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GLYCEROL FATTY ACID PARTIAL ESTER GELS

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7 Claims. (Cl. 252—316)

This invention relates to glycerol fatty acid partial ester compositions and more particularly, to high purity monoglyceride compositions.

High purity monoglyceride compositions can be readily prepared by the methods disclosed by Kuhrt in U.S. Patents 2,634,234, 2,634,278 and 2,634,279. In accordance with Kuhrt's methods, a fatty material such as a triglyceride or a fatty acid is interestified with glycerine in the presence of an interesterification catalyst. The resulting interesterification reaction mixture is thereafter subjected to thin film high vacuum distillation to separate a high purity monoglyceride composition.

It is an object of this invention to provide high purity monoglyceride compositions in a new and useful form.

It is another object of this invention to provide high purity monoglyceride compositions in an improved form that is particularly suitable as a carrier material for medicaments.

It is a further object of this invention to provide low melting, high purity, distilled monoglyceride compositions in a new and useful form.

These and other objects are attained by means of this invention as described hereinafter with particular reference to certain preferred embodiments.

In accordance with the invention, new and useful gels can be formed with water and certain especially prepared glycerol fatty acid partial ester compositions.

The glycerol partial ester compositions employed to prepare the present gels contain at least 75%, desirably at least 85%, and preferably at least 90% by weight of monoglycerides having fatty acid radicals with at least 16 carbon atoms and more generally from 16 to 22 carbon atoms. Also, the glycerol partial ester compositions used in the present invention contain less than 10% and preferably less than 5% by weight of glycerides having saturated fatty acid radicals with more than 11 carbon atoms. Partial ester compositions containing glycerides having such 18 carbon atom unsaturated fatty acid radicals as oleic, linoleic and linolenic acid radicals, and admixtures in all proportions thereof, are preferably employed. Particularly suitable are high purity, normally liquid partial ester compositions comprised of a major proportion of such polyunsaturated monoglycerides as monolinolein and monolinolenin or admixtures thereof. Commercial oleic acid mixtures which contain at least 90% by weight of oleic acid can be utilized to prepare the partial ester compositions used in the present gels. Also, the partial ester compositions can be prepared from solvent wintered fatty acid mixtures prepared by saponifying and acidulating such glyceride materials as cottonseed oil, corn oil, poppyseed oil, sunflower oil, safflower oil, linseed oil, peanut oil, soybean oil and the like, the solvent wintering removing substantial amounts of such saturated fatty acids as stearic acid, palmitic acid, myristic acid and lauric acid from the mixtures. For example, a fatty acid mixture consisting essentially of linoleic acid and oleic acid can be prepared from saponified and acidulated cottonseed oil fatty acids by dissolving a cottonseed

oil fatty acid mixture in an equal weight of acetone, chilling the mixture to −15° C. and holding the mixture at this temperature for 24 hours, filtering out the resulting crystallized higher saturated fatty acids, and thereafter distilling the acetone from the filtrate to recover a fatty acid mixture suitable for preparing the high purity monoglyceride compositions used in making the gels described herein. Similarly, a fatty acid mixture consisting essentially of oleic acid, linoleic acid and linolenic acid can be prepared by wintering a linseed oil fatty acid mixture.

The present glycerol fatty acid partial ester compositions can be prepared by reacting glycerol and triglycerides or fatty acids containing the suitable fatty acid moieties described above in the presence of a basic interesterification catalyst, and thereafter separating by thin film high vacuum distillation a composition containing at least 75% by weight of monoglyceride, the balance consisting essentially of diglycerides and triglycerides.

Any of the well known alkali metal and alkaline earth metal interesterification catalyst materials can be employed as the catalyst to prepare the present glycerol fatty acid partial ester compositions. Particularly suited are the alkali and alkaline earth metal oxides, hydroxides, carbonates, alcoholates, hydrides and glyceroxides. Particularly effective are the bivalent metal compounds such as calcium oxide, barium oxide, strontium oxide, strontium hydroxide,, calcium hydroxide, barium hydroxide, etc. Likewise, the catalyst can be added to the reaction mixture in the form of such soaps as sodium stearate, strontium oleate and other higher fatty acid soaps of alkali and alkaline earth metals. The amount of catalyst material can be varied in accordance with usual interesterification practice, with amounts of at least about 0.005% to about 1.0% by weight based on the total weight of the reaction mixture being preferably employed.

The interesterification reaction is preferably carried out with an excess of glycerol over the calculated stoichiometric proportions based on the weight of the fatty acids or triglycerides in the reaction mixture. The reaction is effected at elevated temperatures for optimum results, with temperatures of at least 180° C. and particularly temperatures from about 200° C. to about 280° C. being eminently suitable. The reaction time is usually varied from about 15 minutes to about 6 hours depending upon the ratio of the reactants, concentration of catalyst, reaction temperature and similar variables which affect the speed of the reaction.

The resulting reaction mixture is preferably cooled and a large proportion of the unreacted glycerol phased off. Thereafter, the remaining unreacted glycerol is distilled or "stripped" off the reaction mixture by thin film vacuum distillation, typical distillation conditions being pressures of 10 microns at 90° C. to 300 microns at 150° C. A glycerol fatty acid partial ester composition is then distilled from the reaction mixture, typical distillation conditions being pressures of from 1 micron at 150° C. to 10 microns at 200° C. The pressures referred to above are in microns of mercury. Such distillation conditions are merely illustrative and considerable variations can be made in accordance with usual distillation practice. High vacuum thin film centrifugal distillation is desirably employed for separating the partial ester composition. The interesterification reaction mixture is readily spread in a thin film, usually less than 5 mm. and more generally less than 1 mm. in thickness, on the heated distilling surface of the still, and the partial ester composition rapidly distilled therefrom. The distillations are made without prior "killing" or inactivation of the interesterification catalyst.

The present gels are prepared by incorporating water

into the above described glycerol fatty acid partial ester compositions. As the amount of water incorporated into the present partial ester compositions is increased, the gel becomes increasingly firmer until no more water can be incorporated. Water in amounts of at least 10% of but less than 90% of the weight of the partial ester composition, and preferably from 15% to 50% by weight of the weight of the partial ester composition is incorporated into the partial ester composition to form the present gels. The present gels can be readily formed by combining the partial ester composition with water and heating the resulting mixture until a gelatinous composition is formed. A firm, substantially clear gel is formed on cooling which resembles in appearance petroleum jelly. Gels containing up to about 40% by weight of water based on the partial ester composition can be prepared by this method. Also, the present gels can be prepared by thoroughly mixing or kneading the partial ester composition and water at room temperature. Up to about 90% by weight of water based on the partial ester composition can be incorporated into the partial ester composition by such a mixing or kneading action. Uncombined or excess water can be easily separated by decanting or pouring it from the gel. X-ray diffraction patterns of the present gels indicate that they are in an amorphous form. The common "monodiglyceride" mixtures of commerce which contain about 40% to 50% monoglyceride, about 40% to 50% diglyceride and about 5% to 20% triglyceride do not form gels with water as do the present high purity monoglyceride compositions.

The gels of the present invention can be employed in a diversity of products such as in cosmetics and related products. Likewise, the present gels can be used as carrier materials for medicaments. Medicaments can be incorporated into the gel in amounts up to about 15%, although much smaller amounts are usually employed. Such medicaments as vitamins, amines, enzymes, hormones and the like can be incorporated into the gel. As the present gels are combinations of water and fatty materials, these gels can be utilized as carrier materials for water soluble and fat soluble medicaments and admixtures thereof. Thus for example, a multivitamin gel containing both water soluble and fat soluble vitamins can be prepared. Typical of the vitamins that can be incorporated into the present gels are such water soluble vitamins as thiamin, riboflavin, pyridoxin, nicotinic acid, pantothenic acid, inositol, p-amino benzoic acid and vitamin C; and such fat soluble vitamin materials as vitamin A and fatty acid esters thereof, beta-carotene, vitamin D, vitamin E and fatty acid esters thereof, and vitamin K. To prepare a gel containing water soluble and fat soluble medicaments, the water soluble medicament is dissolved in water, the fat soluble medicament is dissolved in glycerol fatty acid partial ester composition, and thereafter the medicament-containing aqueous solution is incorporated into the medicament-containing fatty acid partial ester composition to form a gel as described hereinabove.

This invention is illustrated by the following examples of preferred embodiments thereof.

Example 1

To a 12 kilogram sample of a mixture of fatty acids comprised of about 57% linoleic acid, about 40% oleic acid, about 2% linoleic acid and about 1% palmitic acid, was added 7.5 kilograms of glycerol and 14 grams of strontium hydroxide. The resulting mixture was heated to 250° C. and maintained at that temperature for 60 minutes during which time the resulting water of esterification was allowed to evaporate from the reaction mixture. The reaction mixture was then cooled and a substantial portion of the unreacted glycerol decanted therefrom. Substantially all of the remaining glycerol was next distilled from the remaining mixture at a pressure of about 10 microns of mercury and at a temperature of 130° C. on a centrifugal, thin film, molecular still having a 14-inch rotor. Thereafter the temperature of the distillation was raised to 180° C., the pressure being maintained at about 10 microns of mercury, and a glycerol partial ester composition distilled over. The resulting distilled product contained about 95% by weight of monoglyceride, was liquid at room temperature, remained a clear liquid to about 23° C., congealed at about 14.5° C. and had an iodine value of 110.

(*a*) A 10 gram portion of the distilled glycerol partial ester composition was thoroughly stirred with 2.8 grams of water at room temperature. A transparent, firm, gel resulted.

(*b*) 8 parts by weight of the distilled glycerol partial ester composition, 2 parts by weight of cottonseed oil and 2 parts by weight of water were thoroughly stirred at room temperature. A firm, substantially clear gel resulted.

Example 2

A distilled glycerol partial ester composition was prepared by the method described in Example 1 except that USP oleic acid was used in lieu of the fatty acid mixture used in the reaction mixture in Example 1. The resulting distilled glycerol partial ester composition contained about 95% by weight of monoglyceride, was a soft white solid at room temperature, melted to clarity at 35° C. and had an iodine value of about 70.

(*a*) Portions of the distilled glycerol partial ester composition prepared from oleic acid were heated at about 90° C. with varying amounts of water and the resulting mixtures cooled to about 20° C. to form compositions having varying physical properties as indicated in the following table. The proportions of partial ester composition and water set out in the table are indicated in percent by weight.

Partial ester Composition, percent	Water, percent	Physical State at 20° C.
100		Soft, opaque solid.
95	+5	Translucent, pourable gel.
90	+10	Transparent, firm gel.
67	+33	Do.

(*b*) A portion of the distilled glycerol partial ester composition prepared from oleic acid and water in an amount slightly in excess of the weight of the partial ester composition were thoroughly stirred at room temperature. Thereafter, the water that did not combine to form a gel with the partial ester composition was decanted, and a transparent, firm, gel resulted which was comprised of about 10 parts by weight of partial ester composition and 9 parts by weight of water.

(*c*) A 5 gram sample of a vitamin A acetate concentrate prepared by chemical synthesis and having a potency of about 2,600,000 U.S.P. units per gram was dissolved in 50 grams of the distilled glycerol partial ester composition prepared from oleic acid. Thereafter, 15 grams of a 1% aqueous nicotinic acid solution were added. The resulting mixture was liquefied by heating to about 60° C. On cooling to room temperature, the liquefied mixture formed a multivitamin-containing gel having the general appearance of petroleum jelly.

(*d*) An 87 gram sample of the distilled glycerol partial ester composition prepared from oleic acid was intimately mixed with 180 grams of water at a temperature of about 50° C. This mixture was then cooled to room temperature, excess water poured off, and a clear, firm gel weighing 129.3 grams resulted. The gel remained stable in a clear, firm state for more than 18 months at room temperature in a closed container.

While the invention has been described in considerable detail with reference to certain preferred embodiments

thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

This application is a divisional application of our copending application, U.S. Serial No. 653,728, filed April 19, 1957, now U.S. Patent No. 2,895,879.

We claim:

1. A firm, substantially clear gel consisting essentially of a glycerol fatty acid partial ester composition containing at least 75% by weight of monoglycerides having fatty acid radicals with at least 16 carbon atoms and having incorporated therein water in an amount of from 10% to 90% by weight based on said glycerol fatty acid partial ester composition, said glycerol fatty acid partial ester composition containing less than 10% by weight of glycerides having saturated fatty acid radicals with more than 11 carbon atoms.

2. A firm, substantially clear gel consisting essentially of a distilled glycerol fatty acid partial ester composition containing at least 85% by weight of monoglycerides having fatty acid radicals with at least 16 carbon atoms and having incorporated therein water in an amount of from 10% to 90% by weight based on said glycerol fatty acid partial ester composition, said glycerol fatty acid partial ester composition containing less than 5% by weight of glycerides having saturated fatty acid radicals with more than 11 carbon atoms.

3. A firm, substantially clear gel consisting essentially of a distilled glycerol fatty acid partial ester composition containing at least 90% by weight of monoglycerides having unsaturated fatty acid radicals with 18 carbon atoms and having incorporated therein water in an amount of from 10% to 90% by weight based on said glycerol fatty acid partial ester composition, said glycerol fatty acid partial ester composition containing less than 5% by weight of glycerides having saturated fatty acid radicals with more than 11 carbon atoms.

4. A firm, substantially clear gel consisting essentially of a distilled glycerol fatty acid partial ester composition containing at least 90% by weight of monoolein and having incorporated therein water in an amount of from 10% to 90% by weight based on said glycerol fatty acid partial ester composition, said glycerol fatty acid partial ester composition containing less than 5% by weight of glycerides having saturated fatty acid radicals with more than 11 carbon atoms.

5. A firm, substantially clear gel consisting essentially of a distilled glycerol fatty acid partial ester composition containing at least 90% by weight of a mixture of monoolein, and monolinolein and having incorporated therein water in an amount of from 10% to 90% by weight based on said glycerol fatty acid partial ester composition, said glycerol fatty acid partial ester composition containing less than 5% by weight of glycerides having saturated fatty acid radicals with more than 11 carbon atoms.

6. A firm, substantially clear gel consisting essentially of a distilled glycerol fatty acid partial ester composition containing at least 90% by weight of a mixture of monoolein, monolinolein and monolinolenin, and having incorporated therein water in an amount of from 10% to 90% by weight based on said glycerol fatty acid partial ester composition, said glycerol fatty acid partial ester composition containing less than 5% by weight of glycerides having saturated fatty acid radicals with more than 11 carbon atoms.

7. A firm, substantially clear gel consisting essentially of a distilled, normally liquid, fatty acid partial ester composition containing at least 90% by weight of monoglycerides having fatty acid radicals with at least 16 carbon atoms, a major portion of said monoglycerides containing polyunsaturated radicals having at least 16 carbon atoms, and having incorporated therein water in an amount of from 10% to 90% by weight based on said glycerol fatty acid partial ester composition, said glycerol fatty acid partial ester composition containing less than 5% by weight of glycerides having saturated fatty acid radicals with more than 11 carbon atoms.

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