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**STABILIZED UNSATURATED COMPOSITIONS
AND STABILIZER THEREFOR**

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This invention relates to stabilized compositions containing unsaturated organic material normally subject to oxidation, and to improved stabilizers for such unsaturated material.

Unsaturated compositions, such as fats, oils, polyenes, and the like, are normally subject to attack at the unsaturated linkages. In the case of fats and oils the oxidation results in rancidity and decomposition. In the case of polyenes, including terpenes such as vitamin A, the oxidation results in a loss in potency due to a change in the chemical composition of the unsaturated material.

It is accordingly an object of this invention to provide unsaturated organic compositions of improved stability.

It is a further object of the invention to provide stabilized compositions containing unsaturated organic material normally subject to oxidation and also containing new and improved stabilizers therefor.

Another object of the invention is to provide new stabilizers adapted to protect unsaturated materials against oxidation.

Another object of the invention is to provide new compositions of matter stabilized against objectionable peroxide formation.

Another object of the invention is to provide improved unsaturated glyceride compositions stabilized against rancidity.

Another object of the invention is to provide compositions containing unsaturated monoglycerides normally subject to oxidation and having new and improved stabilizers incorporated therein.

Another object of the invention is to provide new and improved compositions containing a predominantly non-polar unsaturated vehicle stabilized against oxidation.

Other objects of the invention will be apparent from the description and claims which follow.

These and other objects of the invention are attained by means of this invention as described more fully hereinafter.

The stabilization of unsaturated compounds is of particular importance in the field of fats and oils containing a greater or lesser amount of unsaturated glycerides. These materials are readily subject to peroxide formation resulting in oxidation and rancidity. The development of rancidity makes such materials unfit for use. Other unsaturated and normally unstable materials such as vitamin A and similar polyenes are also subject to a serious loss in potency due to saturation unless adequate steps are taken to stabilize them.

One of the important classes of materials normally subject to oxidation is the class of fatty acid partial esters of polyhydric alcohols and particularly the unsaturated monoglycerides and diglycerides. Peroxide formation in such partial ester compositions is particularly objectionable because of the inherent instability of such partial esters. Because of this inherent instability, the decomposition due to oxidation takes place at an accelerated pace.

By means of this invention compositions containing a predominantly non-polar unsaturated vehicle are effec-

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tively stabilized against oxidation. Many of the common antioxidants which normally function by ion-interchange in polar media are totally ineffective to stabilize fats, oils and similar predominantly non-polar materials. The materials which are stabilized in accordance with this invention include the unsaturated glycerides such as are found in the vegetable oils as typified by cottonseed oil, soybean oil, coconut oil, peanut oil, and the like, as well as the animal fats such as lard, tallow, and the like.

Other materials which are stabilized in accordance with this invention are the unsaturated free fatty acids such as linolenic acid, linoleic acid, and similar unsaturated fatty acids either alone or as a constituent of other compositions. The partial esters which are stabilized in accordance with this invention include mono- or diglycerides as well as mixtures of such mono- and diglycerides with each other and/or with triglycerides.

The monoesters are commonly produced by reacting a fatty acid or acids, or a fatty material containing triglycerides, with a polyhydric alcohol, such as glycerine, in the presence of an ester-interchange catalyst in accordance with well-known practice.

The compositions embodying the present invention comprise a vehicle as described hereinabove and normally subject to oxidation, and a stabilizer comprising a hydrohalide of ethylene diamine tetra-acetic acid incorporated in such vehicle. For purposes of brevity, ethylene diamine tetra-acetic acid will hereinafter be referred to as EDTA. I have discovered that the hydrohalides such as the hydrochloride, hydrobromide, and the like, of EDTA effectively stabilize the non-polar unsaturated materials against oxidation. The stabilizer is preferably incorporated in the vehicle in an amount equal to at least 0.01% by weight of stabilizer based on the weight of the vehicle. Amounts of stabilizer such as 0.05%, 0.1%, 0.5% or 1.0% also are effectively used and higher amounts can be employed although further enhancement of stability is not attained in most cases by the use of higher amounts.

In some cases, particularly in the case of solid vehicles such as lard, solid fats, solid partial esters and the like, it is desirable to dissolve the stabilizer in a small amount of a suitable liquid medium in which the stabilizer and the vehicle are soluble and incorporate the solution of stabilizer in the vehicle. The polyhydric alcohols such as glycerine, glycols and the like are preferably employed as solvents. If desired, the solvent can be removed from the composition by vaporization or similar means, after incorporation of the stabilizer into the composition.

The free acid herein designated as EDTA has been employed for stabilization in polar media, but is not effective as a stabilizer in the predominantly non-polar compositions such as are employed in the present invention.

The hydrohalides of EDTA, employed as stabilizers in accordance with this invention, are readily prepared by reacting the free acid, EDTA, with the desired hydrohalic acid such as hydrochloric acid, hydrobromic acid or the like.

The effectiveness of the hydrohalides of EDTA in stabilizing a non-polar unsaturated vehicle normally subject to oxidation is clearly shown in Table I. The vehicle which was stabilized consisted predominantly of cottonseed oil monoglycerides prepared by reacting cottonseed oil with an excess of glycerine in the presence of an alkaline ester-interchange catalyst and vacuum distilling the monoglyceride from the resulting reaction product. The monoglyceride composition obtained thereby was, of course, a mixture of monoesters including unsaturated monoesters. The stability of the compositions set out in Table I was determined by an accelerated oxidation test which involved heating the samples in a bath at 98° C. while blowing air through the sample. The peroxide con-

tent was determined by chemical analysis, a peroxide value of 20 being considered the upper permissible limit.

Table I

Additive	Percent	Peroxide Value				
		0 hrs.	5 hrs.	7 hrs.	24 hrs.	28 hrs.
None.....		8	34	-----	-----	-----
EDTA.....	0.05	8	32	-----	-----	-----
Sodium salt of EDTA.....	0.05	8	22	-----	-----	-----
EDTA hydrochloride.....	0.05	8	7	8	177	-----
Do.....	0.075	8	6	7	30	366
Do.....	0.10	8	6	7	15	24
Sodium salt of EDTA.....	0.10	8	19	28	-----	-----

As can be seen from Table I, the glyceride composition containing no stabilizer was rancid in less than 5 hours. Similarly, the composition stabilized with free EDTA was also rancid in less than 5 hours. The composition stabilized with a sodium salt of EDTA showed a slight improvement but became rancid in about 5 hours and was considered unsuitable for commercial use. On the other hand, EDTA hydrochloride effectively stabilized the monoester composition for more than 24 hours in the case where 0.10% of the stabilizer was employed.

In Table II, the results of tests employing very low levels of the stabilizer are shown. In the accelerated test employed, a peroxide value of 20 in 3 hours was considered to be the permissible maximum for commercial compositions. The material employed as a vehicle was a cottonseed oil monoglyceride composition. The vehicle had an initial peroxide value of 4. As shown by the data in Table II, an amount of stabilizer equal to 0.0025% of stabilizer prepared on the weight of vehicle gave a peroxide value of 20 in 3 hours and a peroxide value of 104 in 7 hours.

Table II

Additive	Percent	Peroxide Value				
		0 hrs.	3 hrs.	7 hrs.	12 hrs.	16 hrs.
EDTA hydrochloride.....	0.0025	4	20	104	-----	-----
Do.....	0.005	4	20	98	-----	-----
Do.....	0.01	4	7	23	-----	-----
Do.....	0.025	4	4	8	16	30

Other predominantly non-polar unsaturated vehicles, including other unsaturated glyceride compositions as well as terpenes, polyenes and similar well-known oxidizable materials are also stabilized by any of the hydrohalides of EDTA in corresponding amounts.

Thus, by means of this invention unsaturated compositions of improved stability are obtained. Although 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 without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A stabilized composition of matter comprising a pre-

dominantly non-polar unsaturated vehicle normally subject to oxidation stabilized by a hydrohalide of ethylene diamine tetra-acetic acid incorporated in said vehicle, said vehicle being selected from the class consisting of fats containing substantial amounts of unsaturated glycerides, oils containing substantial amounts of unsaturated glycerides, unsaturated free fatty acids, and unsaturated fatty acid partial esters of polyhydric alcohols.

2. A stabilized composition of matter comprising an unsaturated glyceride normally subject to oxidation, and a stabilizing amount of a hydrohalide of ethylene diamine tetra-acetic acid incorporated in said glyceride.

3. A stabilized composition of matter comprising a predominantly non-polar unsaturated vehicle normally subject to oxidation and being stabilized by a hydrochloride of ethylene diamine tetra-acetic acid incorporated in said vehicle, said vehicle being selected from the class consisting of fats containing substantial amounts of unsaturated glycerides, oils containing substantial amounts of unsaturated glycerides, unsaturated free fatty acids, and unsaturated fatty acid partial esters of polyhydric alcohols.

4. A stabilized composition of matter comprising an unsaturated glyceride normally subject to oxidation stabilized by a hydrochloride of ethylene diamine tetra-acetic acid incorporated in said glyceride.

5. A stabilized composition of matter comprising an unsaturated fatty acid partial ester of polyhydric alcohol stabilized by a hydrohalide of ethylene diamine tetra-acetic acid incorporated in said partial ester.

6. A stabilized composition of matter comprising an unsaturated monoglyceride normally subject to oxidation and a stabilizer therefor comprising a hydrochloride of ethylene diamine tetra-acetic acid.

7. A stabilized composition of matter comprising a predominantly non-polar unsaturated vehicle normally subject to oxidation and at least 0.01% by weight based on the weight of said vehicle of a hydrochloride of ethylene diamine tetra-acetic acid incorporated in said vehicle, said vehicle being selected from the class consisting of fats containing substantial amounts of unsaturated glycerides, oils containing substantial amounts of unsaturated glycerides, unsaturated free fatty acids, and unsaturated fatty acid partial esters of polyhydric alcohols.

8. A stabilized composition of matter comprising an unsaturated glyceride normally subject to oxidation and at least 0.01% by weight based on the weight of said glyceride of a hydrochloride of ethylene diamine tetra-acetic acid incorporated in said glyceride.

9. A stabilized composition of matter comprising an unsaturated monoglyceride and at least 0.01% by weight based on the weight of said monoglyceride of a hydrochloride of ethylene diamine tetra-acetic acid incorporated in said composition.

References Cited in the file of this patent

UNITED STATES PATENTS

2,371,623	Henderson	Mar. 20, 1945
2,428,353	Bersworth	Oct. 7, 1947
2,463,015	Bersworth	Mar. 1, 1949