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MAKING PEROXIDIC COMPOUNDS

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The present invention relates to the process of producing peroxidic compounds and particularly to the production of such compounds from fatty materials which are solid and of the consistency of butter at ordinary temperatures, with melting point from 28° C. up.

Among such materials having the consistency of butter may be mentioned beef and mutton tallows, lard and any stearines, vegetable or animal, chaulmoogra, hydnocarpic oils, or hydrogenated oils containing acids having more than 10 carbon atoms.

Compounds produced from buttery, fatty materials seem to possess advantages in the industrial arts and from the standpoint of economy they can be produced with relative ease and cheapness in contrast with similar materials made from predominantly unsaturated fatty materials that are normally liquid at ordinary temperatures.

The peroxidic compounds of the buttery materials, when not associated with peroxides of acids lower than 10 carbon atoms, have many advantages over those produced in prior art from coconut oil.

They are extremely stable and approach in stability benzoyl-peroxide which is recognized as a standard of stability.

They are almost substantially non-oxidizing in comparison with peroxidic compounds known heretofore. In this connection it should be remembered that while inorganic peroxidic compounds act both as reducing and oxidizing agents, the organic peroxidic compounds known in prior art have been substantially oxidizing agents only. The peroxidic compounds of the buttery materials are low in oxidizing power compared with the organic peroxides known heretofore.

Not only are these compounds low in oxidizing power, but they definitely act as inhibitors of oxidation. Thus they can be used in inhibiting rancidity, in the prevention of gum-formation in petroleum oils and of aging phenomena.

From the bacteriological standpoint they are many times more deadly than peroxidic compounds of coconut oil and peroxidic compounds made from phthalic, malic, fumaric, camphoric and succinic acids. Thus, peroxidic compounds made from stearic acid or from the total acids of cocoa butter or from the chaulmoogric or hydnocarpic acids, are many times more germicidal than the peroxidic compounds of the total acids of coconut oil. Benzoyl-peroxide is absolutely inert from the germicidal standpoint. For this reason peroxidic compounds made in accordance with our present invention are more suitable for use in cosmetics and medicinal applications. The active oxygen of these compounds is many hundred times more powerful than the oxygen of inorganic peroxidic compounds, as well as organic peroxidic compounds which are insoluble in water, like benzoyl peroxide. From the standpoint of phenol potency based on the oxygen content in dilution, they range from several hundred to 1500 times more powerful than carbolic acid. They promote the growth of enzymes, although they are deadly to pathogenic bacteria.

It is a well known fact that mixed peroxidic compounds are generally unstable. Hydrogen peroxide when mixed with other oxidizing materials depreciates very rapidly. Permanganate of potash when brought in contact with hydrogen peroxide not only instantly decomposes hydrogen peroxide, but in the process destroys itself. This fact has been made use of in the analysis of hydrogen peroxide by permanganate of potash.

In a prior patent of Kokatnur and Stoddard, No. 1,718,609, mixed peroxidic compounds of the total fatty acids of coconut oil were first described. Known methods of producing the peroxidic compounds in general are by means of either (1) acid anhydrides, or (2) acid chlorides. Both these methods are in substance very old. The main novelty in our present process consists in the adjustment of conditions, the order of steps and the concentration primarily of the alkali used. Prior patents of Kokatnur disclose that the mixed peroxidic compounds of the total fatty acids of coconut oil, contrary to the common belief, are relatively stable. They also disclose that the yield of such peroxidic compounds is almost quantitative when the alkali concentration is adjusted to a given degree.

We have now found that coconut oil peroxides, although relatively stable, are not stable enough from a commercial standpoint and this may be one reason why they have not found practical use. Further, contrary to the disclosure in these prior patents, the yield of peroxidic compounds of buttery materials is very small, if the method of these patents is followed. Experimental work has indicated that low yields of peroxidic compounds of buttery materials are due to the inclusion of the acid chloride by a crust of the newly formed solid peroxidic compound. It would be somewhat like the deposit on a surface by a solid substance dissolved in a volatile solvent, during evaporation of the solvent. To understand the difficulty one may visualize a globule of an acid chloride (liquid at ordinary tempera-

tures) in reaction at the surface with an inorganic peroxide. The newly formed peroxidic material becomes a solid shell with a liquid core of acid chloride. There is lack of minute subdivision at contact.

Whether this theory is true or not, the fact remains that the yields of peroxidic compounds from buttery materials are very low, that is, of the order of 25% to 40%. And we have found that prior methods of producing these compounds have to be radically modified if better yields are to be obtained. For this purpose we have found it extremely advantageous either to use a solvent for acid chloride and hydrogen peroxide, or to decrease the particle size of the globule of the acid chloride by dissolving in an inert solvent, so that a homogeneous precipitate, not encrusted globules, is produced.

We have found that water-soluble alcohols, ketones and ethers are satisfactory as neutral media. As neutral media for reducing the size of the acid chloride globule, we have found low-boiling hydrocarbons both of the aliphatic and the aromatic type, are best suited. We prefer to use in this connection an aromatic hydrocarbon such as benzene as it seems to combine molecularly with the newly formed peroxidic compounds as benzene of crystallization.

The process of this invention satisfactorily produces either pure or mixed peroxidic compounds.

The peroxidic compounds above discussed can be prepared from the total fatty acids of natural fats with butter-like consistency. These fatty acids are often available on the market and are generally prepared by the ordinary saponification process or by the Twitchell process. We, however, prefer to use fatty acids prepared from non-aqueous saponification or splitting as disclosed in U. S. P. 1,913,454 of July 7, 1931. We have found that the fatty acids produced by this method yield more stable and purer peroxidic compounds than those prepared from ordinary fatty acids available on the market or from those prepared by the ordinary saponification or Twitchell splitting method.

In trying to account for this strange difference, we have come to the conclusion that in the ordinary method of saponification or splitting by watery solutions, certain changes in fatty acids occur. What the nature of such changes is, we have so far not been able to determine. We are inclined to believe that during the long boiling operation in the presence of water possibly certain hydroxylation reactions take place. Whether this is so or not, the fact remains that the peroxidic compounds produced from acids which in turn are produced by non-aqueous saponification, are relatively more stable and purer than similar compounds produced from acids produced by the older methods.

The preferred method of the embodiment of our invention is described below. But it should be understood that such appropriate changes as may be obvious to one skilled in the art, may be made without departing from the spirit of the invention as disclosed herein.

Example I

In a suitable vessel fitted with agitator, 30–35 parts by volume of 28 to 30% hydrogen peroxide, and 100 parts by volume of acetone are added. To this mixture of hydrogen peroxide and acetone 100 parts by volume of the acid chloride of the total acids of cocoa butter (designated hereafter as cocoa butter chloride) with an average molecular weight of around 300, and 110 to 115 parts by volume of a 10% solution of caustic soda are added simultaneously in substantially equal amounts gradually and piece-meal. During this addition the agitation is continued vigorously, taking care that the temperature does not exceed 35° C. to 40° C. The addition of the cocoa butter chloride and the caustic soda solutions is so adjusted as to occupy about one hour. By this addition a critical alkalinity is maintained in the solution throughout the experiment. After about one-half hour the agitation may be discontinued if found desirable. The end of the reaction is determined by the color and the state of the subdivision of the reaction mass. The color is generally slightly brownish white and the original liquid thickens uniformly without any lumps. At the end of the reaction the reaction mass or mother liquor is filtered and washed with cold water, temperature between 10° and 18° C. containing 1 to 2% of acetone. The washing is continued until the wash liquor shows no trace of acid chloride or of free hydrogen peroxide. The wet pulverulent and white crystalline material is dried at a temperature not to exceed 37° until it is free from water or acetone. The purity of the material is about 75% and the yield is about 80% of the theoretical. This material may be recrystallized from solvents like petroleum ether, benzene or acetone, etc. to produce a material of 99% purity. If the solution during recrystallization is found to be acidic it should be neutralized and the solvent separated and dried before recrystallizating the peroxide product. To avoid losses of acetone a closed vessel with a distilling as well as a reflux attachment should be used.

Example II

In an apparatus similar to that used in Example I, 30 to 40 parts by volume of hydrogen peroxide, strength 28% to 30% by weight, and 200 parts by volume of commercial benzene are added. It should be noted that the hydrogen peroxide is not soluble in benzene and being heavier stays at the bottom. To this, after the agitation is started, 126 parts of 10% sodium hydroxide solution and 100 parts by volume of cocoa butter chloride are added slowly and simultaneously, keeping the alkali solution, however, in slight excess throughout the addition period.

During the addition the temperature should not be allowed to go substantially above 10° C. and the time of addition and operation should be approximately an hour. During the operation the benzene dissolves the cocoa butter chloride instantly and this solution comes in contact with the dispersing hydrogen peroxide and the added caustic soda solution. The reaction seems to be instantaneous and the peroxide separates in a crystalline mass forming with benzene what appears to be a combination as benzene of crystallization and appearing as a homogenous viscous crystalline slurry.

During the operation the alkali should be added uniformly in excess. The agitation may be stopped after about one-half hour. At the end of the reaction the excess of alkali is neutralized by dilute hydrochloric acid and the excess of benzene distilled under vacuum at a temperature not to exceed 40°. When most of the benzene is substantially removed, the reaction slurry is filtered and washed with water containing about ¼% hydrogen peroxide. Without this small amount of hydrogen peroxide in the water, the

washing and filtration becomes well nigh impossible. After the washing is completed the filter cake is dried as mentioned in Example I. The purity of this material is between 85% and 90%. The yield is between 85% and 88% of the theoretical.

The term, inert diluent, as used herein, is intended to include solvents which are not acted upon by hydrogen peroxide or by the acid chloride. For example, the various ethers, alcohols, ketones or hydrocarbons and their derivatives are suitable to carry out the invention. These may be solvents of one or both of the reacting components, namely hydrogen peroxide and acid chloride. Although alcohols react with acid chlorides to produce esters, in the presence of hydrogen or other peroxides, they do not so react. Thus alcohols are inert in these reactions.

The expressions, integral mixing or fine division or dispersion as used herein are meant to signify mixing of two immiscible materials in a very thorough intimate manner either by the use of a solvent, a diluent, or by merely a mechanical action.

We claim:

1. The process of producing peroxidic compounds of fatty acids from natural fats of butter-like consistency containing acids of more than 10 carbon atoms only, comprising reacting the acid chlorides of the said fatty acids with hydrogen peroxide of about 30% strength, the reacting materials being in a finely divided condition, and neutralizing the chlorine acids as fast as they are produced during the reaction and at a temperature below about 50° C. while maintaining a predetermined slight alkalinity.

2. The process of producing peroxidic compounds of fatty acids from natural fats of butter-like consistency containing acids of more than 10 carbon atoms only, comprising reacting the acid chlorides of the said fatty acids with hydrogen peroxide of about 30% strength in the presence of an inert solvent of said acid chlorides, and neutralizing the chlorine acids as fast as they are produced during the reaction by the progressive addition of alkaline solution whose concentration slightly exceeds that necessary to completely neutralize the chlorine of the acid chloride during the reaction and at a temperature below about 50° C.

3. The process of producing peroxidic compounds of fatty acids from natural fats of butter-like consistency containing acids of more than 10 carbon atoms only, which comprises adding progressively and simultaneously the acid chlorides of the said fatty acids and an alkaline peroxide solution in an inert solvent of said acid chlorides with agitation, the said chlorides and alkaline solution being added in proportions so as to keep the reaction mass slightly alkaline throughout the process and at a temperature not to exceed about 50° C.

4. The process of producing peroxidic compounds of mixed fatty acids derived from cocoa butter which comprises reacting the acid chlorides of the said fatty acids with hydrogen peroxide of about 30% strength, the reacting materials being in a finely divided condition, and neutralizing the chlorine acids as fast as they are produced during the reaction and at a temperature below about 50° C. while maintaining a predetermined slight alkalinity.

5. The process of producing peroxidic compounds of mixed fatty acids derived from cocoa butter which comprises reacting the acid chlorides of the said fatty acids with hydrogen peroxide of about 30% strength in the presence of an inert solvent which has a solvent action on at least said acid chlorides, and neutralizing the chlorine acids as fast as they are produced during the reaction and at a temperature below about 50° C., while maintaining a predetermined slight alkalinity.

6. The process of producing peroxidic compounds of mixed fatty acids derived from cocoa butter which comprises reacting the acid chlorides of the said fatty acids with hydrogen peroxide of about 30% strength in the presence of an inert solvent of said acid chlorides, and neutralizing the chlorine acids as fast as they are produced during the reaction by the progressive addition of alkaline solution whose concentration exceeds that necessary to completely neutralize the chlorine of the acid chloride during the reaction and at a temperature below about 50° C.

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