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OXIDATION OF SULFURIC ACID HEAVY ALKYLATE

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The present invention relates to the treatment of heavy alkylate and, more particularly, to the production of liquid and semi-solid products containing high molecular weight acids and esters thereof.

At the present time in the production of aviation fuel base stocks by alkylation of isoparaffins with olefins it is customary to top the alkylate to 350° F. to 400° F. dependent upon the degree of volatility desired. The residue, known as heavy alkylate, has an initial boiling point of about 350° F. to about 400° F. and an end point of about 750° F. In other words, heavy alkylate is that fraction of hydrocarbon material produced by the alkylation of isoparaffins with olefins which boils above about 350° F. to about 400° F. and has an end point of about 750° F. The heavy alkylate has an iodine number appreciably higher than that of slack wax and usually of the order of about 75. It is customary to add the heavy alkylate to some other fraction, such as automotive fuel, fuel oil or cracking stock which will not be depreciated in value by the addition. In other words, at the present time heavy alkylate is a low value product which is dumped into any fraction which will not be lowered in value by the addition in order to dispose of the heavy alkylate as easily as possible with the least additional cost. It has now been discovered that this low value product can be treated to provide valuable materials containing organic acids and esters thereof of high molecular weight.

It is an object of the present invention to provide a method of treating heavy alkylate to produce products containing organic acids and alcohols having high molecular weight and/or esters thereof. It is another object of the present invention to provide a method of treating sulfuric acid heavy alkylate to produce products containing organic acids and alcohols having high molecular weight and/or esters thereof. It is a further object of the present invention to provide a method of treating material composed of saturated and unsaturated isoparaffinic polymers having an initial boiling point of about 350° F. to about 400° F. and an end point of about 750° F. to produce products containing acids, alcohols and/or esters thereof having high molecular weights. The present invention also has as an object to provide a method of treating sulfuric acid alkylate having an initial boiling point of about 350° F. to about 400° F. and an end point of about 750° F. to produce products containing acids and/or esters thereof having high molecular weights. Other objects and advantages will become apparent from the following description.

As has been pointed out in a recent article by

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Dr. R. Strauss, entitled "Fatty acids by oxidation of hydrocarbons" translated by E. J. Barth and published in Petroleum Refiner, February 1945 (117–120) the source of the paraffins has an effect upon the character of the products produced. Thus, according to N. J. Tschernoshukow and S. Krein, paraffins from Grossny yielded the greatest amount of condensation products and only a small quantity of acid products; whereas, the solar oils from Baku furnished small amounts of resins and a high percentage of acid products.

In general, the method of treating heavy alkylate and, particularly, sulfuric acid alkylate bottoms having an initial boiling point of about 350° F. to about 400° F. and an end point of about 750° F., comprises heating heavy alkylate within the temperature range of about 100° F. to about 400° F. at pressures from atmospheric to about 350 atmospheres in the presence of about 0.1 per cent to about 10 per cent, and preferably about 1 per cent to about 3 per cent, of an oxidation promoter consisting of "per" compounds such as inorganic peroxides, organic peroxides and salts of "per" acids, for periods of time dependent upon temperature. Among the oxygen promoters preferred for the purposes herein set forth are lauroyl peroxide, tertiary butyl peroxide, benzoyl peroxide, urea peroxide, hydrogen peroxide, sodium peroxide, ammonium persulfate, pyrophosphate peroxide and the like. Those oxidation promoters are especially preferred which are substantially completely soluble in the heavy alkylate per se and in the products of the reaction. Of the foregoing catalysts, at this time lauroyl peroxide provides the highest yield of acids and esters thereof. During the reaction air or other free oxygen-containing gas is passed through the reaction mixture.

As has been pointed out hereinbefore, the treating time is dependent upon the temperature and the pressure at which the reaction is carried out and, in addition, upon the degree to which the oxidation promoter is soluble in the heavy alkylate and the products of the reaction. For example, at a reaction temperature of 200° F. and at a pressure of one atmosphere about 250 hours of treatment are required to produce an appreciable amount of petroleum acids and esters of high molecular weight. On the other hand, at higher pressures and/or higher temperatures substantially the same conversion can be obtained in a shorter treatment period.

Illustrative of some of the conditions under which heavy alkylate can be treated in accordance with the present method are the following examples.

EXAMPLE I

Temperature	200° F.
Pressure	1 atmosphere
Oxidation promoter	Benzoyl peroxide
Concentration of benzoyl peroxide	1% by weight
Time	240 hours
Agitation	Continuous
Product:	
Acid No.	27.7
Ester No.	70.1
Saponification No.	97.8
Iodine No.	64
Separated acids (per cent weight)	28.4
Neutralization number of separated acids	141
Iodine number of separated acids	31
Titer	Liquid at room temperature (70° F.)

The characteristics given above are to be compared with the corresponding properties of the untreated heavy alkylate as set forth in Table I:

Table I

Gravity, °A. P. I.	48.0
Flash, C. O. C. °F.	175
S. U. V. @ 100° F.	35 sec.
Aniline point	185
Pour point	Below minus 100° F.
Calculated average molecular weight	182
Iodine No.	75
Neutralization No.	0.03
A. S. T. M. color	1

EXAMPLE II

Temperature	380 F.
Pressure	1 atmosphere
Oxidation promoter	Benzoyl peroxide
Concentration of benzoyl peroxide	1% by weight
Agitation	Continuous
Time	As indicated

Table II

Time, Hours	Iodine No.[1]	Acid No.[1]	Ester No.[1]	Saponification No.[1]
0	83.4	Nil	Nil	Nil
4.5		4.5	2.4	6.9
13	74.6	5.1	7.1	12.2
35.5	63.1	23.3	37.8	61.1

[1] These headings have the conventional meanings.

The final product separated on standing and cooling into a mixture of liquid and solid materials, representing respectively 35 per cent and 15 per cent by weight of the original charge. The liquid portion was distilled under vacuum. The characteristic properties of the fractions are given in Table III and are quite different from those of the original material (heavy alkylate) given in Table I.

Table III

Cut No.	Wt. Percent	Cum. Wt. Percent	Cut Point Temperature, °C.	Pressure, mm.	Iodine No.	Acid No.	Ester No.	Saponification No.
1	18.6		78	1.5	52.4	7.1	10.7	17.7
2	18.6	37.2	86	1.0	61.7	7.4	12.1	19.5
3	18.2	55.4	121	2.0	58.9	9.3	16.7	26.0
4	17.8	73.2	170	4.5	69.1	15.2	32.8	48.0
5	7.2	80.4	185	4.5	57.5	38.5	88.0	126.5
Residue (semi-solid)	19.6	100.0	above 185	4.5	43.5	49.9	92.7	142.6

Upon referring to Table II it will be noted that the original heavy alkylate had an iodine number of 83.4 which was reduced to 63.1 after 35.5 hours. This decrease in iodine number is indicative that at least some of the oxidation is taking place at the unsaturated linkages. It will also be noted that the material boiling at and above 170° C. at 4.5 millimeters of mercury pressure contained a greater amount of acids and esters than the lower boiling fractions. In fact the major portion of the acids and esters produced are recovered in the material boiling at and above 170° C. at 4.5 millimeters.

EXAMPLE III

Temperature	200° F.
Pressure	1 atmosphere
Oxidation Promoter	As indicated hereinafter
Concentration of Oxygen Donor	As indicated hereinafter
Agitation	Continuous at 200 R. P. M.
Time	258 hours

	1 per cent Lauroyl Peroxide	10 per cent Benzoyl Peroxide	1 per cent Ammonium Persulfate
Yield, Wt., per cent	17.8	27.6	17.2
Color	(1)	(2)	(3)
Specific gravity 60°/60° F.	0.947	0.946	0.879
Viscosity at 100° F. (S. U. S.)	9619	5366	567
Viscosity at 210° F. (S. U. S.)	115	86.5	51.7
Iodine Number	43.2	54.7	59.1
Acid Number	30.4	30.5	10.0
Ester Number	78.8	67.4	28.4
Saponification Number	109.6	97.9	38.4
Separated Acids (Wt. per cent)	30.3	22.5	16.8
Neutralization No. of separated acids	143.5	175.3	133.5

[1] Light 6-A. S. T. M.
[2] Light 5-A. S. T. M.
[3] Brown.

The tabulation of the characteristics of the products in Example III provide data for several generalizations. One per cent by weight of lauroyl peroxide is more effective on the basis of quantity of acids produced than either benzoyl peroxide or ammonium persulfate. In the presence of lauroyl peroxide or ammonium persulfate greater amounts of esters are produced than in the presence of benzoyl peroxide. The ratio of ester to free acid in the products being for oxidation in the presence of lauroyl peroxide, benzoyl peroxide and ammonium persulfate

$$\frac{78.8}{30.4}=2.6 \qquad \frac{67.4}{30.5}=2.2 \qquad \frac{28.4}{10.0}=2.8$$

respectively. In addition, a comparison of the results produced when employing one per cent benzoyl peroxide and when employing ten per cent peroxide for substantially equal reaction times at the same reaction temperature and pressure indicate that under present conditions there is no appreciable advantage in the use of amounts of oxidation promoter greater than about one per cent. This can be understood readily after consideration has been given to the data presented in Table IV.

Table IV

Oxidation promoter	Benzoyl peroxide	
Concentration	1% by wt.	10% by wt.
Temperature	200° F.	200° F.
Pressure	1 atmosphere	1 atmosphere
Time	240 hours	258 hours
Acid No.	27.7	30.5
Ester No.	70.1	67.4
Saponification No.	97.8	97.9
Iodine No.	64	54.7
Separated acids (per cent weight)	28.4	22.5
Neutralization No. of separted acids	141	175.3

We claim:

1. The method for producing a mixture of oxidation products of unsaturated and saturated nature, which comprises: heating sulfuric acid heavy alkylate produced by the alkylation of isoparaffins with olefins and having an iodine number of about 75, in the presence of a peroxide to elevated temperatures whilst passing air through said heavy alkylate, until the reaction mixture contains oxidation products.

2. The method for producing a mixture of oxidation products of unsaturated and saturated nature, which comprises: heating sulfuric acid heavy alkylate produced by the alkylation of isoparaffins with olefins and having an iodine number of about 75, in the presence of a peroxide, to a temperature of at least 100° F. whilst passing air through said heavy alkylate, until the reaction mixture contains unsaturated and saturated oxidation products.

3. The method for producing a mixture of oxidation products of unsaturated and saturated nature, which comprises: heating sulfuric acid heavy alkylate produced by the alkylation of isoparaffins with olefins and having an iodine number of about 75, in the presence of lauroyl peroxide, to a temperature of about 200° F. whilst passing air through said heavy alkylate, until oxidation products are produced.

4. The method for producing a mixture of oxidation products of unsaturated and saturated nature, which comprises: heating sulfuric acid heavy alkylate produced by the alkylation of isoparaffins with olefins and having an iodine number of about 75, in the presence of benzoyl peroxide, to a temperature of about 200° F. whilst passing air through said heavy alkylate, until oxidation products are produced.

5. The method for producing a mixture of oxidation products of unsaturated and saturated nature, which comprises: heating sulfuric acid heavy alkylate produced by the alkylation of isoparaffins with olefins and having an iodine number of about 75, in the presence of ammonium persulfate, to a temperature of about 200° F. whilst passing air through said heavy alkylate, until oxidation products are produced.

6. The method for producing a mixture of oxidation products of unsaturated and saturated nature, which comprises: heating sulfuric acid heavy alkylate produced by the alkylation of isoparaffins with olefins and having an iodine number of about 75, in the presence of a peroxide, to a temperature of at least 100° F. whilst passing air through said heavy alkylate, until the reaction mixture has an acid number of at least 10 and an iodine number not less than about 40.

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