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PROCESS FOR PRODUCING HIGH VISCOSITY WAX OXIDATE

John K. McKinley, Gordon S. Bright, and Roy F. Nelson, Port Arthur, Tex., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

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This invention relates to a method for oxidizing high molecular weight paraffins so as to produce a high ester content, high viscosity oxidate. This type of oxidate is an excellent additive for mineral oil to produce specialty lubricants.

Oxidation of high molecular weight hydrocarbons with air or oxygen results in the production of a heterogeneous mixture of oxygenated compounds. Not only are many different types of oxygenated hydrocarbons produced, but oxygenates of a wide molecular weight range result because the oxidation is accompanied by substantial chain degradation even when a relatively close boiling charge material is employed. The complexity of the oxidation product is apparent from a brief review of the types of oxygenates obtained. Acids, alcohols, aldehydes and ketones are all produced directly in the oxidation reaction. Acids are the main reaction product, with hydroxy hydrocarbons constituting the second largest product. Further oxidation of the acids leads to the production of hydroxy acids and keto acids. In addition, at the oxidation temperatures ordinarily employed, which are in the range of 200 to 400° F., a number of secondary reaction products are formed; in particular, there is a substantial amount of thermal esterification of organic acids with hydroxy acids and with alcoholic components of the reaction mixture.

Despite the extensive nature of the prior art on wax oxidation, both the technical and patent literature are deficient in teaching how to control the oxidation reaction so as to produce a product oxidate characterized by both high ester content and high viscosity. The prior art does disclose that a relatively high ester content oxidate is normally produced in the oxidation reaction but is devoid of any teaching how the viscosity of the high ester content oxidate can be controlled as desired. The subject application provides a method for producing a high ester content oxidate in which the Saybolt Univ. viscosity at a temperature of 210° F. is higher than 4000. Hight ester content, high viscosity wax oxidate is useful as a lubricating oil additive to impart corrosion resistance and emulsibility and possesses exceptional and surprising solubility in lubricating oil fractions.

In accordance with the process of this invention, a wax oxidate of high ester content and high viscosity is obtained by reacting high molecular weight hydrocarbons of the class comprising petrolatum and lubricating oil fractions with air in the presence of a catalyst at an air feed rate of 15 to 35 standard cubic feet of air per pound of hydrocarbon per hour, at a temperature between 270 and 400° F. and at atmospheric pressure. The critical features are choice of charge material, use of catalyst, maintenance of prescribed temperature and pressure conditions, and use of an air rate within the prescribed region. Employing the prescribed conditions, a product oxidate having a ratio of Neut. No. to Sap. No. less than about 0.25 and a Saybolt Univ. viscosity at 210° F. greater than 4000 is obtained by oxidation of a petrolatum. Even when the charge material is a viscous lubricating oil fraction, an oxidate having a Saybolt Univ. viscosity at 210° F. greater than 1500 is obtained employing the oxidation conditions prescribed in this invention.

The subject invention in contrast with prior art processes affords a means of producing oxidates whose ester content is approximately 2 times its acid content, as indicated by a ratio of Neut. No. to Sap. No. less than 0.40, and which have a Saybolt Univ. viscosity at 210° F. between 1500 and 11,000. In general petrolatums oxidized under the prescribed conditions yield oxidates whose ratio of Neut. No. to Sap. No. is less than 0.25 while lubricating oils yield oxidates whose ratio of Neut. No. to Sap. No. is less than 0.40. In addition, the product of the aforementioned characteristics is obtained in a short reaction time under the prescribed reaction conditions.

The discovery that the viscosity of a high ester content oxidate can be controlled as desired by selection of charge stock, use of catalyst and critical control of temperature, pressure and air rate is a significant advance in the field of wax oxidation. The process of this invention results in the formation of a high viscosity, high ester content oxidate which is an excellent additive for lubricant compositions wherein anti-corrosive properties in combination with good water emulsification are required specifications. The high ester content, high viscosity oxidate produced in accordance with this invention is an excellent additive for marine oil to which it imparts desired anti-corrosive and emulsibility properties.

The selection of charge material has a significant and substantial effect on the type of oxidate produced. Petrolatums and lubricating oil fractions are the requisite charge materials to produce high ester content, high viscosity oxidate. Petrolatum is obtained by the solvent dewaxing of residual oils. It is not feasible to prepare high ester content oxidate having SUS viscosities well over 1500 at 210° F. from deoiled waxes. With petrolatum as a charge stock it is possible to produce high ester content oxidates whose Saybolt Univ. viscosity at 210° F. is higher than 6000.

In general, the production of high ester content, high viscosity oxidate is effected in an aluminum-lined reactor in the presence of a catalyst. Particularly preferred catalyst is potassium permanganate which is charged to the reactor in an aqueous solution together with petrolatum. A potassium permanganate catalyst of this nature is employed in amounts ranging from 0.01 to 1.0 per cent of the total wax charge; 3 to 10 per cent aqueous solutions of potassium permanganate are ordinarily used to introduce the required catalyst into the reaction zone. Excellent distribution of the potassium permanganate throughout the hydrocarbon charge is obtained in the induction period during which air is blown through the reaction mixture and the reaction mixture is raised to the specified temperature range. The water evaporates during the induction period, leaving the catalyst distributed throughout the charge very uniformly. Although potassium permanganate in the form of an aqueous solution is the preferred oxidation catalyst, oil-soluble catalysts such as manganese stearate, zinc stearate, manganese and zinc salts of previously oxidized wax fractions may also be employed in the process of this invention to produce a high ester content, high viscosity oxidate.

The oxidation temperature must be maintained between 270 and 400° F. in order to produce a high ester content, high viscosity oxidate. The preferred temperature range is 300 to 380° F. Control of reaction temperature is ordinarily effected by indirect heat exchange. An alternative means of temperature control involves continuous introduction of water into the reaction zone, which results in removal of exothermic heat of reaction by evaporative cooling.

Atmospheric or sub-atmospheric pressure is prescribed to produce a high ester content, high viscosity oxidate. It is important to maintain pressures below about 20 pounds per square inch gauge in the process of this invention because higher pressures result in the production of a more acid-like oxidate.

The final decisive factor in the process of this invention is the rate at which air is passed through the oxidate. Air rates of 15 to 35 standard cubic feet of air per pound of petrolatum per hour must be employed to obtain the desired product. The air rate is particularly decisive in determining the viscosity of the high ester content oxidate. Apparently air rates of the prescribed range result in the proper correlation of agitation and contact of reactants to produce a high ester content, high viscosity oxidate at the prescribed temperature and pres-

sure conditions. It should be noted that the amount of air passed through the reaction mixture is considerably in excess of that which actually enters into the oxidation reaction.

The process of the invention is illustrated in detail in the following examples wherein petrolatum and lubricating oil fractions are oxidized in accordance with the process of this invention. Examples I and II illustrate the production of high ester content, high viscosity oxidates from petrolatum, whereas Examples III and IV illustrate the preparation of high ester content, high viscosity oxidates from lubricating oil fractions.

Example I

There was charged to an aluminum reactor provided with heat exchange surface 150 pounds of petrolatum obtained by centrifuge dewaxing of a refined residuum; the charge petrolatum had the following properties:

Gravity, ° API	20.5
Flash, O. Cleve., ° F	520
Fire, Cleve., ° F	590
Visc., Say. Univ., at 210° F	86.6
Color, T. R	1/4
Melting point, ° F	151.8
Ash, per cent	.008
Sulfur, per cent	.19
Oil, per cent (ASTM)	13.39

There was also charged to the reactor an aqueous solution of potassium permanganate prepared by dissolving 0.6 pound of potassium permanganate in 10 pounds of water. Air blowing was initiated as soon as the total charge mixture was introduced into the reactor. The reaction mixture was rapidly heated to a temperature of about 350° F. by heat exchange in order to initiate the reaction. After the initiation of reaction was indicated by the evolution of heat, the reaction mass was cooled to an operating temperature of 330° F. The oxidation was effected at atmospheric pressure and at an air rate of 20 cubic feet of air per pound of petrolatum per hour. The reaction was continued at these conditions for a period of about 6¼ hours, at which time the oxidate had reached a Neut. No. of 26 and a Sap. No. of 126. There was obtained a yield of approximately 86 per cent oxidate on the basis of hydrocarbon charged. The product obtained had a Saybolt Univ. viscosity at 210° F. of 6211 and was characterized by the following tests:

Neut. No	26
Sap. No	126
Ester No	100
Ratio Neut. No./Sap. No	0.21
Unsaponifiable, per cent	37.3
Gravity, ° API	17.3
Flash, O. Cleve., ° F	475
Fire, Cleve., ° F	510
Visc. SU, 210° F	6211
Pet. melting point, ° F	142
Ash, per cent	0.56

Example II

100 pounds of petrolatum of the type described in Example I was charged to an aluminum reactor. There was also charged to the reactor an aqueous solution of potassium permanganate prepared by dissolving 0.4 pound of potassium permanganate in 10 pounds of water. After the induction period, the reaction was effected for a period of about 5½ hours at an average reaction temperature of 360° F. and at atmospheric pressure; the air rate was 30 cubic feet of air per pound of petrolatum per hour. The yield of oxidate was approximately 96 per cent of the hydrocarbon charged. The product oxidate had a Saybolt Univ. viscosity at 210° F. over 11,000 and was characterized by the following properties:

Neut. No	2.3
Sap. No	65
Ester No	62
Ratio, Neut. No./Sap. No	.05
Unsaponifiable, per cent	32
Gravity, ° API	17.6
Flash, O. Cleve., ° F	495
Fire, Cleve., ° F	550
Visc., Say. Univ., at 210° F	11,038
Ash, per cent	.61

Example III

There was charged to an aluminum reactor provided with heat exchange surface 100 pounds of lubricating oil which was produced by refining a paraffin distillate with sulfur dioxide; the charge oil had the following properties:

Gravity, ° API	31
Flash, O. Cleve., ° F	295
Fire, Cleve., ° F	335
Visc., Say. Univ., at 100° F	48.7
Pour, ° F., maximum	—75
Viscosity index, minimum	60

There was also charged to the reactor an aqueous solution prepared by dissolving 0.4 pound of potassium permanganate in 10 pounds of water. The oxidation procedure was the same as that described in Example I; the reaction was effected at a temperature of 330° F., at atmospheric pressure and at an air rate of 30 cubic feet of air per pound of charge oil per hour. At the end of 5⅓ hours there was obtained an oxidate having a Saybolt Univ. viscosity at 210° F. of 1631. The product oxidate was characterized by the following tests:

Neut. No	82
Sap. No	222
Ester No	140
Ratio, Neut. No./Sap. No	0.37
Unsaponifiable, per cent	32.3
Gravity, ° API	3.2
Flash, O. Cleve., ° F	320
Fire, Cleve., ° F	410
Visc., Say. Univ., at 210° F	1631
Color, ½" Lovi. Cell	85

Example IV

In an aluminum reactor provided with heat exchange surface a lubricating oil fraction having been obtained by solvent dewaxing paraffin distillate 40 was oxidized in accordance with the procedure described in Example I. The charge oil had the following properties:

Gravity, ° API	27.3
Flash, O. Cleve., ° F	495
Fire, Cleve., ° F	560
Visc., Say. Univ., at 210° F	77.2
Visc., Say. Univ., at 100° F	824
Color, Lovi. ½" Cell	40
Pour, ° F	—5

The oxidation was effected in the presence of a permanganate catalyst at a temperature of 330° F., at atmospheric pressure and at an air rate of 30 cubic feet of air per pound of oil per hour. At the end of 5½ hours there was obtained a product oxidate having a Saybolt Univ. viscosity at 210° F. of 2515. The yield of oxidate was 92 per cent. The product oxidate was characterized by the following properties:

Neut. No	34
Sap. No	110
Ester No	76
Ratio, Neut. No./Sap. No	0.31
Unsaponifiable, per cent	41.5
Gravity, ° API	10.2
Vis., SU, 210° F	2515
Pour, ° F	95

It will be observed that oxidation of petrolatum and mineral oils in accordance with the process of this invention results in the production of high ester content, high viscosity oxidates. The oxidates produced from petrolatum have Saybolt Univ. viscosities at 210° F. higher than 6000 and are characterized by a ratio of Neut. No. to Sap. No. less than about .25. The oxidates produced by oxidation of mineral oils have a Saybolt Univ. viscosity at 210° F. higher than 1600 and are characterized by a ratio of Neut. No. to Sap. No. less than 0.40.

The oxidates produced in accordance with the process of this invention possess excellent solubility in lubricating oil fractions and are excellent additives for imparting emulsibility and corrosion resistance to the lubricating fractions in which they are incorporated.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, there-

fore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A wax oxidate derived by the catalytic liquid phase oxidation of petrolatum at a temperature between 270 and 400° F., at a pressure below 20 pounds per square inch gauge and at an air feed rate of 15 to 35 cubic feet of air per pound of petrolatum per hour, said oxidate being characterized by a Neut. No. to Sap. No. ratio less than 0.25 and a Saybolt viscosity at 210° F. greater than 4,000.

2. A process for producing a high viscosity, high ester content petrolatum oxidate characterized by a Neut. No. to Sap. No. ratio less than 0.25 and an SUV at 210° F. greater than 4,000, which comprises reacting petrolatum with air in the presence of a catalyst at a temperature between 270 and 400° F., at a pressure below 20 p. s. i. g. and at an air rate between 15 and 35 cubic feet of air per pound of petrolatum per hour.

3. A process according to claim 2 in which petrolatum is reacted with air at a temperature between 300 and 380° F. and at atmospheric pressure.

4. A process according to claim 2 in which the catalyst is a 3 to 10 weight per cent solution of permanganate in such proportions that potassium permanganate constitutes 0.01 to 1.0 weight per cent of the petrolatum charge.

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