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SOLVENTS FOR FAT AND OIL ANTIOXIDANTS

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This application is a continuation-in-part of copending application Ser. No. 532,123 filed September 1, 1955, which is abandoned in favor of this continuing application.

This invention relates to antioxidant compositions for fats and oils. In particular, it relates to acetins and their utilization as solvent materials for various antioxidant compositions. These acetins can be used alone, as mixtures with themselves or as mixtures with other antioxidant solvents such as the mono- and diglycerides.

Most fat and oil antioxidants are solid materials. However, commercial use often necessitates that these antioxidants be liquid. Consequently, it is necessary to employ some solvent or mixture of solvents. Such a solvent should dissolve a high concentration of the antioxidants; it should be inexpensive, odorless, colorless, tasteless, compatible with fats and oils, and preferably, it should be non-toxic.

Various solvents for fat and oil antioxidants are known and are currently in use. Perhaps the most widely used solvent is propylene glycol. This solvent is not completely satisfactory in certain cases; furthermore, a solution containing a high concentration of citric acid is impossible to achieve. Moreover, other antioxidants are only sparingly soluble in propylene glycol.

Although certain monoglycerides are good solvents for butylated hydroxytoluene, butylated hydroxyanisole, and propyl gallate, these monoglycerides are not useful in some applications requiring higher concentrations of an acid synergist, such as citric acid, because they are extremely poor solvents for citric acid. In these cases where a high concentration of acid synergist is desired, it is desirable to maintain the antioxidant concentration at as high a level as is possible and yet increase the acid synergist concentration.

Since many antioxidant compositions are mixtures of several components which usually include citric acid or other acid synergist, it is highly desirable to have a solvent which will allow the preparation of such solutions.

An object of this invention, therefore, is to provide solvents for antioxidant compositions for which there are no other satisfactory solvents at present which fulfill the desired characteristics to the requisite degree.

Another object is to provide solvents for the various acid synergists which are used in antioxidant compositions, said solvents being compatible with fats and oils and with other known solvents.

Another object of our invention is to provide solvents for antioxidant compositions which are acceptable for food use.

A still further object of this invention is to provide an inexpensive and effective means for making solutions of the various antioxidant compositions, particularly those which comprise acid synergists.

Other objects will be apparent from the description and claims that follow.

We have found that the acetins, i.e. mono-, di-, and tri-acetin, are excellent solvents for fat and oil antioxidants. They are particularly good solvents, when used alone or in combinations of the acetins themselves or in combinations of one or more of the acetins with other solvents, for the acid synergists as typified by citric acid, phosphoric acid, and the like. When they are used alone, or in combination with themselves or other solvents, the acetins very satisfactorily dissolve the various antioxidant compositions.

Because of the several-component composition of most antioxidant compositions, different acetins are often advantageously employed as solvents for separate materials which will make up the final solution, utilizing those acetins which are the best solvents for the respective materials. Then, since the acetins are compatible with each other, the different component solutions can be brought together to form the final antioxidant solution. As an example, monoacetin can be used as a solvent for an acid synergist, while triacetin can be used as a solvent for a specific antioxidant; then the two solutions can be brought together, forming a compatible antioxidant mixture in solution. In a like manner, diacetin and triacetin can be used, and other combinations of the acetins, antioxidants, acid synergists, and other solvents can be used, depending upon the type of composition which is desired as an end product. Thus, antioxidant compositions can be produced in solvent media, namely one or more of the acetins, which permits the combination of separate solutions without undergoing undesirable effects such as salting out of components or separation into phases upon combination.

We have found that diacetin particularly is an excellent solvent for citric acid, and, like the other acetins, is compatible with other antioxidants and with fats and oils. Triacetin is a good solvent for all of the common fat and oil antioxidants. Mixtures of di- and triacetin are very good solvents for any of the combinations of the common fat and oil antioxidants, and especially for the antioxidant compositions containing acid synergists. Monoacetin is particularly valuable as a solvent for the various acid synergists which are employed in antioxidant compositions. It has been found to be very useful when incorporated with other solvents for antioxidants, including propylene glycol and the other acetins.

One or more of the acetins can thus be used as solvents for any of the well-known antioxidants or synergists. Among the antioxidants which may be dissolved in the acetins are the phenolic antioxidants, the acetins being particularly useful as solvents for phenolic antioxidants such as butylated hydroxyanisole, butylated hydroxytolu-

ene, propyl gallate, nordihydroguaiaretic acid, gum guaiac, the tocopherols, hydroquinone, 2,4,5-trihydroxybutyrophenone, 2,4,5 - trihydroxyacetophenone, 5 - acenaphthenol, etc. The acetins are also useful as solvents for other classes of fat and oil antioxidants such as glycine, lecithin, 3,3'-thiodipropionic acid and esters thereof, etc. as well as various mixtures of any of these or similar materials.

The acetins are valuable solvents for synergists such as citric acid, phosphoric acid, ascorbic acid, isopropyl citrate, and other similar materials. This is one of the most advantageous and unobvious features of this invention since a common solvent for various solutes including synergists is quite unexpected. Synergists are sometimes called metal deactivators.

The following table illustrates the solubility of typical antioxidants and synergists in the acetins when used singularly.

TABLE I

Solubility (percent by weight)

	Citric acid	Propyl Gallate	Butylated Hydroxyanisole	Butylated Hydroxytoluene	2,4,5-Trihydroxybutyrophenone	Hydroquinone
Monoacetin	25	15	----------	----------	10	10
Diacetin	30	25	30	5	25	10
Triacetin	5	10	50	30	30	5

As is apparent from Table I, individual acetins or mixed acetins can be used without any other solvent components to dissolve various antioxidant and synergistic components. These and other stabilizers mentioned above can be readily dissolved in acetin solvents (various acetic acid esters of glycerine). The invention is particularly concerned with acetin solutions of mixtures of synergists and phenolic antioxidants (one or more of each type of component).

Any of the well-known solvents can be used in combination with the acetins and antioxidant compositions. Certain embodiments comprise using glycerine, propylene glycol, acetic acid, naturally occurring fats and oils, and products derived from naturally occurring fats and oils such as higher fatty acid monoglycerides, diglycerides, etc. in various combinations with one or more of the acetins.

The following compositions were prepared and tested. These data are given in order to illustrate the type compositions that can be made, and to indicate the Active Oxygen Method (AOM) stability provided by the particular compositions. These data are based on tests conducted under equivalent conditions employing similar samples of lard in each instance. The AOM figures are in hours required for formation of 20 milliequivalents of peroxide per kg. of fat, with air bubbling through the samples at 98° C. A peroxide value of 20 was taken, according to normal practice, as corresponding to a commercially objectionable rancidity level.

In Table II, BHA represents a mixture of isomers consisting of 3-tertiarybutyl-4-hydroxyanisole and 2-tertiarybutyl-4-hydroxyanisole; BHT represents 3,5-ditertiarybutyl-4-hydroxy toluene. These antioxidants are frequently referred to in the art as butylated hydroxyanisole and butylated hydroxytoluene respectively. The latter compound is sometimes referred to as butylated p-cresol.

TABLE II

Components of Antioxidant Composition	Concentration, Weight Percent	AOM Stability in Hours
(a)		
25% Solute composed of: 40% BHA (10% of overall); 40% BHT (10% of overall); 20% Citric Acid (5% of overall). 75% Solvent composed of: 4% Propyl gallate (3% of overall); 48% Diacetin (36% of overall); 48% Corn oil monoglyceride (36% of overall)	0.05	63
(b)		
30% Solute composed of: 66.7% BHA (20% of overall); 20.0% Propyl gallate (6% of overall); 13.3% Citric acid (4% of overall). 70% Solvent composed of: 100% Diacetin (70% of overall)	0.05	93
(c)		
50% Solute composed of: 100% BHA (50% of overall). 50% Solvent composed of: 100% Triacetin (50% of overall)	0.04	31
(d)		
30% Solute composed of: 100% BHA (30% of overall). 70% Solvent composed of: 100% Diacetin (70% of overall)	0.067	31
(e)		
30% Solute composed of: 100% BHT (30% of overall). 70% Solvent composed of: 100% Triacetin (70% of overall)	0.067	52
(f)		
25% Solute composed of: 100% 2,4,5-Trihydroxybutyrophenone (25% of overall). 75% Solvent composed of: 100% Diacetin (75% of overall)	0.08	180
(g)		
30% Solute composed of: 83.3% 2,4,5-Trihydroxybutyrophenone (25% of overall); 16.7% Citric acid (5% of overall). 70% Solvent composed of: 100% Diacetin (70% of overall)	0.08	190
(h)		
10% Solute composed of: 100% Hydroquinone (10% of overall). 90% Solvent composed of: 100% Diacetin (90% of overall)	0.20	150

Since most antioxidant compositions are mixtures of several components, it is impossible to assign specific limits to the concentration of acetins used. If the concentration of one component is varied, there will be an effect on the maximum concentration of the other components. However, as indicated in Table I, certain maximum concentrations are possible to achieve and, generally, the maximum concentration is the desirable one. Therefore, although rather specific solubilities may be determined for the acetins and one other material as shown by Table I, since the application of this invention to actual antioxidant compositions quite frequently deals with compositions having several components, no one of which is fixed except by the use for which the overall composition is intended, the invention is not to be limited by any specific expressed concentrations of acetins which can be used.

The antioxidant compositions with which this invention is concerned can be used to stabilize any of the various fatty materials subject to rancidity such as solid or liquid fats and oils, including the free fatty acids such as oleic acid, the animal fats such as lard and tallow,

the vegetable oils such as soybean oil, corn oil, cottonseed oil, and peanut oil, the partial esters of any mono- or diglycerides, and similar well-known fatty materials.

Thus, the acetins are useful and valuable as solvents, alone and in combination with themselves and other solvents, for fat and oil antioxidant compositions, particularly those including difficultly fat soluble acid synergists, and provide a means whereby the antioxidant field is expanded toward more useful commercial antioxidant compositions.

Although this invention has been illustrated to a considerable extent by Tables I and II, the data provided in Table III, as presented hereinbelow, is illustrative of other examples of this invention.

tion for addition to fats and fatty oils, which composition consists essentially of a homogeneous solution of the following components by weight: (1) from 5 to 50% of a solute essentially composed of 0–10 parts of a synergist and 5–42 parts of at least one compound normally effective in stabilizing fats and fatty oils against oxidative degradation and (2) from 95 to 50% of a solvent essentially composed of 10–95 parts of at least one acetic acid ester of glycerine and from 0–69 parts of at least one organic compound effective as a solvent for the solute. Of course, those components (synergists and supplemental solvents) where the parts can be 0 part by weight are optional components but if they are present there can be one or more of each of such optional components.

TABLE III*a*

Components of Antioxidant Composition	Antioxidant Compositions Giving Approximate Percentages by Weight (±0.1%) of (a) Solute, (b) Solvent and (c) Overall Weight											
	A		B		C		D		E		F	
Solute components:												
Hydroquinone												
BHT	a32.6	c15	a33.3	c10	a33.3	c10	a30.0	c15	a31.2	c10	a75	c30
BHA	a32.6	c15	a33.3	c10	a33.3	c10	a30.0	c15	a31.2	c10		
Propyl gallate	a13.1	c6	a33.3	c10	a20.0	c6	a24.0	c12	a18.8	c6		
2,4,5-Trihydroxybutyrophenone												
Citric acid	a21.7	c10			a13.3	c4	a16.0	c8	a18.8	c6	a25	c10
Ascorbic acid												
Total solute	a100	c46	a100	c30	a100	c30	a100.0	c50	a100.0	c32	a100	c40
Solvent components:												
Monoacetin												
Diacetin	b33.3	c18	b14.3	c10	b14.3	c10	b30	c15	b14.7	c10	b33.3	c20
Triacetin												
Glyceryl monooleate	b66.7	c36	b42.8	c30	b28.6	c20	b40	c20	b29.4	c20	b66.7	c40
Corn oil			b42.8	c30	b57.1	c40	b30	c15	b55.9	c38		
Propylene glycol												
Total solvent	b100	c54	b100	c70	b100	c70	b100	c50	b100	c68	b100	c60

TABLE III*b*

Components of Antioxidant Composition	Antioxidant Compositions Giving Approximate Percentages by Weight (±0.1%) of (a) Solute, (b) Solvent and (c) Overall Weight									
	G		H		I		J		K	
Solute components:										
Hydroquinone							a100	c5	a33.3	c5
BHT	a75	c30	a75	c30						
BHA										
Propyl gallate										
2,4,5-Trihydroxybutyrophenone					a50	c5			a33.3	c5
Citric acid	a25	c10	a25	c10	a50	c5				
Ascorbic acid									a33.3	c5
Total solute	a100	c40	a100	c40	a100	c10	a100	c5	a100	c15
Solvent components:										
Monoacetin					b44.4	c40			a9.4	c8
Diacetin	b16.7	c10	b16.7	c10	b44.4	c40				
Triacetin							b100	c95	a9.4	c8
Glyceryl monooleate	b50.0	c30	b66.7	c40					a18.8	c16
Corn oil	b33.3	c20	b16.7	c10					a62.4	c53
Propylene glycol					b11.1	c10				
Total solvent	b100	c60	b100	c60	b100	c90	b100	c95	a100	c85

The antioxidant compositions shown in Table III were subjected to storage at −12° C. for more than 90 hours with no apparent adverse effects. Some of these compositions were rather viscous liquids at sub-zero temperatures but upon warming to room temperature, no separation was observed. Compositions F, G and H solidified at −12° C. but upon warming to room temperature they were completely miscible. Antioxidant potencies for the compositions of Table III were analogous to those illustrated in Table II and depended upon the concentration of the solutes in the fat or oil serving as the substrate during the tests.

Analysis of the data presented in Tables I, II and III shows that advantageous embodiments of this invention are provided by a normally liquid antioxidant composi-

The various numerical values for the parts by weight are based on the figures shown in the various tables and can be varied somewhat without departing from the scope of the invention.

The optional organic solvents which can be present are preferably one or more higher fatty acid glycerides (mono-, di- and triglycerides) which are normally liquid. Such glycerides can be readily obtained from fats and fatty oils, e.g. animal or vegetable fats or oils. These glycerides are well known in the art as solvents for antioxidants. Quite obviously, those which are normally solids are not considered as useful solvents. The higher fatty acid glycerides can be obtained by reacting a fat or fatty oil with glycerine, usually in the presence of a catalyst.

Although the synergists are optional components, the use of acetins as solvents produces its most advantageous and unobvious results as to compositions containing synergists. As shown in Table III, from 5 to 10 parts of a synergist such as citric acid, phosphoric acid, ascorbic acid, or the like can be employed to achieve especially advantageous antioxidant compositions. The use of citric acid is normally of especially useful advantage.

Since, as already indicated, mixtures of antioxidants with higher fatty acid glycerides are well known in the art, care should be taken not to confuse the present invention with such disclosures as illustrated in U.S. Patent 2,745,749 where there is disclosed an acetylated monostearate described as a colorless, odorless and tasteless oil to which enough propyl gallate was added to prevent the oxidation of the oleoyl radical (present due to the fact that the mono-stearate used contained about 3% olein) when subjected to aeration for more than 700 hours at 208° F. It is obvious that disclosures of this type involve the employment of very small percentages of antioxidant compounds in the total mixture. As those skilled in the art well know, the use of about 0.02% of an antioxidant is normally adequate and percentages higher than 0.1 are rarely employed. In contrast, the antioxidant compositions of this invention contain at least 5% of a solute essentially composed of stabilizing compounds. According to most commercial applications of this invention, the percentage of solute would be at least 25% by weight of solute. Although the range from 5% to the probable commercial minimum of 25% is somewhat arbitrary, it is conceivable that some situations may exist where antioxidant compositions of advantageous utility would contain solute within this range. In any event, the especially preferred embodiments of this invention containing solute in the range of from 25 to 50% are not even remotely conceivable as a result of any reasonable analysis of the prior art.

Since the acetins with which this invention is concerned are specific compounds and are vastly different from the higher fatty acid glycerides, it should be noted that the acetins are by definition acetic acid esters of glycerine. The three acetins can also be called the monoacetate, the diacetate and the triacetate of glycerine. The term acetin is not generic to acetic acid esters of higher fatty acid mono- and diglycerides. The term acetin as used in this specification is only generic to the three acetic acid esters of glycerine specifically encompassed within the term acetin.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A normally liquid antioxidant composition for addition to fats and fatty oils consisting essentially of from 5 to 50% by weight of active constituents composed of from 5 to 42 parts by weight of a phenolic antioxidant out of a total of 5 to 52 parts by weight of active constituents and from 95 to 5% by weight of a solvent composed of from 10 to 95 parts by weight of an acetic acid ester of glycerine out of a total of 10 to 164 parts by weight of solvent.

2. An antioxidant composition as defined in claim 1 wherein the active constituents are present in an amount of from 25 to 50%.

3. An antioxidant composition as defined in claim 2 wherein the active constituents contain from 5 to 10 parts of a synergist selected from the group consisting of citric acid, phosphoric acid and ascorbic acid and from 5 to 42 parts of said phenolic antioxidant, and said solvent is essentially entirely composed of at least one member selected from the group consisting of an acetic acid ester of glycerine, propylene glycol and a normally liquid higher fatty acid glyceride from fats and fatty oils.

4. An antioxidant composition as defined in claim 3 wherein the synergist is citric acid.

5. An antioxidant composition as defined in claim 4 wherein the solvent is composed entirely of at least one acetic acid ester of glycerine.

6. An antioxidant composition as defined in claim 4 wherein said solvent contains from 35 to 69 parts of at least one of said normally liquid higher fatty acid glycerides obtained from fats and fatty oils.

7. An antioxidant composition as defined in claim 6 comprising tertiary butylhydroxyanisole, 3,5-ditertiary-butyl-4-hydroxytoluene, propyl gallate, citric acid, diacetin, and glyceryl mono-oleate.

8. An antioxidant composition as defined in claim 6 comprising tertiary butylhydroxyanisole, propyl gallate, citric acid and diacetin.

9. An antioxidant composition as defined in claim 6 comprising tertiary butylhydroxyanisole, propyl gallate, citric acid, diacetin and glyceryl mono-oleate.

10. An antioxidant composition as defined in claim 2 comprising tertiary butylhydroxyanisole and diacetin.

11. An antioxidant composition as defined in claim 2 comprising tertiary butylhydroxyanisole and triacetin.

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