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2,964,545

DIMERIC FATTY ACIDS AND ESTERS THEREOF

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5 Claims. (Cl. 260—407)

The present invention relates to a novel process of producing dimeric fatty acids and monohydric alcohol esters thereof having conjugated double bonds. Polyesters, polyamides, and other derivatives of these dimeric fatty acids have the unique property of readily undergoing further polymerization because of the conjugated unsaturation. They are, therefore, useful in the coating, resin and fiber fields. The present application is a division of my co-pending application, Serial No. 341,343, filed March 9, 1953, now abandoned, which in turn is a continuation-in-part of my application Serial No. 168,659, filed June 16, 1950, now abandoned.

It is well known that dimerization of unsaturated fatty acids may readily be effected either by straight thermal polymerization without catalysts or by thermal polymerization in the presence of catalysts. It is well known, however, that these processes of thermal polymerization of unsaturated fatty acids actually destroy oxidative drying power, since the polymerization is effected through reduction in unsaturation. The more rapid drying properties of a heat-bodied oil as compared with the same oil which has not been heat-bodied, are largely attributed to the fact that thermal polymerization has already carried the cross linking process part way so that less oxidation is required in the film to carry the film to a hard state than would be required for a film of oil that had not been heat-bodied.

The invention involves the process of cross linking fatty acids and at the same time retaining substantially their capacity to further cross link through oxidative polymerization. The dimeric products of the present invention not only retain the oxidative properties of the unsaturated fatty acids from which they are made, but actually possess enhanced oxidative acceptability in view of the fact that the unsaturation has been converted to a conjugated form. The products obtained are acyclic and contain substantially the same total unsaturation as the materials from which they are derived and in addition a portion at least of the unsaturation is in the conjugated form.

It is, therefore, an object of the present invention to provide a novel process for producing dimeric fatty acids and monohydric alcohol esters thereof having conjugated double bonds therein.

The process involves the treatment of fatty acids or monohydric alcohol esters of fatty acids containing two double bonds separated by a methylene group, with certain organic peroxides at temperatures in excess of 50° C. and usually in excess of 100° C., the temperature depending on the particular peroxide used. The process is applicable to a variety of fatty acid materials including free fatty acids and lower aliphatic esters of these fatty acids such as, for example, the methyl esters. The fatty acid materials employed should contain some fatty acid groups containing two double bonds separated by a methylene group. Typical of these fatty materials are linoleic acid and linolenic acid and the above-mentioned derivatives thereof.

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It will be appreciated that the fatty acid material employed may be composed entirely of the fatty acid materials containing the two double bonds separated by a methylene group or may contain these materials in admixture with other fatty acid materials, either saturated or unsaturated. Thus, the most useful materials are the mixed fatty acids or mixed monohydric alcohol esters of the fatty acids of the drying and semi-drying fatty oils, especially those having an iodine value of at least 120. Typical of the materials which may be employed are soybean oil fatty acids and the methyl esters of the soybean oil fatty acids. These materials may also be subjected to some fractionation in order to get materials of higher degrees of unsaturation and the more unsaturated fractions thus obtained may be used for the present invention.

It is believed that the reaction proceeds through a radical mechanism. The various fatty acid groups in the reaction mixture form radicals through the loss of hydrogen atoms. The fatty acid group containing the two double bonds separated by a methylene group forms a radical by the loss of a hydrogen atom from the methylene group. The radical thus obtained then isomerizes at least in part to the conjugated form. These conjugated diene radicals may combine with conjugated or non-conjugated radicals and also with mono-olefinic and with saturated radicals formed from other fatty acid groups present in the reaction mixture. The reaction product is composed of a mixture of dimers resulting from the various combinations of the radicals present. The union of the radicals occurs without the loss of any double bonds. Where the starting material contains a substantial quantity of fatty acid groups having two double bonds separated by a methylene group, the product of the reaction will contain a substantial amount of conjugation.

The products of the present invention are to be distinguished from the products obtained by ordinary thermal polymerization products in that in the latter the fatty acid groups themselves combine in a cyclic structure, whereas in the products of the present invention the fatty acid groups combine in a linear manner. Of the products of the present invention those derived from the free fatty acids or the monohydric alcohol esters thereof are preferred in that by employing these materials as starting materials it is possible through regulation of the amount of catalyst employed to obtain end products which are almost exclusively dimers. This is of particular value where it is desired to produce a largely dimeric material.

Any organic peroxide having the formula $ROOR^1$ in which R is selected from the group consisting of hydrogen and hydrocarbon radicals and in which R^1 is a hydrocarbon radical may be employed for the purpose of conjugating and dimerizing the fatty acid group. In view of their stability, however, it is preferred to employ such peroxides as those containing a tertiary-alkyl peroxy radical, for example ditertiary butyl peroxide, tertiary butyl hydroperoxide, cumene hydroperoxide and the like.

The temperature which is employed depends upon the particular peroxide employed and upon the time period desired. In general, temperatures should be in excess of 50° C. and preferably in the range of 100–250° C. The maximum temperature which may be employed is the decomposition temperature of the material being treated, and generally is in the neighborhood of 250° C. It is preferred, however, not to employ temperatures as high as 250° C. inasmuch as at these high temperatures the peroxides decompose more rapidly than is desirable, and in addition thermal polymerizations accompany the polymerizations due to the peroxide. Thermal polymerization becomes significant in rate at temperatures in excess of 200° C., and accordingly, it is preferred to

operate at temperatures below 200° C. The preferred range of temperature, therefore, is 100–200° C.

The quantity of peroxide which may be employed, likewise, may vary with the other variables such as the material being employed, the temperature and the time. In general, from a small but definite quantity of peroxide, the quantity may vary up to 10–15% by weight. Usually it is not desirable to employ less than ½ of 1%.

The time period employed likewise varies with the rest of the reaction conditions, but generally is within the range of 5–50 hours. The process involves the mere admixture of the fatty acid or its ester with the peroxide and the heating of the mixture in an inert atmosphere for the desired time and at the desired temperature. At the completion of the process the reaction product may, if desired, be stripped under vacuum to remove all the decomposition products of the peroxide as well as unreacted fatty acids or esters. It will be appreciated, however, that it is not essential that these decomposition products or the unreacted materials be removed if it is not essential to have a material consisting essentially of the dimeric conjugated acid.

Example 1

Methyl linoleate (87%) 100 g. and di-tert-butyl peroxide 3.0 g. were treated without agitation in sealed bottles under nitrogen. The temperature was maintained at 130±.5° C. for 24 hours. An additional 3.0 g. of di-tert-butyl peroxide was then added and the heating continued for another 24 hours. The reaction product was then stripped under vacuum to remove volatile decomposition products of di-tert-butyl peroxide and unreacted methyl linoleate. The residue remaining weighed 20 g. This was analyzed and gave the following results:

Sap. No.	188
Iodine No.	168.3
Sp. $\alpha_{234}^{m\mu}$	42.8

Since alkali isomerized methyl linoleate has a specific α_{232} value of 84.3, the value obtained for the residue indicates that on the average there is one pair of conjugated double bonds per each two methyl linoleate units. An ebullioscopic molecular weight determination on another sample made in the same manner showed the average molecular weight to be about 600–640. This indicates that the residue is largely dimeric.

Further evidence of the fact that the residue was largely dimeric was obtained as follows: Twelve grams of the residue was catalytically hydrogenated in 6 hours at 130–160° C. at atmospheric pressure using 0.4 g. of Harshaw nickel catalyst Ni 0501 F (24.2% nickel). The reduced product had a specific α_{234} of 1.2, showing virtual elimination of conjugation. This reduced product was vacuum distilled at 0.05 mm. to yield a main fraction boiling at 240–250° C. at 0.05 mm. and having a saponification value of 188. This boiling range indicates the ester to be largely dimeric.

Example 2

The procedure of Example 1 was followed employing cumene hydroperoxide in place of the di-tert-butyl peroxide. The same type of product resulted.

The dimer ester of Example 1 was used in the preparation of a polyamide by reacting it with ethylene diamine according to the following procedure:

The dimer ester (50 g.) and a 65% aqueous solution of ethylene diamine (7.25 g.) were placed in a 250 cc. three-necked round bottom flask equipped with stirrer, thermometer and 2 ft. Vigreux column carrying an alembic head for removing water and alcohol. The mixture was brought up to 200° C. and held there for two hours, while keeping under nitrogen atmosphere. The mass was heated at 200° C. for another hour under a vacuum

of 0.4 mm. The product was then poured over Dry Ice. The resulting polyamide was more rubbery and tackier than a polyamide prepared in essentially the same manner and from the same components except that ordinary thermally polymerized fatty acid methyl esters were substituted for the dimerized methyl esters of Example 1. This polyamide is referred to as product B. A 35% solution in a 50–50 mixture of toluene-butanol was more viscous than the same concentration of product B. Cobalt drier (0.1% cobalt) was added to the solution and 0.005 inch thick films were spread. These remained tacky until the fourth day when they became harder and tougher than the films similarly prepared from product B.

Example 3

15.0 grams of methyl linoleate and 0.45 gram of di-tertiary butyl peroxide were placed in a 1-ounce small mouth screw cap bottle and the bottle was closed and placed in an oil bath at 130° C.±5° C. The bottle was allowed to remain in the oil bath at this temperature for approximately 27 hours, at which time 0.3 gram of di-tertiary butyl peroxide was then added to the bottle, and the bottle again placed in the oil bath at 130° C. for an additional 24 hours. The monomeric material was stripped off to leave a residue. The residue had a specific alpha at 236 of 48.6. Molecular weight was approximately 625.

I claim as my invention:

1. Process of dimerizing and conjugating a compound selected from the group consisting of higher fatty acids, containing at least two double bonds separated by a methylene group, and monohydric alcohol esters thereof, which comprises heating solely said compound to a temperature within the approximate range of 100–250° C. in the presence of ½ to about 15% by weight based on said compound of an organic peroxide having the formula ROOR¹ in which R is selected from the group consisting of hydrogen and hydrocarbon radicals and R¹ is a hydrocarbon radical.

2. Process of dimerizing and conjugating lower aliphatic esters of higher fatty acids containing at least two double bonds separated by a methylene group, which comprises heating solely said esters to a temperature within the approximate range of 100–250° C. in the presence of ½ to 15% by weight based on said esters of an organic peroxide having the formula ROOR¹ in which R is selected from the group consisting of hydrogen and hydrocarbon radicals and R¹ is a hydrocarbon radical.

3. Process of dimerizing and conjugating methyl linoleate which comprises heating solely methyl linoleate in the presence of ½ to 15% by weight based on said methyl linoleate di-tert-butyl peroxide to a temperature within the approximate range of 100–250° C.

4. Process of dimerizing and conjugating methyl linoleate which comprises heating solely methyl linoleate in the presence of ½ to about 15% by weight based on said methyl linoleate cumene hydroperoxide to a temperature within the approximate range of 100–250° C.

5. The product prepared by the process as defined in claim 1.

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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 46, after "to" insert -- about --;
line 52, after "to" insert -- about --.

Signed and sealed this 6th day of June 1961.

(SEAL)

Attest:

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