of the present invention.

As stated above, the oxidation of a petroleum fraction, and particularly of one containing naphthenic constituents, gives rise to an oil-insoluble phase which is heavier than the conjugate phase comprising the unreacted hydrocarbons and products soluble therein. The oil-insoluble phase may be recovered by settling and decantation or by other obvious means, which process constitutes the first step in the treatment. By means of this step the oil-insoluble phase is recovered relatively free from unreacted hydrocarbons and from such oxidation products as are soluble in the oil phase. More prolonged settling, or washing with a light hydrocarbon solvent such as naphtha may be resorted to in order to free more completely the oil-insoluble phase from occluded or emulsified portions of the conjugate phase. If desired, the oil-insoluble phase may then be further subjected to a dehydrating step, such as to evaporative heating or refluxing with toluene with a trapped return, in order to remove any associated or dissolved water.

The oil-insoluble phase obtained as a result of the first step of phase separation with or without the additional steps of naphtha washing and/or dehydration, is a mass having a fluid to highly viscous consistency, and is of a brown to black color. This mass is substantially soluble in caustic alkaline solutions and substantially insoluble in light paraffinic hydrocarbons and heavier paraffin or naphthenic hydrocarbons, such as the stock from which it was produced, even when the solvent power of such hydrocarbons is enhanced by the presence of soluble oxidation products. It is distinguished from the oxidation product in toto by the absence of the more soluble or less oxidized oxidation products and also by the substantial absence of unreacted hydrocarbons. Chemically it is preponderantly acidic in character and may be roughly classed as consisting predominantly of oxy-acids such as hydroxy acids, keto acids, lactones, lactides, etc., on the basis of the observed acid numbers, saponification values, and oxygen contents, al-

though such evidence is of course far from conclusive as to the exact character of such a complex mixture. More particularly, it has been found that the oil-insoluble phase comprises fractions which vary greatly in their chemical and physical properties, and that for some uses the action of one fraction is antagonistic to that of another, so that the full utility of the product is available only upon resolution into simpler and more coherent fractions.

It has now been discovered that oxygen-containing di- and tri-basic inorganic acids, such as sulfuric or phosphoric acids are effective solvents or reagents in resolving the oil-insoluble phase into constituent fractions thereof, especially when used in conjunction with organic diluents or solvents in a manner which will be more fully described hereinbelow. It is therefore still a further object of the present invention to provide a process whereby the complex oil-insoluble phase obtained as a product of liquid phase oxidation of hydrocarbons may be treated with oxygen-containing di- or tri-basic inorganic acids to produce and/or isolate therefrom simpler fractions of a more homogeneous or purer character and of consequently greater utility.

For purposes of exposition, the invention will be more fully described in conjunction with a typical example, the various phases of the invention being discussed at greater length in connection therewith.

Approximately 38,000 grams of an untreated topped light gas-oil fraction obtained from naphthenic or asphalt base crude oil, and having a boiling point range of from 393 to 612° F. and a gravity of about 33° A. P. I. were oxidized by agitating with air for a period of seven hours at a pressure of 100 lbs. gauge and at an average temperature of 300° F. in the presence of approximately 210 grams of a magnesium oxide catalyst. By separation of the soluble and insoluble phases, an oil-insoluble phase was obtained which weighed 9580 grams or 25.2% on the basis of the original charge. In order to treat the oil-insoluble phase with sulfuric acid or the like in the most advantageous manner, it has been found essential to form a fluid and more or less dilute solution of said oil-insoluble phase. This is produced with the aid of a solvent which is relatively substantially inert to the sulfuric acid. It is, however, not necessary to choose a powerful solvent, such as chloroform or carbon disulfide, which is capable of dissolving the entire oil-insoluble fraction. In most instances preference is given to a moderately powerful solvent, such as benzene or toluene or mixtures of naphtha and chloroform, etc., which will dissolve and extract a relatively more liquid fraction and leave as a residue a highly viscous or even solid fraction which may subsequently be worked up or treated along different lines, which do not constitute any part of the present invention. By thus extracting the oil-insoluble phase with a selective solvent, an extract is obtained which is more amenable to treatment with sulfuric acid than when the entire oil-insoluble fraction is thus treated. Furthermore the products resulting from the subsequent acid treatment of this extract encompass a smaller variety of constituents, which is in line with the objects of the invention. The selective solvent used need not be indifferent to the sulfuric acid, and may comprise such materials as acetone or ethyl alcohol, provided that such solvent is supplanted by an indifferent solvent before treating with the sulfuric acid.

In the present instance, about 7500 grams of a substantially oil-free oil-insoluble phase was extracted with benzene to yield, after evaporation of the benzene, about 4000 grams of a benzene-soluble fraction. This extract fraction was redissolved in nine parts of benzene and the solution treated twice with one volume per cent portions of 60% sulfuric acid, the treatments being carried out at room temperature. The acid sludges were combined and set aside. The treated benzene solution was then extracted with dilute caustic to remove the free organic acids, and the aqueous soap solution thus obtained was decomposed with requisite quantities of a mineral acid to yield or liberate about 1350 grams of organic acids hereinafter referred to as the "refined benzene-soluble acids." The caustic washed benzene solution was then evaporated to yield approximately 1200 grams of material hereinafter referred to as "benzene-soluble neutrals." By hydrolyzing the acid sludge, as by strong dilution with water, or by the addition of aqueous alkali up to incipient neutralization, a still further oily water-insoluble fraction was obtained with a yield of 1000 grams, which fraction is hereinafter referred to as "sludge acids." Finally, the two aqueous phases representing the wastes from the above caustic extraction and the sludge hydrolysis were worked up to yield, respectively, 330 and 30 grams of "water soluble acids," this treatment being realized by extracting the aqueous phases with ethyl ether, or by salting out, by evaporation, etc.

Thus the oil-insoluble phase, apart from the initial formation of a benzene-insoluble fraction, has been resolved into four fractions, namely the refined benzene-soluble acids, the benzene-soluble neutrals, the sludge acids, and the water soluble acids, all of which, as will be shown subsequently, are substantially distinct in their chemical and physical properties.

In the present instance the crude benzene-soluble fraction was a black highly viscous material with an acid number of about 150, and a saponification number around 280. The iodine number and acetyl value indicated the presence of 0.62 double bonds and 2.1 hydroxyl groups per acid equivalent.

The refined benzene-soluble acids represented a material of tacky consistency and much better color than the crude benzene-soluble fraction; indeed they were transparent and red when viewed in thin layers. These refined acids had an acid number of 208, a saponification number of 234, an iodine number of 33.3, and an acetyl value of 198. These figures indicate the presence of 0.35 double bonds and 1.1 hydroxyl groups per acid equivalent. It is thus seen that the number of double bonds and hydroxyl groups were decreased substantially by 50% when compared to the number thereof in the crude benzene-soluble acids. Many uses suggest themselves for refined acids of this character, particularly in view of their solubility characteristics. In addition, they possess the unusual property of forming excellent resins when heated by themselves or with an equivalent quantity of glycerin. This property of resinification is also displayed to some extent by the crude benzene-soluble fraction, but the resins obtained from this latter material are less satisfactory from the viewpoint of color and consistency.

The sludge acids were approximately of the same consistency as that of the refined acids, and had an acid number of 71, a saponification num-

ber of 98, an iodine number of 105, and an acetyl value of 112. On the basis of these figures, 3.26 double bonds and 1.7 hydroxyl groups are indicated per acid equivalent. Such relatively high unsaturation and hydroxylation make this acidic fraction of interest for many uses, in addition to which it displays resinifying properties approaching, but not equalling, those of the refined benzene-soluble acids.

The benzene-soluble neutral fraction is a fluid material with a terpene-like odor, having an acid number of 6, a saponification number of 119, an iodine number of 35.4, and an acetyl value of 112. It can thus be characterized as consisting largely of esters and similar saponifiable materials, which apparently bear free hydroxyl groups. The characteristics of this fraction adapt themselves well for use in the manufacture of solvents, plasticizers, resins, etc.

The water-soluble acids are of syrupy consistency, and have an acid number of 372, a saponification value of 383, an iodine number of 12.2, and an acetyl value of 200. These figures indicate the presence of 0.07 double bonds and 0.7 hydroxyl groups per acid equivalent. This fraction thus represents a cheaply produced mixture of water-soluble hydroxy acids, and as such should find many uses in the arts.

The treatment of the crude benzene-soluble acids with a di- or tri-basic inorganic oxygen-containing acid may obviously be realized under various conditions. Thus, the optimum concentration of the inorganic acid depends on the character of the material treated, its degree of dilution in an inert diluent, the type of inorganic acid employed, as well as the degree of purification desired. Sulfuric acid has been found to be effective in concentrations ranging from 40 to 95%, and even higher, the most economic concentrations being in the neighborhood of 60 to 80%. However, to realize the same degree of purification or treatment with phosphoric acid as the treating agent, it has been generally found that a slightly higher range of concentration is generally necessary. Obviously the quantity of inorganic acid used must vary according to the character of the acid employed and the degree of refining desired. The most practical results have been obtained by the use of from 1 to 5 volume percent of the inorganic acid as calculated on the basis of the volume of the solution treated. Generally speaking sharper separation and more effective treatment is realized by increasing the degree of dilution of the organic acids with the inert solvent. Obviously, such dilution must be maintained within limits since excessive dilution will necessitate the handling of a large bulk of solute, and the use of unnecessarily large quantities of inorganic acid. Such procedure would thus become cumbersome and probably uneconomical. The optimum dilution, from a practical and economical standpoint, has been found to fall within the range of the use of from 5 to 15 volumes of diluent-solvent to one volume of the organic acids to be treated. This range, however, varies to some extent with the character of the solvent and of the material treated.

It has been also found that the above described process of treatment with an inorganic acid in the presence of a solvent or diluent is not limited to the refining of crude benzene-soluble acids, but is also applicable, without essential modifications, to the treatment of other acidic fractions arising from the oxidation of petroleum oils, their fractions or distillates. Thus, the above process may be used to refine or purify the oil-insoluble phase, the oil-soluble phase, or any and all fractions or cuts thereof. In case of acid treatment of the oil-soluble phase, the unreacted stock may form a portion or even all of the diluent. It is obvious that in these diverse applications the diluent-solvent must be so chosen that it is capable of dissolving the material to be treated.

In general, it is advantageous to use a solvent with a boiling point range differing from that of the material treated. In such a case, the solvent which may be dissolved in or emulsified with the soap phase (during the alkali extraction which follows the acid treating step) may then be readily removed for example by evaporation or distillation. The use of such solvents having a different boiling point range from that of the organic acids dissolved therein, is however not essential if the presence of small traces of such solvents in the refined organic acids is not objectionable. Furthermore, it is to be noted that the presence of the diluent-solvent tends to suppress the aforementioned emulsification during the saponification step.

In case it is not deemed advantageous or desirable to separate the neutral oils as a separate fraction, the solvent may be removed from the treated acidic material by a simple evaporation or distillation. Obviously, such a procedure necessitates the initial use of a solvent which has a different and preferably a lower boiling point range from that of the organic acidic fraction treated.

The acid numbers and saponification values presented hereinabove refer to the milligrams of potassium hydroxide necessary to neutralize or saponify respectively, one gram of the acidic material. It is obvious that the acid numbers, saponification values, iodine numbers and acetyl values, as well as the number of double bonds and hydroxyl groups per acid equivalent, are only specific to the particular fraction when obtained from the given original stock by the various steps of operation described hereinabove. These specific characteristics will naturally vary to a certain degree with a change in the original stock and the degree and character of oxidation and subsequent treatment. It has however been found that the general physical and/or chemical features of these various fractions will remain substantially constant, or at least similar to those described hereinabove.

It is to be understood that it is desired to comprehend within this invention such modifications and changes as may adapt it to varying conditions and uses, the various phases of the invention being limited only by the scope of the appended claims.

I claim:

1. In a process of treating products of liquid phase oxidation of hydrocarbons, the steps of separating said products of oxidation into a phase soluble in the unreacted hydrocarbons and a phase insoluble therein, extracting said hydrocarbon insoluble fraction with a selective solvent selected from the class consisting of benzene, toluene, ethyl alcohol, acetone and mixtures thereof with naphtha and chloroform, and treating the fraction soluble in said selective solvent with an inorganic acid selected from the class consisting of the oxygen-containing di- and tribasic acids.

2. In a process according to claim 1 wherein

the acid treatment is realized in the presence of the selective solvent employed for the above-mentioned extraction of the hydrocarbon insoluble fraction.

3. A process for treating products of liquid phase oxidation of naphthenic petroleum oils which comprises separating said products of oxidation into a phase soluble in the unreacted oils and a phase insoluble therein, commingling said oil-insoluble fraction with a selective solvent selected from the class consisting of benzene, toluene, ethyl alcohol, acetone, and mixtures thereof with naphtha and chloroform, separating the phase insoluble in said selective solvent from the phase soluble therein and treating the phase soluble in said solvent with an inorganic acid selected from the class consisting of the oxygen-containing di- and tri-basic inorganic acids.

4. In a process according to claim 3 wherein the acid treating step is realized in the presence of a solvent inert to the action of the inorganic acid but in which the material treated is soluble.

5. A process for treating products of liquid phase oxidation of naphthenic petroleum oils which comprises separating said oxidation products into a phase soluble in the unreacted oils and a phase insoluble therein, commingling said oil-insoluble fraction with benzene to cause phase separation between the fractions soluble in said solvent and a fraction insoluble therein, and treating said benzene-soluble phase with an inorganic acid selected from the class consisting of the oxygen-containing di- and tri-basic inorganic acids.

6. In a process according to claim 5 wherein sulfuric acid is employed in the acid treating step.

7. In a process according to claim 5 wherein sulfuric acid in concentrations ranging from approximately 40 to 95% is employed in the acid treating step.

8. A process for treating products of liquid phase oxidation of naphthenic petroleum oils which comprises separating said products of oxidation into a phase soluble in the unreacted oils and a phase insoluble therein, extracting said oil-insoluble phase with benzene to separate therefrom the benzene soluble phase, commingling said benzene soluble phase in solution in said benzene with sulfuric acid of a concentration ranging from about 45 to 90% and in quantities ranging from about 1 to 5 volume percent as calculated on the basis of the volume of the solution treated, separating the sludge acids thus produced, and further treating the acid treated solution thus produced to extract therefrom the resin-forming acids present therein.

9. In a process according to claim 8 wherein the last mentioned treatment comprises saponification of the organic acids present in said acid treated solution, separation of the soap solution thus produced from the unsaponified materials, and the liberation of the resin-forming acids from said solution by addition of necessary quantities of an inorganic acid.

ARTHUR L. BLOUNT.