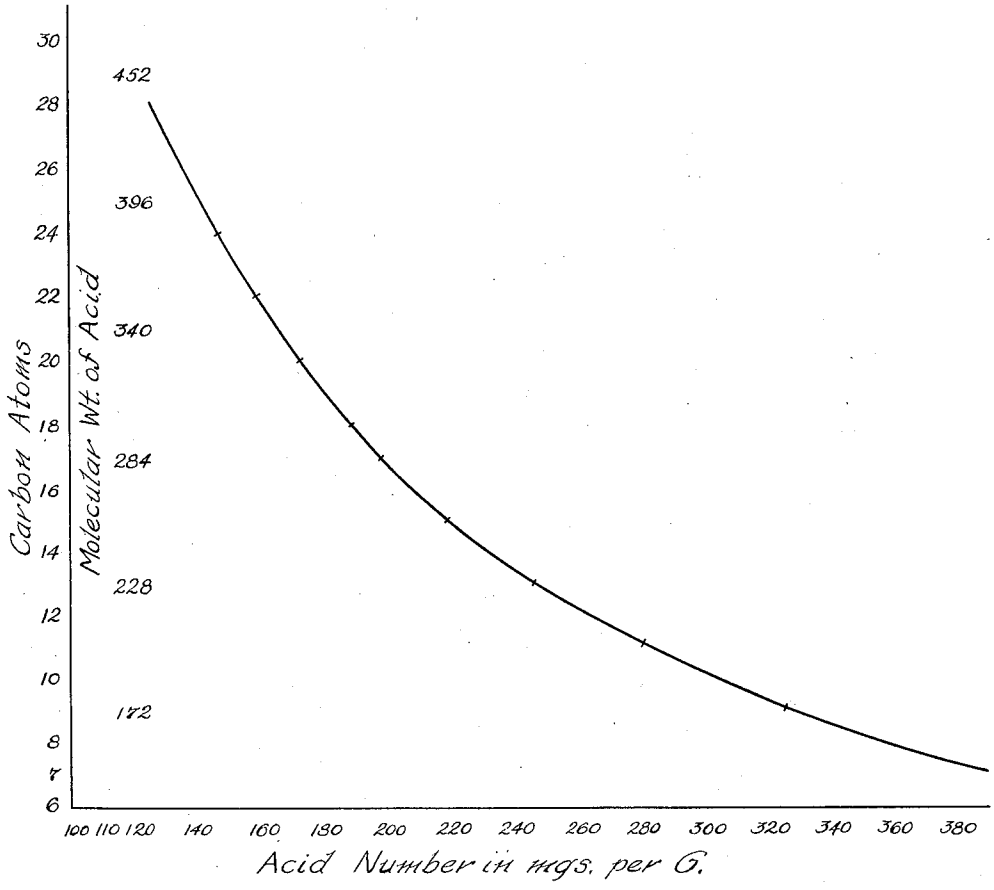
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MANUFACTURE OF OXIDIZED PETROLEUM ACID COMPOUNDS

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MANUFACTURE OF OXIDIZED PETROLEUM ACID COMPOUNDS

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In the preparation of carbon acids or higher molecular weight fatty acids from hydrocarbons by oxidation, the known commercial procedure involves oxidation particularly of paraffin wax by application of air and maintenance of a rather high temperature. A yield of acids extending over quite a wide molecular range results, and for many desired usages it has been impracticable to effect a separation to such an extent as to permit commercial adaptability to certain specific usages. The conglomerate mixture product has had to be employed practically as an indiscriminate mixture, and with its consequent limited capabilities of usage. In accordance with the present invention however, carbon acids of selectively desired character may be made from petroleum hydrocarbons, and such as to have applicability to purposes involving exacting requirements.

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 and the annexed drawing 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.

In said annexed drawing the sole figure is a graph illustrating the relation of stocks to products.

Instead of starting with very high molecular hydrocarbons and depending upon more or less breaking down to attain lower molecular products, the present invention selects hydrocarbon raw material in view of the characteristics of the product which it is desired to make. Thus, for a given desired acid number product, hydrocarbon or petroleum raw material is taken, and there being a definite relation establishable between acid number (determined as milligrams per gram of sample) in the product desired, with relation to the molecular weight or carbon atoms of the acid, correspondingly, the hydrocarbon raw material is selected by its boiling point. Closely cut distillate fractions of petroleum can thus be taken, and with corresponding carbon atom composition, and by the avoidance of molecular breakdown, because of the low conversion rate per pass and the closely controlled operations characteristic of the invention, the desired properties may be attained in the product. Petroleums of different source may be employed, depending upon the products desired, for most practical applications, acid products of acid number 100–300. A close cut liquid petroleum fraction corresponding to the selected acid number desired in such range is thus taken as raw material. The selected raw material is initially brought up to reaction temperature range by heating, and then oxygen or more commonly, air, is blown into the liquid under controlled conditions. The initial temperature depends somewhat upon the particular hydrocarbon being treated, whether of low or higher molecular weight and boiling point, but it must be low enough to avoid heating to excessive vaporization under the pressure conditions prevailing. Generally the pressure may be about sixty to one hundred pounds per square inch, and the temperature about 300–330° F. In the oxidational process, exothermic in character, heat is generated, and in the operation of the present process control of the temperature is carefully maintained, the reaction vessel desirably having a temperature control jacket or coils for such purpose, and the temperature is maintained in a desired reaction range. Vapors which form are caught by suitable condensing means, and condensed water is separated out, and condensed oil is returned to the reaction mass. Desirably, fresh feed hydrocarbon distillate is introduced into the reaction mass continuously, preferably at the lower portion, and with an acid number attained and thence continuously maintained at a desired rate in the reaction mass, as for instance an acid number of from 25, and best 10–20, liquid is drawn off, preferably at the upper portion, and preferably also continuously. The air introduced into the reacting hydrocarbon liquid may be at some convenient operating pressure, up to several hundred pounds or more, desirably for instance 78–100 lbs. per sq. in., and is disseminated thoroughly into the liquid by suitable dividing means to effect a good distribution and action. The air feed rate is desirably from about 2 to about 100 cu. ft. per hour per gal. of oil being reacted, and preferably not over 40 cu. ft. per gal, per hour.

The liquid withdrawn from the reaction zone is mixed with an alkali metal neutralizant, desirably a caustic soda or sodium carbonate solution, as for instance 0.5–5 N. for caustic soda, or 0.5 to saturated at room temperature for sodium carbonate. After thorough mixing and settling, the acid product may be set free from the alkali metal salt so formed, if desired; or a selective fractional precipitation may be carried out by successive precipitations with heavy metal ions, as by additions of manganese, cobalt, iron or the like, chlorides, hydroxides, etc.

Desirably, a catalyst may be added to the hydrocarbon liquid initially. With an accumulation of produced acid in the reaction zone a catalytic effect therefrom however ultimately is available. As a catalyst, manganese naphthenate or stearate is advantageous. The amount may be 0.2–0.8 or more, and desirably about 0.4 per cent. Similar other high molecular compounds of manganese, cobalt, etc. may be employed.

As an illustrative example: For a product of acid number 265, a petroleum distillate fraction of 300 to 310° F. I. B. P. 370 to 390° F. F. B. P. is heated to about 305° F. to 320° F. and air is blown therein at, e. g., 80 lbs. pressure and about 20 cu. ft. per hour per gal, in the reaction vessel in the presence of about 0.4 per cent of manganese stearate. The temperature is controlled at about 320° F., and when the acid number in the reaction zone samples at about 20, fresh feed is started at the bottom and the drawoff from the upper portion. The drawn off liquid is mixed with, e. g., 2.5 N. caustic soda solution. After settling, the pH is adjusted to barely acid and heavy metal salts are precipitated in successive fractions by separate precipitating additions of, e. g., lead nitrate. The thus selectively separated products are available for application to usages where a particularly definite material is desired. Of course, where such close splitting down is not desired, the products may be employed directly, without the fractional precipitation separation.

Or the acid may be freed from the sodium salt solution, e. g., by adding just enough sulphuric acid. The thus freed acids may be subjected to fractional distillation.

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.

I therefore particularly point out and distinctly claim as my invention:

1. In a process of making an oxidized petroleum acid compound, heating to about 305° F. a petroleum fraction of 300–390° F. B. P., blowing air therein at about 80 lbs. pressure and about 20 cu. ft. per hour per gal., controlling the temperature at 310–330° F., and maintaining the acid number in the reaction mass at not exceeding about 25, while continuously introducing fresh petroleum below and drawing off liquid above.

2. In a process of making an oxidized petroleum acid compound, heating a petroleum fraction of 300–390° F. B. P., blowing air therein at about 80 lbs. pressure and about 20 cu. ft. per hour per gal., while controlling the temperature at 300–330° F., maintaining the acid number in the reaction mass at 25, and drawing off liquid.

3. In a process of making an oxidized petroleum acid compound, heating to about 305° F. a petroleum fraction of 300–390° F. B. P., blowing air therein at about 80 lbs. pressure and about 20 cu. ft. per hour per gal., controlling the temperature at 300–330° F., maintaining the acid number in the reaction mass at not exceeding about 25, and drawing off liquid.

4. In a process of making an oxidized petroleum acid compound, heating a petroleum fraction of 300–390° F. B. P., blowing air therein at about 20 cu. ft. per hour per gal., while controlling the temperature at 300–330° F., and maintaining the acid number in the reaction mass at 5 to 25, and drawing off liquid.

5. In a process of making an oxidized petroleum acid compound, selecting a liquid petroleum material of boiling point chosen by reference to the carbon atom content of the acid product ultimately desired, heating such petroleum material and blowing air therein at about 20 cu. ft. per hour per gal., controlling the temperature and preventing excessive vaporization, maintaining the acid number in the reaction mass at 10–25, and drawing off liquid.

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