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PROCESS FOR THE PRODUCTION OF HIGH-MOLECULAR COMPOUNDS CONTAINING EPOXIDE GROUPS

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This invention relates to an improved process of producing epoxidized high-molecular weight organic compounds and to the compounds so prepared.

I have found that high-molecular weight organic compounds containing epoxide groups can be obtained by reacting high-molecular weight olefinically-unsaturated compounds containing lipophilic radicals with di- or polycarboxylic acids in the presence of activators capable of forming mixed anhydrides, treating the mixture with hydrogen peroxide and isolating the epoxide compounds formed thereby. The total amount of di- or polycarboxylic acid and acid activator should, as a rule, be no greater than 0.5 mol per double bonds of the starting material calculated on a molar basis. The reaction temperatures to be applied lie between 0 and 100° C., preferably between 40 and 60° C.

Examples of suitable olefinically-unsaturated high-molecular weight starting components are the following: aliphatic high-molecular weight olefinic hydrocarbons, derivatives of olefinically-unsaturated high-molecular weight hydrocarbon alcohols, such as the esters of alcohols obtained by reduction of natural-occurring vegetable or animal olefinically-unsaturated fatty acids under preservation of the double bond hereinafter sometimes referred to as olefinically-unsaturated fatty alcohols, or esters of olefinically-unsaturated alcohols which are obtained by splitting natural wax esters, such as esters of olefinically-unsaturated fatty alcohols having from 14 to 18 carbon atoms, especially of oleyl alcohol and other mono- or poly-olefinically-unsaturated alcohols formed with any desired low-molecular weight or high-molecular weight carboxylic acids. Also suitable are the corresponding ethers of the above-mentioned unsaturated alcohols formed preferably with low-molecular weight alcohols.

Furthermore, derivatives of olefinically-unsaturated high-molecular weight fatty acids, such as their esters, amides or nitriles may be used as starting materials. Especially suitable are the natural-occurring glycerides, the fatty acid moiety of which may be mono-unsaturated or poly-unsaturated, such as the semi-drying oils, primarily soybean oil, cottonseed oil and linseed oil. Similarly suitable are olive oil, neat's foot oil, sperm oil and other aquatic animal oils. Examples of other esterifying components for the unsaturated fatty acids are the following alcohols: ethyl, isopropyl, n-butyl, secondary butyl, tertiary butyl, tertiary amyl, n-octyl, 2-ethylhexyl, dodecyl, octadecyl, octadecenyl, cyclohexyl, methylcyclohexyl, naphthenyl, benzyl alcohols, and the like, polyvalent alcohols, such as ethylene glycol, 1,2-propylene glycol, 2-ethylhexanediol - 1,3,butanediol - 1,2,butanediol - 1,3,butanediol-1,4,dodecanediol-1,12, glycol, polyalkylene glycols, such as diethylene glycol, glycerin, pentaerythrite, and the like. Similarly, esters formed by the unsaturated fatty acids and alcohol mixtures may be used as starting materials as well as mixed esters formed by polyvalent alcohols and varying unsaturated fatty acids; for example, the mixed esters formed by ethylene glycol with oleic acid and linseed oil fatty acid. Finally, the esters in which the alcohol moiety as well as the acid moiety possesses a high-molecular weight aliphatic mono-unsaturated or poly-unsaturated hydrocarbon radical may also

be used. In addition to the esters, amides of olefinically-unsaturated fatty acids may be used as starting materials, such as the amidation products of unsaturated fatty acids or fatty acid mixtures produced with ammonia, dimethylamine, dodecylamine, oleylamine, ethylenediamine, cyclohexylamine, benzylamine, etc. Examples of nitriles of unsaturated fatty acids which may be used are tetradecenyl nitrile, hexadecenyl nitrile or also mixtures of alkenyl nitriles having from 14 to 18 carbon atoms in the molecule.

In accordance with the present invention, the above-mentioned starting materials are treated with an epoxidizing mixture containing di- or polycarboxylic acids. Di- or polycarboxylic acids which are suitable for this purpose are, for example, succinic acid, adipic acid, maleic acid or its halogen-substitution products, fumaric acid, citric acid, acetonedicarboxylic acid, sebacic acid, phthalic acids, benzenepolycarboxylic acids or their halogenation products, polyacrylic acids or other polycondensation products containing several carboxyl groups, base-exchange resins containing carboxyl groups, and so forth. It is also possible to use mixtures of di- or polycarboxylic acids for the epoxidation. Furthermore, polybasic carboxylic acids or their mixtures which have been obtained by oxidation cleavage of saturated or unsaturated fatty acids, or their esters, may also be used.

Examples of activators accelerating peracid formation which are capable of forming mixed anhydrides with the above-mentioned di- or polycarboxylic acids are organic or inorganic acids or acid halides, such as mineral acids, including phosphoric acid, nitric acid and sulfuric acid, perchloric acid, borontrifluoride or boron trifluoride-water adducts, acid phosphoric acid esters, p-toluenesulfonic acid, high-molecular weight resins containing sulfonic acid groups, and the like. Some of these activators are known under the name of Lewis acids. These activators are capable of facilitating or accelerating the peracid formation in that they combine with the di- or polycarboxylic acids in an intermediate step to form energy-rich mixed anhydrides.

The epoxidation takes place by virtue of the fact that the di- or polycarboxylic acids are rendered capable of reacting with the hydrogen peroxide and forming organic peracids in the presence of the high-molecular weight olefinically-unsaturated compounds, due to the influence of the activators, and that the peracids cause the transfer of the active oxygen to the double bond of the high-molecular weight olefinically-unsaturated compounds.

The quantitative ratios of the reaction components which are used according to the present invention depend primarily upon the number of double bonds present in the starting material which are to be transformed into epoxide groups.

The concentration of active oxygen—that is, the content of hydrogen peroxide—should lie between 1.1 and 2 mols per molar equivalent of double bonds. In general, the required maximum amount of di- or polycarboxylic acids and activator should not exceed a total of 0.5 mol per molar equivalent of double bonds. However, in those cases where a base-exchange resin containing carboxyl groups is used as an oxygen-transfer agent larger quantities can be used. For reasons of economy and for the purpose of suppressing side-reactions, it is advantageous to maintain the amount of di- or polycarboxylic acids as low as possible. When excessive quantities of di- or polycarboxylic acids are used, the reaction rate and the reaction temperature may be increased to such an extent that the epoxide groups are cleaved and dihydroxy and acyloxy derivatives are formed with a corresponding decrease in the value of the epoxide compounds formed by the reaction.

The process according to the present invention is car-

ried out by first admixing the starting material to be epoxidized with the di- or polycarboxylic acids and the acid activators in the reaction vessel and then raising the mixture to temperatures of preferably 40 to 60° C. Thereafter the calculated amount of an at least 30%, but preferably 50 to 60%, aqueous hydrogen peroxide solution is added slowly and gradually over a period of several hours, accompanied by vigorous stirring, while maintaining the reaction temperature at the indicated value by cooling, if necessary. After the addition of hydrogen peroxide has been completed, it is in many cases advantageous to increase the temperature of the reaction mixture by discontinuing the cooling and supplying additional heat, if necessary, in order to bring the reaction to completion.

The process according to my invention has a number of advantages over other known epoxidizing processes. By continuing the addition of hydrogen peroxide over a period of several hours, the oxidizing agent is always present in such dilute form that the limits of explosive concentration of the organic peracids which form as intermediate products are not reached. Moreover, the organic peracids formed from di- or polycarboxylic acids are not nearly as explosive as the peracetic acid or performic acid formed during the known epoxidation processes. In comparison with known processes in which the total required amount of hydrogen peroxide is added to the reaction mixture at the beginning, the process according to my invention makes it easier to control the epoxidation process by controlling the course of the exothermic reaction. Because of the delayed course of reaction, the danger of formation of undesirable dihydroxy or acyloxy compounds by cleavage of the epoxide ring is also reduced. In those cases where synthetic resins containing carboxyl groups are used, as the required polycarboxylic acid component, a further advantage is derived in that they do not cause a cleavage of the epoxide groups formed during the reaction, even when present in amounts above 0.5 mol per molar equivalent of double bonds. Moreover, the reaction product obtained in accordance with the present invention is much easier to work up after completion of the reaction than when formic acid or acetic acid is used, because the di- or polycarboxylic acids used as oxygen-transfer agents in accordance with the invention are present in solid form after cooling of the reaction mixture, and may thus be separated from the epoxide compounds by filtration and may be reused without further regeneration treatment.

The high-molecular weight epoxide compounds obtained in accordance with the above method are of manifold technical interest. For example, because of their excellent compatibility and resistance to migration, they are useful as auxiliary agents in the production of synthetics, e.g. in the role of softeners and stabilizers for polyvinyl chloride and its mixed polymerizates. Furthermore, they may be used as lubricants and lubricating oil additives or textile oils.

The following examples will further illustrate the present invention and enable others skilled in the art to understand it more completely. It will be understood, however, that the invention is not limited to these particular examples.

Example I

Into a stirring vessel made of VA-steel and provided with a coil heater and a cooling jacket, 750 parts by weight of a soybean oil (acid number 0.2; esterification number 188; hydroxyl number 2; iodine number 122), 100 parts by weight of technical-grade succinic acid and 10 parts by weight of 70–80% sulfuric acid were placed. The contents of the vessel were then heated to a temperature of 40–45° C. Thereafter, 300 parts by weight of a hydrogen peroxide solution containing 50% by weight hydrogen peroxide were added to the mixture during the course of 3–4 hours, accompanied by stirring, while maintaining the temperature at 40–45° C. by cooling the vessel. After completion of the hydrogen peroxide addition, the temperature of the contents was allowed to rise to 50–60° C. by reducing the cooling. At this temperature the reaction product was stirred for 10–12 hours and was then washed with water until neutral. In order to remove small residual amounts of acid components, the reaction product was refined with dilute alkali and finally washed until neutral.

By heating the resultant product to a temperature of 70–90° C. under reduced pressure, a dry epoxidized soybean oil having an epoxide-oxygen content of 5.3% (iodine number 31.2; acid number 0) was obtained.

Example II

The procedure described in Example I was repeated except that in place of succinic acid 50 parts by weight of adipic acid and 50 parts by weight of concentrated phosphoric acid were used in the reaction. After a reaction period of 15 hours, an epoxidized soybean oil having an epoxide-oxygen content of 4.3% (acid number 0; iodine number 50.2) was obtained.

Example III

A synthetic-ion-exchange resin containing carboxyl groups (Levatit CNO) was allowed to swell in dilute phosphoric acid and after 2 to 3 hours standing was squeezed free from excess acid. 100 parts by weight of the resin thus pretreated were suspended in 50 parts by weight of concentrated phosphoric acid. The resultant suspension was stirred for a few hours and then again squeezed to remove excess liquid components. 750 parts by weight of a thoroughly deacidified soybean oil (acid number 0.2; esterification number 188.5; hydroxyl number 2.9; iodine number 129) were added to this resin, and then 300 parts by weight of a 60% by volume hydrogen peroxide solution was added thereto at a temperature of about 40–45° C., accompanied by stirring. The hydrogen peroxide was added over a period of 3 hours. Thereafter, the temperature was allowed to rise to about 50–60° C. and the mixture was stirred for 10–12 hours. Subsequently, the solid components of the reaction mixture were separated from the raw epoxide with the aid of a filter. The raw epoxide was refined in accordance with known methods, washed and dried. A product having an epoxide-oxygen content of 3.24% (acid number 0; iodine number 67.7) was obtained.

Example IV

1000 parts by weight of a cottonseed oil fatty acid-methylcyclohexyl ester (produced from the liquid components of cottonseed oil fatty acids and methylcyclohexanol; saponification number 147; iodine number 97; acid number 0.17; hydroxyl number 1.4) were admixed with 131.5 parts by weight of succinic acid and 13.2 parts by weight of 70–80% sulfuric acid, and the mixture was heated to a temperature of 40–45° C. Thereafter, 400 parts by weight of a hydrogen peroxide solution containing 60% by volume hydrogen peroxide were added to the mixture over a period of 4 hours, while carefully maintaining the temperature of 45° C. Subsequently, the temperature of the reaction mixture was allowed to increase to 50–60° C. and the mixture was stirred for 12–14 hours. The contents of the reaction vessel were allowed to cool and were then filtered to remove the succinic acid which had precipitated mostly in crystalline form. About 75–80% of the original amount of catalyst was thus recovered. The succinic acid can be reused in a subsequent run. The reaction product was then deacidified in a refining container, washed and then freed from water under reduced pressure. The epoxide thus obtained had an epoxide-oxygen content of 4.2% and an iodine number of 12.4.

Example V

By proceeding in accordance with the procedure described in Example 1, but using 100 parts by weight of

citric acid instead of succinic acid, a product having an epoxide-oxygen content of 3.0% (acid number 0; iodine number 76) was obtained.

Example VI

200 parts by weight of a soybean fatty acid-butyl ester (acid number 0; saponification number 165; hydroxyl number 2; iodine number 110) were epoxidized in accordance with the procedure described in Example I in the presence of 60 parts by weight of succinic acid and 12 parts by weight of 70–80% sulfuric acid with 360 parts by weight of a hydrogen peroxide solution containing 60% by volume hydrogen peroxide. After working up the reaction mixture, an ester-epoxide with an epoxide-oxygen content of 4.10% and an iodine number of 15.0 was obtained.

Example VII

A synthetic ion-exchange resin containing sulfonic acid groups (Amberlite I.R. 120) is preliminarily treated with diluted mineral acid, washed and dried.

To a mixture of

68 parts by weight of this resin,
140 parts by weight adapic acid and
2500 parts by weight synthetic soybean oil fatty acid glycerin ester (acid number 0.3, iodine number 121, hydroxyl number 3.0)

obtained by reesterification of the fluid portions of soybean oil fatty acid and glycerin, are added, while stirring during 4–5 hours at a temperature not exceeding 65° C. in a steel vessel, 1300 parts by weight of 50% by weight hydrogen peroxide. During the epoxidation process the temperature is kept at 60–75° C. After a reaction time of about 20–28 hours the mixture is cooled down and the solid portions of the mixture are separated from the fluid portions in a usual manner. The thus obtained synthetic ion-exchange resin is washed and dried and may be reused in the next charge. The fluid raw product is freed from the acid portions by washing with diluted soda lye, washed with water until neutral and dried.

The soybean oil epoxide is refined by treating with fuller's earth and active carbon and shows after that an epoxide-oxygen content of 6.06% and an iodine number 1.6.

Instead of the above described synthetic ion-exchange resin one may use in the like manner other high-molecular weight resins containing free acid especially sulfonic acid

groups as they are described e.g. in "Plaste und Kautschuk," 1955, pages 74–78.

In like manner other high-molecular weight fatty acid derivatives such as the fatty acid amides and fatty acid nitriles and the high-molecular weight fatty alcohols can also be epoxidized by my invention.

While I have disclosed various specific embodiments of my invention, it will be apparent to persons skilled in the art that the present invention is not limited to these specific embodiments and that various changes and modifications may be made without departing from the spirit of the invention or the scope of the appended claim.

I claim:

A process for the introduction of 1,2-epoxy groups into esters of high-molecular weight, olefinically-unsaturated fatty acids containing from 12 to 26 carbon atoms comprising (A) mixing said fatty acid ester with a synthetic ion-exchange resin containing free carboxyl groups and an acid activator capable of forming a mixed anhydride with said free carboxyl groups and accelerating per acid formation selected from the group consisting of mineral acids, organic sulfonic acids and synthetic resins containing sulfonic acid groups which serve as proton donors, said ion-exchange resin containing free carboxyl groups and said acid activator being added in an amount in combination of less than 0.5 mole for each double bond in each mole of said fatty acid, (B) adding slowly over a period of several hours from 1.1 to 2.0 moles for each double bond in each mole of said fatty acid ester of hydrogen peroxide in a solution containing at least 50% hydrogen peroxide while stirring vigorously and maintaining the reaction temperature between 40° C. and 60° C., (C) allowing the reaction to proceed to completion and (D) isolating the epoxidized fatty acid esters.

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