Patented Apr. 8, 1941 2,237,301

UNITED STATES PATENT OFFICE

2,237,301

MANUFACTURE OF OXIDIZED PETROLEUM ACID COMPOUNDS

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No Drawing. Application February 10, 1938, Serial No. 189,896

10 Claims. (Cl. 260—452)

In making carbon acids for higher molecular weight fatty acids by oxidizing hydrocarbons the known commercial procedure has been based more particularly upon oxidation of paraffin wax by means of air and a rather high temperature, and with production of a mixture of acids in quite a wide range molecularly, there apparently being sufficient cracking of the original hydrocarbons to considerably increase the scattering range of the products. With this procedure, a practicable separation has not been possible such as to permit adaptation to certain usages, and a more controllable procedure has been desired in the art. To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

As starting material we employ liquid hydrocarbons or petroleum in a rather narrow cut or fraction, for instance, a fraction below gas oil range, and for example of 350 to 550° F.; such as of stocks of Pennsylvania or Michigan source, that is suitably paraffinic or at least predominantly paraffinic or saturated, being particularly feasible. Desirably, even closer cuts may be employed, as for example 350 to 450° F. B. P., in any case the precise range of fraction depending upon the particular end products in view, and having regard also to consideration of relative costs where more expensive distillation may be involved. For a given desired acid number product, petroleum raw material thus is taken having definite boiling points, that is correlated molecular weight or carbon atoms. And, by the avoidance of molecular break down, because of the low conversion rate per pass and the closely controlled operations characteristic of the invention, liquid petroleum fractions of desired carbon atom number are converted into products of the desired acid number character. For most practical applications, products of acid number 150–350 are particularly desirable, and for the special range of these which may be immediately desired the starting material is chosen as above indicated. This, brought up to reaction temperature by heating, is subjected to the action of oxygen, or more commonly air, blown into the liquid under controlled conditions. The initial temperature depends somewhat upon the particular hydrocarbon treated, whether of low or higher molecular weight, i. e. boiling point; but corresponding thereto the temperature is such as to avoid excessive vaporization of the hydrocarbon under the pressure conditions employed. In general, in accordance with the material operated upon, the pressure may be about 60 to 140 pounds per square inch and the temperature about 290–360° F. The reaction is exothermic, heat being generated, and in the operation of the process the temperature is carefully controlled in a desired reaction range, suitable temperature controlling means being employed. Vapors leaving the reaction zone are condensed and water is separated out, while condensed oil is returned to the reaction zone. With particular convenience, fresh feed hydrocarbon is introduced into the reaction zone continuously, for instance at the top, and on attaining an acid number suitable, as for example between 5 and 20, or 25, liquid is drawn off, for instance at the lower portion and preferably continuously. The air introduced into the reaction zone may be at a convenient operating pressure, desirably for instance 60–150 pounds per square inch, and is thoroughly disseminated into the liquid by suitable means to effect the distribution and action. The air feed rate may be 2 to about 100 cubic feet per hour per gallon of oil being reacted, and preferably about 27 cubic feet per hour per gallon, and usually not over 40. In the oxidizing reaction, it is preferable to recycle unreacted material going through, this being returned in successive passes. With particular advantage in starting, although not indispensable, the reaction may be carried on in the presence of a small amount of an agent acting as a catalyst. This may be for instance a manganese salt of a high molecular acid as manganese stearate, mangnese naphthenate, etc.

The liquid withdrawn from the oxidizing zone is reacted with an alkali metal compound, as sodium carbonate solution or preferably sodium hydroxide, 0.5 N. to saturation at room temperature for sodium carbonate, for instance or 2.5 N. for caustic soda. Thus, 10–20° Bé. NaOH may be used in quantity to give nearly complete consumption thereof. This reaction is carried on at a temperature of 175–320° F., preferably slightly below 212° F., for instance about 210° F., and under the full pressure of the system as afore-mentioned, or at least 20 pounds pressure. Where employing caustic soda solution of about 2.5 N. the reaction time may be 15–60 minutes, depending somewhat upon the particular condi-

tions and efficiency of mixture. Preferably, the reaction is carried out by countercurrent mixing of the acid liquid and the alkaline solution, and this may be effected in two stages or more, and a concentration of 4 N. caustic soda is desirably employed, at least in one of the stages.

The product of the alkali reaction stage contains some unsaponified material which has been carried through, and this tends to emulsify and be held so closely that practical methods of settling, centrifuging, etc., are ineffective to bring about a satisfactory removal. Such material going through into the final products has the result of lowering the acid number and also detracting from the odor of the material. In accordance with our procedure, this may be avoided, and oxidation products whether from the foregoing or from other sources may be brought into particularly pure condition by the operations hereinafter described, or by such portion thereof as may be desired in any given instance.

While the reaction mass or alkali metal salts produced by the alkali reaction upon the oxidation acids may be directly treated to free the acids, it is preferably subjected first to treatment eliminating unsaponified material. For this it is advantageous to flash off the unsaponifiable material by passing in steam or by heating the soap solution. The time should be controlled, to avoid polymerization. Or in some cases, we may subject the mixture to solvent extraction, extracting with such solvents as benzene, petroleum ether, etc., the solvent being employed in amount of ½ to 4 volumes, being thoroughly mixed with the material, and then allowed to settle and stratify into layers. The alkali salt or soap layer retains some solvent, which may be removed therefrom by distillation, and the solvent layer proper which contains the unsaponified material may be also subjected to separation, as by distillation, and the solvent may be returned for re-use in the system.

The alkali salt or soap material obtained is now acidified to obtain the formed oxidation acids. The temperature of this operation is desirably controlled in elevation to at least 125° F. Sulphuric acid may be used as acidifying agent or the light acids produced in the process can replace part of the sulphuric acid in the event such acids are not desired for other uses. Vigorous agitation is applied in the acidification step, and after acidification the material is allowed to settle one-fourth to one-half hour, preferably one-half hour.

Following the acidification to release the oxidation acids the latter are removed, and it is desirable to cleanly recover the acids from the bottoms, this involving a stripping action under conditions not decomposing the acid and not carrying over spray to discolor the product. In this step the maximum bottoms temperature utilized is less than 700° F. or desirably less than 600° F., and the distillation tower is preferably operated at below 100 mm. pressure, for instance 20–25 mm. and with sufficient steam to meet such conditions. For example, about one and one-half parts by weight of steam, based on the distilled acid, may be used; and the linear velocities in the tower should not exceed about 2 feet per second, while the time of distillation should be kept down, for example, in the range of 20 to 30 minutes. If desired, the distillation can be operated to accomplish fractionation of the acids, as for particular products. Or fractionating can be provided by a further special fractionation. The distillations can be carried out either by continuous or batch operation. The freshly distilled acid is clear and pale in color and of satisfactory odor. The acid is useful for further treatment to convert into salts of heavy metals suitable e. g. as siccatives.

For further improvement of the odor, the acid product may be re-dissolved in caustic soda solution, for instance of the initial concentration, and may be subjected to solvent extraction with a solvent selective for contaminating material, such as for instance benzene, petroleum ether, etc. The solvent in amount of about 1 to 4 volumes is thoroughly mixed with the distilled acid and the mixture is allowed to settle and stratify into layers, the solvent containing the impurities, and the other layer being the oxidation acid. The acid product is then released by acidifying as with the original crude product and the acid is distilled off.

The color of the distilled acid may tend to deteriorate, particularly where there has been a solvent extraction of distilled acid redissolved in alkaline solution. Corrective of this, we may treat the acid with zinc and hydrochloric acid, or we may apply to the freshly distilled acid an agent which we have found to inhibit the color change, and which we may term a "coloration-inhibitor." As such agent hydroquinone may be used.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

We therefore particularly point out and distinctly claim as our invention:

1. In a process of manufacturing oxidized petroleum acid compounds, heating in the neighborhood of 320° F. a petroleum fraction of 350–550° F. B. P., blowing air therein at about 120 pounds pressure at the rate of about 27 cubic feet per hour per gallon of petroleum, in the presence of a catalyst, controlling the temperature at 290–360° F., maintaining the acid number in the reaction mass at about 5–20, while continuously introducing fresh petroleum and drawing off liquid, reacting the drawn-off liquid in countercurrent flow with about 4 N. caustic soda solution, at 175–320° F. and 20–140 pounds pressure per square inch, returning unoxidized petroleum to the oxidizing operation, eliminating unsaponified material by extracting the mass with a selective solvent, acidifying the mass at around 125° F. to release the oxidation acid from the alkaline salt, distilling the released acid, re-dissolving the oxidation acid in caustic soda solution, extracting the solution with a selective solvent for odorous contaminants, removing the acid, and treating the acid with material eliminating coloration.

2. In a process of manufacturing oxidized petroleum acid compounds, heating in the neighborhood of 320° F. a petroleum fraction of 350–450° F. B. P., blowing air therein at 78–140 pounds pressure at the rate of about 27 cubic feet per hour per gallon of petroleum, in the presence of a catalyst, controlling the temperature at 290–360° F., maintaining the acid number in the reaction mass at about 5–20, while continuously introducing fresh petroleum and drawing off liquid, reacting the drawn-off liquid in countercurrent flow with about 4 N. caustic soda solution, at 175–320° F. and 20–140 pounds pressure per square inch, returning unoxidized petroleum to

the oxidizing operation, eliminating unsaponified material by extracting the mass with a selective solvent, acidifying the mass at around 125° F. to release the oxidation acid from the alkaline salt, distilling the released acid, re-dissolving the oxidation acid in caustic soda solution, extracting the solution with a selective solvent for odorous contaminants, removing the acid, and treating the acid with zinc and hydrochloric acid.

3. In a process of manufacturing oxidized petroleum acid compounds, heating in the neighborhood of 320° F. a petroleum fraction of 350–550° F. B. P., blowing air therein at 68–140 pounds pressure at the rate of about 27 cubic feet per hour per gallon of petroleum, in the presence of a catalyst at the start, controlling the temperature at 290–360° F., maintaining the acid number in the reaction mass at about 5–20, while continuously introducing fresh petroleum and drawing off liquid, reacting the drawn-off liquid in countercurrent flow with caustic soda solution, at 175–320° F. and 20–140 pounds pressure per square inch, returning unoxidized petroleum to the oxidizing operation, eliminating unsaponified material by extracting the liquid with a selective solvent, acidifying the mass at around 125° F. to release the oxidation acid from the alkaline salt, distilling the released acid, re-dissolving the oxidation acid in caustic soda solution, extracting the solution with a selective solvent for odorous contaminants, removing the acid, and treating the acid with material eliminating coloration.

4. In a process of manufacturing oxidized petroleum acid compounds, oxidizing a petroleum distillate fraction, controlling the temperature at 290–360° F., maintaining the acid number in the reaction mass at about 5–20, while continuously introducing fresh petroleum and drawing off liquid, reacting the drawn-off liquid with caustic soda solution, at 175–360° F. and 20–140 pounds pressure per square inch, eliminating unsaponified material by extracting the mass with a selective solvent, acidifying the mass at around 125° F. to release the oxidation acid from the alkaline salt, and distilling the released acid.

5. In a process of manufacturing oxidized petroleum acid compounds, heating a petroleum distillate fraction, blowing air therein, controlling the temperature at 290–360° F., continuously introducing fresh petroleum and drawing off liquid, reacting the drawn-off liquid with caustic soda solution, at 175–320° F. and 20–140 pounds pressure per square inch, eliminating unsaponified material by extracting the mass with a seletcive solvent, acidifying the mass at around 125° F. to release the oxidation acid from the alkaline salt, and distilling the released acid.

6. In a process of manufacturing oxidized petroleum acid compounds, heating a petroleum distillate fraction, blowing air therein, maintaining the acid number in the reaction mass at about 5–20, while continuously introducing fresh petroleum and drawing off liquid, reacting the drawn-off liquid with caustic soda solution, at 175–320° F. and 20–140 pounds pressure per square inch, eliminating unsaponified material by extracting the liquid with a selective solvent, acidifying the mass at around 125° F. to release the oxidation acid from the alkaline salt, and distilling the released acid.

7. In a process of manufacturing oxidized petroleum acid compounds, heating a petroleum distillate fraction of narrow boiling range, blowing air therein, maintaining the acid number in the reaction mass at about 5–20, while continuously introducing fresh petroleum and drawing off liquid, reacting the drawn-off liquid with caustic soda solution, at 175–320° F. and 20–140 pounds pressure per square inch, distilling off unsaponified material, acidifying the mass to release the oxidation acid from the alkaline salt, and distilling the oxidation acid.

8. In a process of manufacturing oxidized petroleum acid compounds, re-dissolving the acid in a caustic alkali solution and extracting with a selective solvent, removing the acid, and treating the oxidation acid with hydroquinone.

9. In a process of manufacturing oxidized petroleum acid compounds, treating the oxidation acid with hydroquinone.

10. In a process of manufacturing oxidized petroleum acid compounds, heating and blowing air into petroleum hydrocarbons of saturated type, treating the oxidized material with an alkaline neutralizer, acidifying to release the oxidation acid, distilling the oxidation acid from the residual material, and treating for color by a small amount of hydroquinone.

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