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FATTY MONOGLYCERIDE CITRATE AND ANTI-OXIDANT CONTAINING THE SAME

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6 Claims. (Cl. 99—163)

This invention relates to a fatty monoglyceride citrate and also to antioxidant compositions containing the same.

This application is a continuation-in-part of my copending application Serial No. 317,593, filed October 29, 1952 and is a continuation of my pending application Serial No. 393,950, filed November 23, 1953.

The protection of fats against oxidation has long been a problem. Lard, particularly, requires the presence of an antioxidant to avoid rancidity. These antioxidants must be fat soluble in themselves or made so. The antioxidants now primarily in use are propyl gallate, "BHA" (butylated hydroxyanisole) and "NDGA" (nordihydroguaiaretic acid). In connection with all of these antioxidants, it has been customary to use synergists. Of these, citric acid is the most important because it not only improves the action of the antioxidant, but because it is a metal sequestering agent and thus prevents or inhibits color changes and also by its sequestration is in a position to remove metals which may act as pro-oxidants. Citric acid, however, is not fat soluble.

I have now discovered that citric acid may be rendered fat soluble without in any way destroying the value of the citric acid as a synergist or as a metal sequestering material by reacting it under proper conditions with fatty monoglycerides. When so reacted, it may be introduced to the fat in any suitable manner, either together with or separately from the primary antioxidant.

The fatty monoglycerides are, of course, well known as emulsifying or dispersing agents. However, in the present case, they form a new reaction product with citric acid, fatty monoglyceride citrate. The existence of this new compound has been shown definitely by X-ray studies. Microanalysis of the material shows complete absence of citric acid.

The term "fatty monoglyceride" has been employed to cover monoglycerides of the higher fatty acids, particularly those with ten or more carbon atoms. Preferably, of course, the glycerides are of fatty acids of the order of eighteen carbon atoms. The fatty acids need not be saturated.

The preferred monoglycerides actually employed have the following characteristics.

Average chemical and physical data:

(a) Cottonseed monoglyceride:	
Monoester content	90.0% (minimum).
Saponification value	150-160.
Iodine value	80-90.
Glycerol content	1.0% (maximum).
F. F. A. (as oleic)	1.5% (maximum).
Specific gravity	0.96 @ 60° C.
Melting point	45-50° C. (113-122° F.).
(b) Lard monoglyceride:	
Monoester content	90.0% (minimum).
Saponification value	160-170.
Iodine value	45-55.
Glycerol content	1.0% (maximum).
F. F. A. (as oleic)	1.5% (maximum).
Specific gravity	0.96 @ 60° C.
Melting point	50-60° C. (122-140° F.).

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(c) Hydrogenated lard monoglyceride:

Monoester content	90.0% (minimum).
Saponification value	160-170.
Iodine value	3 (maximum).
Glycerol content	1.0% (maximum).
F. F. A. (as stearic)	1.5% (maximum).
Specific gravity	0.96 @ 75° C.
Melting point	70° C., 158° F. (approx.).

As an example of making the new compound fatty monoglyceride citrate, anhydrous citric acid was added to cottonseed monoglyceride previously heated to 265° F. The citric acid was added over a period of approximately 3 minutes and the mixture stirred continuously during this addition, and for 45 minutes thereafter, until substantially complete reaction occurred. During this period the temperature was maintained at about 265° F. An X-ray analysis of the resultant antioxidant product showed that the characteristic diffraction lines for citric acid is such were not present in the X-ray pattern for this composition. Instead, the lines were different and characteristic, thus indicating that a fatty monoglyceride citrate was formed as a new entity or compound.

Instead of employing anhydrous citric acid in the above described example, U. S. P. crystalline citric acid (the monohydrate $C_6H_8O_7 \cdot H_2O$ containing 8.58% H_2O of crystallization) was employed. An X-ray analysis of this resultant antioxidant also indicated the formation of the new entity or compound fatty monoglyceride citrate.

As an example of preparing fatty monoglyceride citrate dissolved in an edible oil, corn oil was then added slowly to the cottonseed monoglyceride citrate solution at 210° F. following which the temperature was dropped down to approximately 120° F. and agitation continued for 20 minutes. The temperature was raised to 160° F. and then propyl gallate was added with vigorous agitation for 15 minutes with the temperature being maintained at 160° F. After cooling the solution to room temperature, "BHA" (butylated hydroxyanisole) concentrate was slowly stirred in for 20 minutes.

Formulations were made as follows:

	Percent
(a) Cottonseed monoglyceride	10.000
Anhydrous citric acid	3.735
Propyl gallate	3.335
Corn oil	49.630
	66.7
(b) Cottonseed monoglyceride	15.000
Anhydrous citric acid	3.735
Propyl gallate	3.335
Corn oil	44.630
	66.7
(c) Cottonseed monoglyceride	20.000
Anhydrous citric acid	3.735
Propyl gallate	3.335
Corn oil	39.630
	66.7
(d) Products a, b or c	66.7
"BHA" concentrate	33.3
Total	100.0
"BHA" concentrate:	
Butylated hydroxyanisole	13.32
Corn oil	19.98
	33.3

In a modified procedure for preparing fatty monoglyceride citrate, citric acid was added to cottonseed monoglyceride previously heated to 265–275° F. and the mix agitated moderately for 1½ hours until substantially complete reaction occurred. Propyl gallate was then added to the resulting fatty monoglyceride citrate solution at 225–265° F. and the mix vigorously agitated for 6–10 minutes. The heat was cut off and the temperature gradually decreased to 210°–220° F. over a period of from 25–35 minutes while moderately stirring the mix. "BHA" concentrate, prepared by dissolving "BHA" in corn oil at 120–130° F. was then added to the fatty monoglyceride citrate-propyl gallate mix at 210–220° F. and the solution agitated for from 5–10 minutes. A preferred formulation used in this modified procedure is as follows:

	Percent
Fatty monoglyceride	26.0
Anhydrous citric acid	5.0
Propyl gallate	5.0
	36.0
"BHA" concentrate	64.0
Total	100.0
"BHA" concentrate:	
"BHA"	11.0
Corn oil	53.0
	64.0

In another example of preparing the new compound, anhydrous citric acid was added to cottonseed monoglyceride previously heated to 245–255° F. and the mix agitated moderately for 3 hours until substantially complete reaction occurred.

Propyl gallate was added to the resulting reaction product at 245–255° F. with moderate agitation for 45 minutes, without application of heat. "BHA" concentrate heated to a temperature of from about 115–130° F. was then added to the fatty monoglyceride citrate-propyl gallate mix at 195–210° F. and the solution agitated for 5–10 minutes until the "BHA" concentrate was completely dissolved.

A preferred formulation used in this procedure is as follows:

	Percent
Fatty monoglyceride	25.0
Anhydrous citric acid	5.0
Propyl gallate	5.0
"BHA" concentrate	65.0
	100.0
"BHA" concentrate:	
"BHA"	11.0
Corn oil	54.0
	65.0

The product of this formulation had a jelling point of 40–42° F., a turbidity point of 54–57° F., and a clearing point of 58–61° F. It took several hours for the product to become turbid at 54–57° F.

The above-mentioned formulation was tested for antioxidant properties when used with commercial lard. Three samples of the lard were used: (1) a control sample containing no antioxidant; (2) a sample impregnated with the above formulation; and (3) a sample impregnated with the above formulation prepared without the addition of citric acid. Each sample was tested for both the time necessary for rancidity to occur and the degree of discoloration effected by the addition of iron. The time required for the sample to become rancid was determined by the standard Active Oxygen Method. The discoloration test consisted of adding 5 p. p. m. of an

alcoholic solution of ferric chloride to each sample. The results are shown in Table I:

Table I

Lard Sample	A. O. M. Hours	Color After Standing 1 Day
1. Containing no antioxidant.....	9	Light Grey.
2. Containing preferred embodiment.....	54	Light, Clear, Transparent.
3. Containing antioxidant without citric acid.	35	Dark Bluish-Grey.

Fatty monoglyceride and citric acid may be reacted at a temperature range of from about 220–300° F. Prolonged heating of the mix above 300–310° F. is destructive to the fatty acid monoglyceride citrate and below 220° F. the product formed is unstable. The preferred reaction temperature range is from about 265–275° F. with about 1½ hours agitation at this temperature range to achieve substantially complete reaction. It is to be noted that one hour of agitation of the mix at 265–275° F. results in a considerable amount of citric acid crystallizing out.

Prolonged agitation of the fatty monoglyceride citrate-propyl gallate mix produces an opaque solution which will result in sedimentation. To prevent this opaqueness, agitation should be limited to not more than about 30 minutes at 260–265° F. and to not more than about 55 minutes at 230–240° F.

The same products may be prepared with cottonseed oil proceeding in identically the same way but substituting cottonseed oil for corn oil. Other vegetable or animal oils may be employed. Selection of an animal as against a vegetable oil normally will be determined by the product in which the material is to be employed.

Formulations were made with the cottonseed oil product as follows:

	Percent
(e) Cottonseed monoglyceride	20.000
Anhydrous citric acid	3.735
Propyl gallate	3.335
Cottonseed oil	39.630
	66.7
(f) Product e	66.7
"BHA" concentrate	33.3
Total	100.0
"BHA" concentrate:	
Butylated hydroxyanisole	13.32
Cottonseed oil	19.98
	33.3

In preparing either the corn oil or cottonseed product, it is important that the mixture be heated sufficiently long, otherwise sedimentation may occur in the final product.

Olive oil may be used in place of corn or cottonseed oil. Preparation of such a fatty monoglyceride citrate was made using the preferred conditions outlined above.

As an example of using olive oil, anhydrous citric acid was added to cottonseed monoglyceride previously heated to 265–275° F. and the mix agitated moderately for 1½ hours until substantially complete reaction occurred. Propyl gallate was then added to the resulting fatty monoglyceride citrate solution at 255–265° F. and the mix vigorously agitated for 5–10 minutes, no heat being added. Agitation was then reduced to a moderate stir for about 35–45 minutes, allowing the temperature of the mix to drop gradually to 200–215° F. "BHA" concentrate, prepared by dissolving "BHA" in olive oil at 115–130° F., was then added to the fatty monoglyceride citrate

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propyl gallate mix at 210–220° F. and the solution agitated for from 5–10 minutes. The formulation was:

	Percent
Fatty monoglyceride	18.0
Anhydrous citric acid	5.0
Propyl gallate	3.34
"BHA"	13.34
Olive oil	60.32
	100.00

When using propyl gallate as one of the antioxidants, darkening will occur at the higher temperatures which will not occur at lower temperatures. In the instances where color is an important item, the slight sedimentation may be disregarded.

Product A above, using only 10% of the monoglyceride and 3.735% anhydrous citric acid appears to be on the borderline, and slight sedimentation may result. At 12%, this slight sedimentation disappears.

The cottonseed oil product gives a slightly better color in the finished material than the corn oil product.

The invention has also been carried out with lard monoglyceride and hydrogenated lard monoglyceride. However, cottonseed monoglyceride is preferred to lard or hydrogenated lard monoglycerides. Less precipitation of waxy substances and greater resistance to cold temperature occurs in the reaction product when using cottonseed monoglyceride.

In the case of the lard monoglyceride, anhydrous citric acid was added to the monoglyceride which had previously been heated to 260° F. The product was continuously agitated and stirred for 45 minutes while maintaining this temperature. It was then cooled to 210° F. and the corn oil added slowly. The temperature was allowed to fall to 120°–125° F. while agitation was continued for about 15 minutes. The temperature was then raised to 150–155° F. and propyl gallate added over a period of about 2 minutes. Stirring was continued for another 25 minutes while maintaining the temperature at about 155° F.

In preparing the "BHA" antioxidant, "BHA" concentrate was then added slowly at room temperature and agitated for 25 minutes.

In the case of hydrogenated lard, the temperatures are necessarily somewhat higher. During the addition of corn oil, the temperature should not be permitted to drop below about 140° F., otherwise the solution becomes too viscous and develops foaming.

Similarly, with this material the temperature is raised to 160–165° F. after the addition of the corn oil.

Furthermore, the temperature is maintained at 160° F. or higher during the addition of the propyl gallate. During the addition of the "BHA" concentrate, the hydrogenated lard compound should be maintained at 160° F. and during the agitation afterward at 135° F.

Combinations of the resulting fatty monoglyceride citrate may be formulated in the case of the lard monoglyceride and hydrogenated lard monoglyceride in the same manner and in the same proportions as above described.

The lard and hydrogenated lard products are stable at higher temperatures than is the case with the cottonseed oil product.

The products made with corn or cottonseed oils added to the fatty monoglyceride-citric acid reaction product were fat and oil soluble and were moderately soluble and dispersible in water.

The formulations may be made in a single batch rather than by forming the "BHA" concentrate separately. As an example, anhydrous citric acid was added to cottonseed oil or lard monoglyceride which had previously been heated to 260° F., and the mixture was stirred for 45 minutes and then cooled to 210° F. Corn or cottonseed oil was then added slowly and agitated for 20 minutes,

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during which time the temperature dropped to approximately 120–125° F. The mixture was then heated to 150–155° F. and propyl gallate added slowly over a period of 2 minutes. This mixture was then agitated for 20 minutes while maintained at 155° F. A completely clear solution was formed. "BHA" was then added at 135–140° F. while agitating for 25 minutes. During the addition of the "BHA" the solution becomes somewhat turbid, but on standing for 48 hours, the solution clears up.

The preferred proportions in the above procedure are as follows:

	Percent
Fatty monoglyceride.....	15.000
Anhydrous citric acid.....	3.735
Propyl gallate.....	3.335
Butylated hydroxyanisole.....	13.320
Corn oil.....	64.610
	100.0

As an example of the single batch method using preferred conditions, anhydrous citric acid was added to fatty monoglyceride previously heated to 265–275° F. and the mix agitated moderately for 1½ hours until substantially complete reaction occurred. The reaction mixture was then cooled to a temperature of about 200° F. by means of a water bath in from 3 to 4 minutes, following which "BHA" was added at 200° F. The resulting mix was agitated for 10 minutes with the mix at a temperature of about 195–200° F. Corn oil was then added and the mix stirred for 30 minutes without further heating to completely dissolve the corn oil. The preferred proportions in the above procedure are as follows:

	Percent
Fatty monoglyceride.....	15.00
Anhydrous citric acid.....	5.00
Propyl gallate.....	3.34
Butylated hydroxyanisole.....	13.32
Corn oil.....	63.34
	100.00

The two batch process, employing a separate mixture of "BHA" and corn oil, olive oil and the like, is preferred as it decreases the probability of volatilizing the "BHA."

Other formulations have been prepared using cottonseed monoglyceride and lard monoglyceride following the same procedures as hereinbefore outlined and employing 30% of the monoglyceride, 6% anhydrous citric acid, 6% propyl gallate, and 58% corn oil. These products are moderately dispersible in water and completely fat and oil soluble.

The antioxidant mixtures are added to oils or fats to be stabilized preferably by first heating the oils or fats to 140° F. to 240° F. Normally, only from .01% to .10% of the antioxidant composition is required, based on the weight of the fat or oil.

A successful rancidity retardant can be prepared by dissolving propyl gallate in fatty monoglyceride citrate. Such a product may be prepared by the steps outlined in the two batch process by eliminating the addition of "BHA" concentrate, or in the single batch process by eliminating the addition of "BHA."

As an example of the production of a propyl gallate rancidity retardant, citric acid was added to cottonseed oil monoglyceride previously heated to 265–275° F., and the mix agitated moderately for 1½ hours until substantially complete reaction occurred. After cooling the mix to 255–265° F., propyl gallate was added, followed by agitation for 20 minutes without application of heat. This mix was cooled to about 200° F. in 5 to 6 minutes and corn oil was then added without any additional heating. The resulting mix was agitated for 10 minutes until the

corn oil was completely dissolved. The proportions used were:

	Percent
Cottonseed oil monoglyceride-----	27.0
Anhydrous citric acid-----	9.0
Propyl gallate-----	6.5
Corn oil-----	57.5
	100.0

The resulting antioxidant product had a jelling point of 44-45° F., a turbidity point of 56-58° F. and a clearing point of 65° F. Constant refrigeration and warming up of the product raised the clearing point to 69° F. and it is preferred to store the product at 70-80° F. to discourage precipitation.

It is to be noted that larger deposits of amorphous substances are present in the fatty monoglyceride citrate-propyl gallate mix than when "BHA" is added.

While I have given examples of particular antioxidants, the fatty monoglyceride citrate is a synergist and ion sequestering agent for antioxidants generally.

Powdered hydrated citric acid may be employed in the procedures outlined above.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations should be understood therefrom as modifications will be obvious to those skilled in the art.

What is claimed is:

1. An antioxidant composition comprising a solution in an edible oil of fatty monoglyceride citrate and an oil soluble antioxidant of the group consisting of butylated hydroxyanisole and propyl gallate.

2. An antioxidant composition comprising a solution in

an edible oil of fatty monoglyceride citrate and propyl gallate.

3. An antioxidant composition comprising a solution in an edible oil of fatty monoglyceride citrate and butylated hydroxyanisole.

4. An antioxidant composition comprising a solution in an edible oil of fatty monoglyceride citrate, propyl gallate and butylated hydroxyanisole.

5. The method which comprises reacting a fatty monoglyceride with citric acid, dissolving the same in a heated edible oil, and then introducing thereto a concentrate of butylated hydroxyanisole in an edible oil to form an antioxidant composition in solution form.

6. The method which comprises mixing citric acid with a fatty monoglyceride at a temperature of from about 220-300° F., agitating the mix at said temperature until substantially complete reaction occurs to form fatty monoglyceride citrate, adding propyl gallate to the reaction product at said temperature, agitating until substantially all of the propyl gallate is dissolved, adding a concentrate of butylated hydroxyanisole and an edible oil to the resulting fatty monoglyceride citrate-propyl gallate mix at a temperature of from about 200-215° F. and then agitating until said concentrate is substantially completely dissolved.

References Cited in the file of this patent

UNITED STATES PATENTS

2,683,694	Hoffman et al.	July 13, 1954
2,699,395	Brown	Jan. 11, 1955
2,701,203	Gooding	Feb. 1, 1955