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SOLVENT EXTRACTION OF OXYGENATED PRODUCTS

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The present invention relates to oxidation, and more particularly pertains to the production of new and useful products resulting from liquid phase oxidation of petroleum hydrocarbons. It is well known that products resulting from liquid phase oxidation of petroleum hydrocarbons comprise a heterogeneous mass containing uncombined or unconverted hydrocarbons, simple carboxylic acids (which may be saturated or unsaturated or both), hydroxy acids, keto acids, resin forming acids, alcohols, ethers, esters, lactones, resinous substances and a mixture of other more or less oxygenated products. It is also known that the liquid phase oxidation of petroleum fractions, and particularly of petroleum fractions which are derived from naphthenic asphalt-base crude oils, produces a mass containing most if not all of the aforementioned as well as other oxygenated products.

It is therefore the main object of the present invention to provide a method for treating complex mixtures of products of oxidation to isolate therefrom one or more new and valuable products or fractions having distinctive characteristics and utilities. A further object of this invention is to treat the products of liquid phase oxidation of petroleum fractions from naphthenic and/or asphalt-base crude oil stocks to recover therefrom the aforementioned new and useful product or products.

As previously stated an oxidation of a petroleum fraction containing naphthenic hydrocarbons, upon oxidation in a liquid phase as by contacting said petroleum fractions with air or a similar oxygen-containing gas at proper or optimum pressures and temperatures, and preferably in the presence of oxidation promoting catalysts, produces a mixture containing some unconverted petroleum hydrocarbons and a heterogeneous mass of products which are oxidized to a greater or less extent. This heterogeneous mixture containing the more or less oxygenated products and the unconverted petroleum hydrocarbons may be easily separated into two fractions, one of which is soluble in the petroleum being oxidized while the other is insoluble therein. This fractionation may be accomplished by a mere decanting of the heterogeneous mixture, the insoluble fraction precipitating out of solution when the mixture is allowed to stand. The present invention deals with that fraction of the oxidized products which is soluble in the petroleum hydrocarbon under treatment, said fraction being hereinbelow referred to as the "oil-soluble fraction," and the acids therein being generally termed as the "oil-soluble acids." Therefore, a still further object of the present invention relates to the treatment of the oil-soluble acids recovered from the above-mentioned liquid phase oxidation of petroleum fractions to isolate from said oil-soluble acids certain types of new and useful acids having certain distinct characteristics and utilities more fully described hereinbelow.

It has now been discovered that the above and other objects may be attained by the use of certain steps described hereinbelow, some of these steps being old when used alone, 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 or processes of oxidation and treatment of petroleum oils, their fractions and/or distillates, and particularly of fractions which are predominantly naphthenic in character.

As stated above, the products of oxidation of petroleum fractions, and particularly of fractions derived from naphthenic and/or asphalt base crude oil stocks, may be separated by decantation into the oil soluble and oil insoluble phases. The oil soluble fraction besides containing the unconverted or unoxidized petroleum fraction, is composed of various simple carboxylic acids, keto acids, hydroxy acids, esters, ethers, lactones, etc. It is therefore a still further object of the present invention to provide a method for treating the oil soluble fractions so as to remove therefrom one or more specific acidic fractions contained therein. A still further object is to recover fractionally one or more of the aforementioned simple carboxylic acids, hydroxy acids, keto acids, esters, ethers, lactones, etc. present in the oil soluble fraction and generally denominated herein as the oil soluble acids.

It has now been discovered that various oil soluble acids may be separated, either fractionally or substantially completely from the oil soluble fraction or phase by the use of certain anti-solvents, which, in conjunction with the unoxidized hydrocarbons, cause said oxygenated products, (or at least certain types thereof) to precipitate out of solution in said oil soluble phase.

It has been further discovered that the quantity of said anti-solvent added to the oil soluble phase, i. e. the ratio of anti-solvent to the oil soluble fraction, determines the quantity and even the type of the oxygenated products precipitated or rejected by such addition of the anti-solvent. Thus, it was found that with a gradual increase in dilution or addition of said anti-solvent, the precipitation of the various types of

oxygenated products increases. It was also found that the acidic fractions rejected by dilution with an anti-solvent contained a comparatively large quantity of esters and similar substances as those shown by the relatively high saponification value of such rejects. Also some of the experiments disclosed that the gradual or further increase in the quantity of anti-solvent added to an oil soluble acidic fraction rejected acidic fractions having progressively or gradually lower acid and saponification numbers. These experiments further disclosed that the rejects produced by the dilution of the oil soluble phase with an anti-solvent of the class described more fully hereinbelow, contained acids which were predominately insoluble in petroleum ether. On the other hand, the acids remaining in the oil soluble phase after such treatment with an anti-solvent were mostly soluble in said petroleum ether.

It has been further found that liquefied normally gaseous hydrocarbons such as liquid propane, butane, or mixtures thereof, may be advantageously used as the anti-solvent adapted to cause the precipitation of the aforementioned oxygenated products. Although these liquefied but normally gaseous hydrocarbons may be employed at ordinary temperatures and high pressures, best results have been obtained when the extraction operation was realized at sub-normal temperatures and even temperatures below 0° F. Thus, the use of liquefied propane at room temperatures may precipitate some of the oxygenated products, while dilution of the oil soluble fraction with the same quantity of liquid propane at temperatures below 0° F. causes the precipitation of greater quantities of oxygenated products, some of which have comparatively lower acid and saponification numbers and may include the less oxidized hydrocarbons.

It is to be noted at this point that some experiments have shown that the dilution of the oil-soluble fraction with petroleum ether, when carried out at normal temperatures and atmospheric pressures, would not produce any precipitation, the whole-oil soluble fraction being apparently soluble in or miscible with said petroleum ether. In other cases, only a very small percentage would be rejected when operating with petroleum ether under the above conditions. On the other hand the same experiments have disclosed that the use of prechilled petroleum ether or the chilling of a solution of oil-soluble fractions in petroleum ether, caused the precipitation of considerable quantities of oxygenated products. The invention, therefore, includes the use of diluents or anti-solvents in which the oxidized products are soluble at normal temperatures but which cause the precipitation of the more or less oxidized fractions when the said diluents or anti-solvents are at sub-normal temperatures.

The above described fractional separation of the oxygenated products is valuable because of the fact that the various products constituting the heterogeneous mixture of oxidized bodies have individual utilities. Thus, certain of the fractions or acids have distinct resin forming characteristics when chemically combined with glycerine or when treated so as to cause polymerization. On the other hand, another group of acids and particularly the so-called simple carboxylic acids have definite characteristics which are similar to those of naphthenic acid and may, therefore, find use as substitutes for such naphthenic acids. The process briefly described hereinabove is highly valuable in that it permits the fractional separation of the various types of kinds of oxygenated products present in the aforementioned oil-soluble fraction obtained by decanting of the mixture produced by liquid phase oxidation of hydrocarbons and particularly of petroleum hydrocarbons containing naphthenic fractions.

Thus, addition of a certain quantity of liquid propane or of chilled petroleum ether to the oil soluble fraction will cause the rejection of an acidic fraction containing a considerable percentage of esters. The acids derived from this reject have a high saponification value and a relatively high acid number. These acids are substantially completely insoluble in petroleum ether. After separation of this acidic group, the addition of certain quantities of anti-solvent such as liquid propane will cause the rejection of another acidic fraction also high in esters. The acids recovered from this acidic fraction although also substantially insoluble in petroleum ether will be found to have saponification values and acid numbers which are lower than those of the acids recovered from the first reject. Further addition of the anti-solvent to the oil soluble fraction thus treated permits the removal of additional quantities of oxygenated products which have progressively relatively lower acid numbers and saponification values. Such a procedure leaves an oil soluble fraction containing an acidic fraction which is substantially free of esters and similar oxygenated products. In fact it may be possible to treat the oil soluble fraction with such quantities of an anti-solvent that the acidic fraction remaining in said oil soluble fraction will consist substantially of acids of the simple carboxylic type.

The separation of the simple carboxylic acids, either alone or in combination with the other acidic fractions remaining in the oil soluble phase after the above treatment with an anti-solvent may be realized in a number of ways. However, it has been found that it is best to remove said acids by an extraction with an alkali. For this purpose the diluted hydrocarbon mixture, containing these simple carboxylic acids and the other oxygenated products remaining in solution, may be first treated to remove the anti-solvent. When using liquid propane or petroleum ether or a similar anti-solvent, this removal may be adequately realized by mere distillation. It is sometimes desirable to retain the diluent through the following alkali extraction in order to prevent excessive emulsification. The oil, freed from diluent or not, may be treated with an alkali which converts the oxygenated products still present in said fraction into their respective salts or soaps, the unconverted or unoxidized hydrocarbons being left in an unchanged form. The aqueous soap solution thus produced may then be decanted and the organic acids liberated therefrom as by addition of optimum quantities of acid such as sulfuric acid. It is obvious that such a procedure is not only advantageous in that it causes fractionation between the various types or grades of acids, etc., but it also eliminates the necessity of employing large quantities of alkali. Thus, if all of the oxygenated products present in the above described oil soluble fraction were to be removed by a mere saponification, it would be necessary to employ excessively large quantities of an alkali. Even then only the relatively highly acidic products will be converted into their soaps and/or salts, while the esters, ethers and like oxygenated prod-

ucts are saponized only when the alkali treatment is carried out or realized under or at relatively high temperatures and/or with strong saponifying agents. These operations are obviously highly cumbersome and expensive and still do not realize the desired fractionation of the various types of oxidized products obtained from the liquid phase oxidation of hydrocarbons of the type described hereinabove.

For purposes of exposition, the invention will be more fully described in conjunction with typical examples, and the various phases of the invention will be discussed at greater length in connection with the description thereof.

Example I

A petroleum hydrocarbon fraction having an average gravity of 60.4° A. P. I. and an Engler distillation range of from 109 to 284° F. was oxidized. An analysis of the hydrocarbon stock showed that it contained approximately 54% by weight of naphthenes, about 43% by weight of paraffines and respectively 1 and 2% by weight of unsaturates and aromatics. The oxidation was carried out at a pressure of approximately 50 lbs. and at a temperature of 270° F., a copper naphthenate catalyst being used in a quantity of about 0.1%. The oxidation reaction was continued for 48 hours, at the end of which period the charging stock was found to have acquired a brownish color and a terpene-like odor. After the cooling of the mixture comprising the reaction products, the oxidized products insoluble in the hydrocarbon stock were found to have precipitated out of solution. The oil-soluble phase was diluted with a cold propane at atmospheric pressure. This dilution caused a precipitation of certain of the hydroxy and keto acids, etc., which were separately removed. The precipitate was found to be viscous, and brown in color and approaching the consistency of a wax. The hydrocarbon-propane mixture still containing certain of the acids in solution was then distilled to remove the propane. The acids were then extracted from the hydrocarbon phase by the addition thereto of optimum quantities of alkali. This caused the saponification of the acids. The aqueous soap solution was then removed as the lower phase, the acids being liberated therefrom by the addition of the proper amount of sulfuric acid. The acids thus recovered were water white in color and quite fluid even at room temperatures. It is thus seen that even from an analysis of the physical appearances of the two types of oxygenated products extracted from the above oxidized hydrocarbon fraction, that the liquid propane had effected a selective separation.

Example II

The following experiment is presented to show the characteristics of rejects obtained by progressive addition of an anti-solvent to the oil soluble phase. In this case two gallons of a topped light gas oil fraction derived from a California Valley crude oil stock and having a gravity of 33.3° A. P. I. and a boiling point range of 383° to 640° F. was oxidized for seven hours at an average temperature of 300° F. and a pressure of 100 lbs. gauge. During this oxidation approximately 300 cubic feet of air was passed through the gas oil, the oxidation reaction being carried out in the presence of 50 grams of magnesium oxide catalyst. The products of oxidation produced by this oxidation were then decanted to separate and remove the oil insoluble fraction.

The supernatant or oil soluble phase was then treated twice with liquid propane to produce two rejects. For this purpose 2400 grams of the oil soluble phase were first commingled with an equal volume of propane, the mixture being maintained at the boiling point of said propane. This amounts to approximately —40° F. at atmospheric pressure. The treatment with this quantity of liquid propane caused the formation of a reject weighing slightly over 80 grams. This reject had an acid number of 80 mg. KOH/g. and a saponification value of 183. The relatively high saponification value as compared to the acid number of this reject indicates the presence of comparatively large quantities of esters and similar oxygenated products. For the purpose of extracting the simple carboxylic acids and similar substances, this reject was treated with an alkali which saponified the simple carboxylic acids and similar substances such as the easily saponifiable lactones. After the separation of the soap solution from the unsaponified phase, and after the liberation of the acids from said soaps, as by the addition of requisite quantities of a mineral acid, the acidic fraction thus recovered weighed 22.3 grams and had an acid number of 163 mg. KOH/g. An extraction with petroleum ether showed that only 3.5 grams, or approximately 13.7% of the acids thus recovered were soluble in petroleum ether. These acids had an acid number of 174 and a saponification value of 253. On the other hand the petroleum ether insoluble acids weighed 18.8 grams, had an acid number of 159 and a saponification value of 225.

To obtain a second reject, additional quantities of liquid propane at the above mentioned low temperatures were added to the oil soluble phase until the mixture contained 300 volume percent of propane. This treatment produced a second reject weighing approximately 137 grams and having an acid number of 64 and a saponification value of 163. As in the previous case, the high ratio of the saponification value to the acid number indicates that this reject contains considerable quantities of esters. When treated as described above with reference to the first reject, this second reject produced about 42 grams of acids having an acid number of 155. This acidic fraction contained slightly less than 7 grams of petroleum ether soluble acids having an acid number of 157 and a saponification value of 231, the petroleum ether insoluble acids having an acid number of 138 mg. KOH/g.

A comparison of the acid numbers and saponification values of the petroleum ether soluble and insoluble acids obtained from both of these rejects showed that the first reject had higher acid numbers and saponification values. Also it is to be noted that both rejects predominated in the petroleum ether insoluble acids as compared to the quantities of acid soluble in this solvent.

The acidic fraction still remaining in the oil soluble phase after the treatment with liquid propane was then extracted by treating the oil soluble phase with cold caustic solution thereby saponifying the acids. These acids were then liberated from the soap solution by the well-known method of adding the requisite quantities of a mineral or inorganic acid. The acidic fraction thus recovered from the propane treated oil soluble phase weighed 141.5 grams, had an acid number of 168 and a saponification value of 192. Of this acidic fraction only 23 grams were insoluble in petroleum ether, this petroleum in-

soluble fraction having an acid number of 163 and a saponification value of 281.

As stated above, most of the acids recovered from the oil soluble phase after treatment with propane were soluble in petroleum ether. These petroleum ether soluble acids, weighing about 118.5 grams were then treated in solution in said petroleum ether with small quantities of sulfuric acid. Although in the instant case this treatment was carried out with two volume percent of 80% sulfuric acid, it is to be understood that other strengths as well as quantities of sulfuric acid or of any other oxygen containing di- or tri-basic organic acid may be used with substantially equivalent results. After the separation of the sludge produced by this acid treatment, the acids recovered after this acid treatment weighed about 50 grams and had an acid number of 210 mg. KOH/g. and a saponification value of 211. This acidic fraction was found to be substantially soluble in propane and had characteristics similar to those of naphthenic acids.

As a further modification, the acid treating step described above may be carried out on the oil-soluble phase soluble in the propane. In such a case, the solution in propane (after removal of the rejects) is treated with necessary quantities of a di- or tri-basic inorganic acid. After removal of the sludge, the solution is commingled with an alkali to saponify the acids. The soap solution may then be removed and treated to liberate the acids. These acids will be substantially similar to the acids obtained by the acid treatment of the aforementioned petroleum ether soluble acidic fraction.

Instead of using reagents of the type of alkalies, the propane solution may be extracted with selective solvents, such as aqueous ethyl alcohol, sulfur dioxide, aqueous acetic acid and the like, thereby extracting the oxygenated products present in the diluted oil-soluble phase.

It is obvious that many other changes and modifications are within the scope of the present invention, and it is therefore to be understood that the invention is not to be limited by any specific details presented herein, but are to be considered as being coextensive with the scope of the appended claims.

I claim:

1. In a process for resolving products of liquid phase oxidation of hydrocarbons, the step of extracting the hydrocarbon soluble fraction of said products of oxidation with a liquefied normally gaseous hydrocarbon adapted to reject an oxygenated fraction containing esters and carboxylic acids predominantly insoluble in petroleum ether.

2. In a process according to claim 1 wherein the selective solvent is liquid propane.

3. In a process according to claim 1 wherein the selective solvent is liquid propane and wherein the extraction step is realized at sub-normal including freezing temperatures.

4. A process according to claim 1 wherein the extraction step is realized at subnormal and even freezing temperatures.

5. In a process for resolving products of liquid phase oxidation of petroleum fractions derived from naphthenic, asphalt-base and similar crude oil stocks, the steps of separating the oil-soluble phase from the fraction insoluble therein, and commingling said oil-soluble phase with successively increasing quantities of liquid propane thereby obtaining a plurality of rejects containing esters, similar oxygenated products and carboxylic acids having progressively lower acid numbers and saponification values, said propane being maintained in a liquid state by proper regulation of temperature and pressure conditions.

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