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PARTIAL FATTY ESTERS OF GLYCEROL AND POLYGLYCEROL STABILIZED WITH ORGANIC PHOSPHITES

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U.S. Cl. 252—356 4 Claims

ABSTRACT OF THE DISCLOSURE

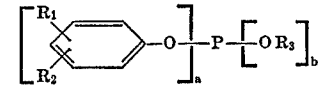
Compositions comprising (1) partial fatty acid esters of glycerol containing at least 40% by weight monoester of glycerol and/or partial fatty acid esters of polyglycerol wherein the polyglyceride has at least one free hydroxyl group and said esters being substantially saturated as indicated by having an iodine number less than about 15 and (2) small amounts of an organic phosphite stabilizer are resistant to deterioration at temperatures in excess of about 200° C. The compositions are widely used as surfactants and dispersing agents.

This invention relates to improved esters of glycerol and polyglycerol. More particularly this invention relates to improved partial glycerol and polyglycerol esters that resist discoloration and deterioration at elevated temperatures.

Various mono- and diesters of glycerol as well as partial esters of polyglycerol with saturated fatty acids have long been known in the art and have been found useful in numerous applications. They are widely used as surfactants and dispersing agents in food, pharmaceutical and cosmetic products. Other applications include lubricating compositions and as plasticizers and emulsifiers for polymers and polymer coating compositions. It has been observed that at elevated temperatures, in the order of 200° C. and above, these predominately saturated fatty glycerides tend to undergo discoloration. These higher temperatures are encountered, for example, when fatty glycerides are used as lubricants in the molding or extrusion of plastics. The use of certain esters of phosphorous-containing acids as stabilizers has been disclosed in the prior art and organic phosphates, phosphites and various derivatives thereof have been employed to prevent deterioration and degradation caused by exposure to oxygen and/or excessive temperatures in a number of materials as, for example, to stabilize soap and soap products, lubricating oils, resins, synthetic rubber, various fats and oils, synthetic lubricants and the like. Examples of the prior art usage of organic phosphite stabilizers may be found in U.S. Pats. Nos. 2,234,379; 2,612,488; 2,717,902; 3,115,463; 3,115,464; 3,115,465 and 3,115,466.

However, there is nothing in the prior art that teaches or even suggests the preparation of partial glycerol esters that are stable at temperatures in excess of 200° C.

In accordance with this invention it has been discovered that compositions comprising (A) a member selected from the group consisting of aliphatic monocarboxylic, particularly fatty acid monoesters and diesters of glycerol and mixtures thereof, mixtures of aliphatic monocarboxylic, particularly fatty acid mono-, di- and triesters of glycerol, said mixtures containing at least about 40% by weight monoester and less than about 25% by weight triester and partial aliphatic monocarboxylic, particularly fatty acid esters of polyglycerols having from 2 to 12 glycerol units and said partial polyglycerol ester having at least one free hydroxyl group, said esters of glycerol and polyglycerol being further characterized as being substantially saturated and having an iodine number up to about 15 and (B) from about 0.1% to 5% by weight based on the weight of constituent (A) of an organic phosphite stabilizer of the formula



where R_1 is selected from the group consisting of hydrogen and alkyl radicals containing at least about 4 carbon atoms and R_2 and R_3 each may be selected from the group consisting of hydrogen and radicals such as alkyl, aryl, alkaryl containing a phenolic hydroxy group, alkaryl and alkaryl containing a phenolic hydroxy group, a is an integer from 1 to 3 and b is an integer equal to $3-a$, are color stable at temperatures in excess of about 200° C.

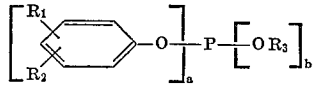
Glycerol esters suitable for use in the compositions of the present invention include aliphatic monocarboxylic, particularly fatty acid mono- and diesters of glycerol and mixtures thereof and preferably C_6 to C_{30} saturated fatty acid esters as well as partial polyglycerol esters of the aforesaid acids, said polyglycerol esters having at least one free hydroxyl group.

Also suitable are mixtures of aliphatic monocarboxylic, particularly fatty acid and preferably C_6 to C_{30} saturated fatty acid mono-, di- and triesters of glycerol, said glycerol ester mixtures containing at least 40% by weight monoester and not more than about 25% by weight triester. Also suitable are partial polyglycerol esters of the aforesaid acids, said polyglycerols having between about 2 and 12 recurring glycerol units. It is essential that the esterified polyglycerol be a partial ester, i.e. it must contain at least one free hydroxyl group. It has been found that glycerides and polyglycerides suitable for use in preparing the compositions of the present invention must be substantially saturated and, therefore, such suitable esters are further characterized as having an iodine number up to about 15, thus indicating the tolerable extent of unsaturation.

Broadly speaking, the fatty acid portion of the ester may contain from about 6 to 30 carbon atoms. Preferably the acyl group will be derived from a long chain, straight chain, substantially saturated, aliphatic monocarboxylic acid containing from about 12 to 18 carbon atoms.

Illustrative esters of saturated fatty acids suitable for use in the compositions of the present invention are glycerol monolaurate, glycerol monopalmitate, glycerol monostearate and mixtures of same, mono- and di-esters of caproic, caprylic, capric, myristic, arachidic and other higher fatty acids and the polyglycerol esters thereof. Also suitable are mixtures of the aforesaid saturated fatty glycerides with various unsaturated fatty acid esters of glycerol and polyglycerol, as for example esters of acids such as caproleic, lauroleic, myristoleic, palmitoleic, oleic, eicosenoic, docosenoic and hexacosenoic acids will be stabilized at high temperatures provided that the degree of unsaturation is such that the iodine number of the glyceride mixture does not exceed about 15. The glycerides and glyceride mixtures which are effectively employed in the compositions of the present invention may be prepared, for example, by the direct esterification of glycerol with the aforesaid acids so as to produce a mixture of mono-, di- and triglycerides. Thus by heating equimolar quantities of stearic acid and glycerol a mixture of monoglycerides and diglycerides with minor amounts of triglyceride is formed. Similar mixtures may be prepared by glycerolysis of a triglyceride. Products with a very high monoglyceride content may be prepared by molecular distillation of commercial monoglyceride mixtures.

Organic phosphite stabilizers suitable for use in the compositions of the present invention may be mono-, di- or triesters of phosphorous acid or mixtures thereof, said esters containing at least one phenyl group and may be represented by the general formula



where R_1 is selected from the group consisting of hydrogen and alkyl radicals having at least 4 carbon atoms and preferably a C_7 to C_{18} alkyl radical, R_2 and R_3 each may be a member selected from the group consisting of hydrogen and radicals such as alkyl, aryl, aralkyl, aralkyl having a phenolic hydroxy group, alkaryl, and alkaryl having a phenolic hydroxyl group, *a* is an integer from 1 to 3 and *b* is an integer equal to 3—*a*. R_2 or R_3 may each be hydrogen, straight or branched chain alkyl radicals, preferably containing up to about 20 carbon atoms including, for instance, methyl, ethyl, butyl, hexyl, octyl and dodecyl radicals, among others aryl and aralkyl radicals, such as, for instance, phenyl, benzyl, methylbenzyl, nonylphenyl, diisobutyl benzyl, phenylethyl, phenylpropyl, phenyloctadecyl radicals, and the like as well as napthyl and alkyl substituted napthyl radicals, aralkyl radicals having a phenolic hydroxyl group such as is exemplified by a p-hydroxycumenyl radical.

Specific examples of suitable organic phosphites useful in the compositions of the present invention are isooctyl dinonylphenyl phosphite, butylated Bisphenol A phosphites and others as disclosed in U.S. Pat. No. 3,112,286, phenyl nonylphenyl dinonylphenol phosphites, p-t-butylphenyl di-isodecyl phosphite, bis(alphamethylbenzylphenyl) 2 - ethylhexyl phosphite, Bisphenol A di-isooctylphosphite, di(hexadecylphenyl) lauryl phosphite, tridecyl diphenyl phosphite, di(2,6 - di-t-butylphenyl) phosphite and 2-t-butyl-2(3-t-butyl - 4 - hydroxyphenyl) bis(p-nonylphenyl) phosphite. Especially suitable and preferred are tris-nonylphenylphosphite, tris - di-nonylphenylphosphite, bis-dinonylphenyl nonylphenyl phosphite, bis-nonylphenyl di-nonylphenylphosphite and mixtures of same.

The proportions of the organic phosphites utilized in the compositions of the present invention should be from about 0.1% to 5% by weight and preferably about 0.5 to 2% by weight based upon the weight of the glyceride component. No beneficial effect is obtained by using more than about 5% by weight of organic phosphite, however, greater quantities of stabilizer may be utilized if so desired. Conventional techniques may be employed to prepare the compositions of the present invention. Preferably the organic phosphite will be added to the thoroughly intermixed with glyceride at a temperature slightly in excess of the melting point of the glycerol ester or mixture of esters.

The invention is further illustrated by the following examples which are not to be considered as limitative of its scope. All percentages stated are by weight.

EXAMPLE I

Heat stability tests were performed at 230° C. upon certain glycerides to which was added 1% stabilizer consisting of a mixture of tris (mono- and dinonylphenyl) phosphites. The glycerides were heated in beakers with occasional stirring and samples were periodically removed and placed on a glass plate to cool and solidify. The degree of discoloration was visually observed. Control experiments were performed with glycerides containing no phosphite stabilizer. The results are tabulated below in Table 1.

Test compositions employed

(A) Glyceride consisting of approximately 40% glycerol monostearate, 45% glycerol distearate and 15% glycerol tristearate

(B) Composition A containing 1% stabilizer

(C) A polyglycerol monostearate containing about 75% by weight stearic acid with a saponification number of 150

(D) Composition C containing 1% stabilizer

TABLE 1

Time (minutes)	Degree of discoloration A	B	C	D
0				
20	Slight	None	Slight	None
40	do	do	Moderate	Slight.
60	do	do	Severe	Do.
80	Moderate	Slight	do	Moderate.
100	do	do	Complete	Do.
120	Severe	do	do	Do.
140	do	do		
160	do	do		

EXAMPLE 2

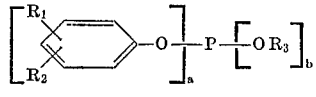
In this example, heat stability tests were conducted at a temperature of 265° C. and samples were taken every 15 minutes. The test compositions A and C were the same as employed in Example 1. Composition B was prepared with Composition A and 2% of the organic phosphite stabilizer of Example 1 and Composition D was prepared with Composition C and 2% of the organic phosphite stabilizer of Example 1.

TABLE 2

Time (minutes)	Degree of discoloration A	B	C	D
0				
15	Slight	None	Slight	None.
30	Moderate	do	Severe	Do.
45	Severe	Slight	Complete	Slight.
60	Complete	do		

What is claimed is:

1. A composition having color stability at temperatures in excess of about 200° C. consisting essentially of (A) a member selected from the group consisting of C_6 to C_{30} aliphatic monocarboxylic acid monoesters and diesters of glycerol and mixtures of same, mixtures of aliphatic monocarboxylic acid mono-, di-, and triesters of glycerol, said mixtures containing at least about 40% monoester and up to about 25% by weight triester and C_6 to C_{30} aliphatic monocarboxylic acid partial esters of a polyglycerol having between about 2 and 12 glycerol units, said partial ester having at least one free hydroxyl group, said ester of glycerol and polyglycerol being further characterized as having an iodine number of up to about 15, and (B) from about 0.1% to 5% by weight based on the weight of the (A) component of an organic phosphite stabilizer of the formula



where R_1 is selected from the group consisting of hydrogen and alkyl radicals containing at least about 4 carbon atoms, R_2 and R_3 are members selected from the group consisting of hydrogen and radicals such as alkyl, aryl, aralkyl, aralkyl containing a phenolic hydroxy group, alkaryl and alkaryl containing a phenolic hydroxy group, *a* is an integer from 1 to 3 and *b* is an integer equal to 3—*a*.

2. A composition according to claim 1 wherein said aliphatic monocarboxylic acid is a substantially saturated long chain fatty acid containing from 12 to 18 carbon atoms.

3. A composition according to claim 1 wherein the composition contains from about 0.5% to 2% by weight of the said phosphite stabilizer.

4. A composition according to claim 1 wherein the phosphite is a member selected from the group consist-

ing of tris-nonylphenylphosphite, tris-dinonylphenylphosphite, bis-dinonylphenyl nonylphenylphosphite and mixtures of same.

References Cited

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RICHARD D. LOVERING, Primary Examiner

U.S. Cl. X.R.

252—54.6, 400; 260—398.5