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PREPARATION OF SALTS OF OXIDIZED PETROLEUM ACIDS

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This invention relates to compounds of quite high molecular weight carboxylic acids as derived by oxidizing petroleum hydrocarbons; and it is among the objects of the invention to provide an improved preparation of salts on such order, having properties applicable to various uses.

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.

In certain aspects the invention is applicable to oxidation acids as produced in known or desired oxidation procedure, however in certain aspects again it is particularly desirable to carry out the oxidation for instance by selecting a stock of liquid hydrocarbon character in a rather narrow fraction, for instance a distillate fraction having a lower boiling range than gas oil, and for example 350 to 550° F., desirable sources being for instance Pennsylvania or Michigan petroleum, that is material which is suitably paraffinic or at least sufficiently predominantly paraffinic or saturated. With particular advantage, even closer distillate cuts may be employed, as for example 400 to 500° F. B. P. In any case however the precise range of fraction depends upon the particular end products in view, etc. Taking a hydrocarbon or petroleum material with a definite relation on boiling points selected, that is with relation to molecular weight or carbon atom contained, corresponding carbon atom compounds in the end products are obtainable, molecular break down being avoided by low conversion rate per pass and closely controlled operations. For most practical applications, products of acid number 150-350 are particularly desirable, and for products in this range the starting material is chosen to take account of the relation as above indicated. The material brought to reaction temperature by heat, 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 lower or higher boiling point, that is molecular weight, but in accordance herewith it is such as to avoid excessive vaporization of the hydrocarbon under the pressure conditions employed. In general the pres-

sure may be about 60 to 140 pounds per square inch and temperature about 290-360° F. Heat is generated, the reaction being exothermic, and the temperature carefully controlled in desired reaction range, suitable control jacket or coils being employed. Vapors from the reaction zone are condensed and water is separated out and oil is returned to the reaction zone. Desirably, fresh feed hydrocarbon is introduced into the reaction zone continuously, e. g. at the upper portion, and on attaining a suitable acid number, for instance between 5 and 20 or 25, reaction liquid is drawn off, e. g. at the lower portion and preferably also continuously. The air feed to the reaction may be at convenient operating pressure, desirably for instance 70-160 pounds per square inch, and is thoroughly disseminated into the liquid by suitable means to effect the distribution and action. The air feed may be at the rate of 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. With especial advantage, although not indispensable, the reaction may be carried on in the presence of a catalyst, for instance a manganese salt of a high molecular weight acid, as manganese stearate, manganese naphthenate, etc. It is generally preferable to re-cycle unreacted material, this being returned to the oxidation.

The liquid withdrawn is then reacted with an alkali metal compound, as sodium carbonate solution or preferably sodium hydroxide, as for instance in 0.5 N. to saturation at room temperature for sodium carbonate, or 0.5-5 N. for caustic soda. Reaction in this stage is carried on at 175-320° F., preferably slightly below 212° F., and may be under the full pressure of the system, or at least 20 pounds pressure desirably. Where employing caustic soda solution of about 2.5 N. the reaction time may be 15-60 minutes depending somewhat upon particular conditions and efficiency of mixture. With advantage the reaction is carried on in 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 especially advantageous, at least in one of the stages. The alkali reaction product or soap is acidified to release the desired acid, and the temperature of this operation is desirably controlled to below 125° F. In the acidifying, concentrated sulphuric acid, or the light acids produced in the process can replace part of the sulphuric acid in the event that such acids are not desired for

other uses. During acidification, vigorous agitation is applied, and finally the material is allowed to settle one-fourth to one and one-half hours, preferably one hour.

The oxidation acid from the reaction mass is then distilled, and it may be reacted with a compound from the group consisting of lead, manganese, cobalt, zinc, sodium, calcium, aluminum, copper, nickel, etc., suitable compounds thereof being reacted directly with the acid, as in the case of oxides or hydroxides for instance, or double decomposition reaction with an inorganic salt of the metal may be effected with the acid. Thus, the acid may be reacted with the lead compound, forming an oxidized hydrocarbon salt of the lead. A peculiarity where relatively low molecular weight oxidation acids as involved from liquid petroleum close cut distillate fractions as particularly instanced above, is the tendency to losses in the double decomposition type of manganese salt formation. However, such oxidized petroleum acid material may be successfully converted as a whole into the manganese compounds by warming the oxidation acid with a salt of a volatile acid, such as manganese acetate, in absence of much water. Acetic acid formed is distilled off, and this may be reacted with manganese carbonate to form manganese acetate which is re-cycled to the reaction with the oxidation acid. Where preferred however, we may, in the distillation as above noted, separate the condensate into two portions, the first 70 per cent of which we react with lead compounds to form lead salts, and the last 30 per cent or higher molecular acid fraction may be reacted with a manganese compound to form the manganese salts, in a double decomposition type of reaction, no loss in water-soluble salts being incurred such as above pointed out, it being found that a segregation of the higher molecular fraction makes possible the necessary reaction in water to form the salt, without having the water dissolve and carry away the salt as formed. And by incorporating the high molecular salt with the low molecular salt of lead more brittleness is imparted to the otherwise undesirably soft lead salt, and the product permits much more convenient manipulation by users.

The salts thus obtained are of value for many purposes. For certain specialized purposes however, for instance siccatives for finish usages etc., we prefer to take the petroleum acid as released by acidification of the material from the reaction with alkali, and subject it to steam and vacuum distillation and then redissolve it in caustic soda solution, then treat it with a solvent, such as benzene, etc., in one-half to four volumes, selective for the unsaponified material. The solvent is thoroughly mixed with the acid and the mixture is allowed to settle and stratify into layers, the solvent layer containing the impurities, and the other layer being a caustic solution of the oxidation acid. In some instances if the color has somewhat deteriorated after this treatment, the acid may be subjected to the action of zinc and hydrochloric acid, or we may apply to the freshly distilled acid an agent which we have found to inhibit color change, and which we may term a "coloration-inhibitor." As such agent hydroquinone may be used. The acid may now be reacted with the inorganic compounds of lead or other metal as above-described, and the resultant products are particularly clear and stable.

Other modes of applying the principles 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 the production of salts of oxidized petroleum acids, heating in the neighborhood of 320° F. a petroleum fraction of 350-550° F., blowing air therein at about 60 to 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 290-340° F., maintaining the acid number in the reaction mass at about 5-20, drawing off reacted liquid, neutralizing and saponifying the same with an alkaline solution, at an elevated temperature, acidifying the resultant mass to release the oxidation acids, distilling the latter into a lighter fraction and a heavier fraction, reacting the lighter fraction with litharge, redissolving the heavier fraction in caustic soda solution and reacting with manganese acetate, distilling off the acetic acid formed and reacting it with a manganese compound, and returning the manganese acetate formed to further reaction with oxidation acids, the heavier fraction being defined as that which produces the least loss in a double decomposition type of manganese salt formation.

2. In the production of salts of oxidized petroleum acids, heating in the neighborhood of 320° F. but without much vaporization a petroleum fraction of 350-450° F., blowing air therein at about 60 to 140 pounds pressure at the rate of about 27 cubic feet per hour per gallon of petroleum, controlling the temperature at 290-360° F., maintaining the acid number in the reaction mass at about 5-20, drawing off reacted liquid, neutralizing the same with an alkaline solution, at an elevated temperature, acidifying the resultant mass to release the oxidation acids, distilling the oxidation acids into a lighter fraction and a heavier fraction, reacting the lighter fraction with a reactive lead compound, and dissolving the further heavier fraction in caustic soda solution and reacting with a reactive manganese compound, the heavier fraction being defined as that which produces the least loss in a double decomposition type of manganese salt formation.

3. In the production of salts of oxidized petroleum acids, heating in the neighborhood of its boiling point but without much vaporization a predominantly paraffinic petroleum fraction of 350-450° F., blowing air therein at about 60 to 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 290-340° F., maintaining the acid number in the reaction mass at about 5-20, drawing off reacted liquid, neutralizing the same with an alkaline solution, at an elevated temperature, acidifying the resultant mass to release the oxidation acids, distilling the oxidation acids, reacting the same with manganese acetate in the absence of any substantial amount of water, distilling off the acetic acid formed and reacting it with a manganese compound, and returning the manganese acetate formed to further reaction with oxidation acids.

4. In the production of salts of oxidized petroleum acids, heating a petroleum fraction of 350-550° F. without much vaporization, blowing air therein at 2-100 cubic feet per hour per gallon of petroleum, maintaining the acid number

in the reaction mass at about 5-20, drawing off reacted liquid, neutralizing the same with an alkaline solution, at an elevated temperature, acidifying the resultant mass to release the oxidation acids, distilling the said acids into a lighter fraction and a heavier fraction, reacting the lighter fraction with a lead compound, redissolving the heavier fraction in caustic soda solution and reacting with a reactive manganese compound, and adding the manganese product to the lead product, the heavy fraction being defined as that which produces the least loss in a double decomposition type of manganese salt formation.

5. In the production of salts of oxidized petroleum acids, heating a petroleum fraction of 350-550° F. without much vaporization, blowing air therein at 2-100 cubic feet per hour per gallon of petroleum, maintaining the acid number in the reaction mass at about 5-20, drawing off reacted liquid, neutralizing the same with an alkaline solution, at an elevated temperature, acidifying the resultant mass to release the oxidation acids, distilling the latter, segregating about the last thirty per cent as the heavier fraction and redissolving it in caustic soda solution, extracting with a volatile solvent and allowing to stratify into layers, separating the solvent, and precipitating a manganese compound of the oxidation acid by adding a water-soluble manganese salt in the absence of any substantial amount of water.

6. In the production of salts of oxidized petroleum acids, segregating a liquid petroleum fraction of boiling point in relation to the acid number desired in the oxidized acid product, heating and oxidizing the same at a temperature of 290-360° F., neutralizing the reacted liquid

with an alkaline solution, acidifying the resultant mass to release the oxidation acids, distilling off the acids into lighter and heavier portions, reacting the lighter portion with a lead compound to form a lead salt, and reacting the heavy portion with a manganese compound to form a manganese salt, the heavier portion being defined as that which produces the least loss in a double decomposition type of manganese salt formation.

7. In the production of salts of oxidized petroleum acids, heating and oxidizing a petroleum fraction of oxidation acids, drawing off reacted liquid, neutralizing the same with an alkaline solution, acidifying the resultant mass to release the oxidation acids, distilling the latter, reacting a lighter portion thereof with a reactive lead compound, reacting a heavier portion with a reactive manganese compound, and embrittling the properties of the obtained lead compound by adding thereto the obtained manganese compound, the heavier portion being defined as that which produces the least loss in a double decomposition type of manganese salt formation.

8. In the production of salts of oxidized petroleum acids, neutralizing with an alkaline solution the acids formed, acidifying the resultant compounds and distilling off the oxidation acids into a lighter and a heavier fraction, reacting the lighter fraction thereof with a reactive lead compound, redissolving the heavier fraction in an alkaline medium and reacting it with a manganese compound, the heavier fraction being defined as that which produces the least loss in a double decomposition type of manganese salt formation.

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