Patented Jan. 4, 1938 2,104,242

UNITED STATES PATENT OFFICE

2,104,242

COMPOSITION OF FATTY MATTER AND PROCESS OF STABILIZING SAME

Albert S. Richardson, Wyoming, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

No Drawing. Application January 30, 1935, Serial No. 4,124

15 Claims. (Cl. 87—9)

This invention relates to the treatment of oils, fats or fatty materials for the purpose of retarding oxidation and the accompanying changes.

This application is a development made by me pursuant to the discoveries made by myself working together with Messrs. Vibrans and Andrews, set forth in application Ser. No. 627,618, filed August 5, 1932.

It is well known that unsaturated vegetable and animal fats or oils are subject to gradual oxidation by air and that such oxidation tends to cause rancid odor and flavor.

It is also known that certain substances added in small proportions to oxidizable materials have the property of retarding oxidation. Such substances have been called antioxidants, or antioxygens; they have achieved extensive commercial use in rubber, but relatively little use in fats and fatty oils, especially those of edible grade. There is apparently no way of predicting what kinds of substances will protect any given oxidizable material, although it has generally been believed that an antioxygen must be oxidized more easily than the material it protects.

I have, however, found a group of substances which are active antioxygens when used in oils and fats and greatly delay rancidity even when used in amounts of less than one per cent, but which are not themselves readily oxidizable by air. This group consists of phosphorous acid together with its acid reacting derivatives. These compounds are not oxidizing agents, like nitric acid and chloric acid, for example, but contain stably bound oxygen. The acid reacting derivative is preferably a simple salt, such as $Ca(H_2PO_3)_2$ or NaH_2PO_3.

The following are examples of my process. To a sample of refined deodorized cottonseed oil were added varying amounts of a fifty per cent solution of phosphorous acid, after which the different samples together with a blank were each subjected to oxidation under identical conditions by inclosing one gram of the oil in a clean, glass flask with about 70 c. c. of air and tested for the time required before rapid absorption of oxygen from the air began. This is a standard method of testing samples of oil for oxidizability. Results are as follows.

H_3PO_3 (50% sol.)	Induction period
Percent	*Hours*
None	26
.001	50
.002	55

These results show that the so-called induction period or the time elapsed before rapid absorption of oxygen begins was almost doubled by the addition of only .001 per cent of 50 per cent phosphorous acid while with the addition of .002 per cent a still longer induction period was found. Other experience shows that similar results are obtainable with the acid reacting derivatives of phosphorous acid.

Phosphorous acid and its acid reacting derivatives appear to be particularly effective in retarding the oxidation of unsaturated fats which happen to be contaminated with a trace of metal such as copper, which is known to exert strong catalytic properties in the oxidation of fatty oils. In a given series of observations a very pure vegetable cooking oil, having an induction period of about 57 hours in the oxygen absorption test mentioned above, was warmed and agitated with 0.05% and 0.1% by weight of an aqueous solution containing 52% NaH_2PO_3, and various tests showed an average resulting increase in the induction period of about 13%. On the other hand, the induction period of a similar vegetable cooking oil contaminated with about one part per million of copper was increased by more than 50% (from about 10 hours to more than 15 hours) after treatment with 0.05% of the same concentrated solution of NaH_2PO_3. Treatment with 0.1% of the acid phosphite resulted in approximately a three-fold increase in the induction period.

This invention, therefore, is not limited to the use of phosphorous acid alone. The action of compounds of this group appears to be similar to that of the group of acids and acid reacting derivatives containing stably bound oxygen mentioned in the said application of Richardson, Vibrans and Andrews.

While I prefer to incorporate a small percentage of these acid antioxidants in the finished fatty product, especially in edible fats or fatty oils during cooling at end of steam deodorization, my invention is also useful for treating oils and fats which are to be exposed to air during factory storage and handling. If the presence of the acid-reacting substance in the finished product is objectionable, my invention may still be used for protection of oils and fats during storage, the antioxidant being eventually removed by alkali refining, water washing, or any other known means, before the final processing.

In practicing my invention it is merely necessary to add to the oil or fat the desired quantity of the antioxidant and mix same uniformly. I may use for this purpose, for example, phosphorous acid or any acid reacting salt or phosphorous acid, such as the acid calcium salt for example. The quantities necessary to obtain good antioxidant action are very small and do not ordinarily exceed .5% on the weight of the oil expressed in terms of phosphorous anhydride. Excellent antioxidant action on ordinary edible

oils such as cottonseed oil, peanut oil, soya bean oil, corn oil, etc., salad oils in general, and shortenings, is obtained through the use of quantities ranging from .0001 to .01% expressed as phosphorous anhydride. With the use of these very minute quantities there is no danger of alteration of the odor or flavor of the oil or fat, nor will darkening or other undesirable changes occur even when the product is heated to a high temperature.

I am aware that certain materials, such for example as phosphoric acid, have been previously used to retard the bacterial spoilage of butter and that other materials of acid reaction have been similarly used to retard the bacterial decomposition of products containing moisture and protein and incidentally containing also fat, and I make no claim to any such process. The present invention is applicable to the retardation of oxidation or rancidity in substantially dry fatty materials which do not contain material subject to bacterial spoilage, but as hereinbefore explained tend to become rancid as a result of atmospheric oxidation. The acid reacting derivatives of phosphorous acid which are suitable for use in my invention must actually have an acid reaction.

The term "fatty materials" as used in this specification and in the claims includes any fat or fatty oil subject to rancidity due to oxidation.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:—

1. The process of stabilizing against rancidity due to oxidation, fatty materials which are substantially dry and substantially free from organic matter subject to bacterial decomposition, which comprises incorporating therewith a small quantity of a compound selected from the group consisting of phosphorous acid and its acid reacting derivatives.

2. The process of stabilizing against rancidity due to oxidation, fatty materials which are substantially dry and substantially free from organic matter subject to bacterial decomposition, which comprises incorporating therewith a small quantity of a compound selected from the group consisting of phosphorous acid and its acid reacting derivatives, and removing said compound after it has served its purpose and prior to using said fatty material.

3. The process of stabilizing against rancidity due to oxidation, fatty materials which are substantially dry and substantially free from organic matter subject to bacterial decomposition, which comprises incorporating therewith a small quantity of phosphorous acid.

4. The process of stabilizing against rancidity due to oxidation, deodorized edible fatty materials which are substantially dry and substantially free from organic matter subject to bacterial decomposition, which comprises incorporating therewith after deodorizing, a compound selected from the group consisting of phosphorous acid and its acid reacting derivatives in quantity such that the phosphorous anhydride so introduced is equivalent to less than .01 per cent in the fatty matter.

5. The process of stabilizing against rancidity due to oxidation, fatty materials which are substantially dry and substantially free from organic matter subject to bacterial decomposition which comprises incorporating therewith an inorganic acid reacting phosphite.

6. Substantially dry, deodorized edible fatty material free from organic matter subject to bacterial decomposition, said fatty material having incorporated therewith a compound selected from the group consisting of phosphorous acid and its acid reacting derivatives in quantity such that the phosphorous anhydride so introduced is equivalent to less than .01 per cent of phosphorous acid in the fatty material, whereby the tendency to develop rancidity due to oxidation is lessened.

7. Lard stabilized against rancidity due to oxidation, said lard having incorporated therewith phosphorous acid in an amount less than .01 per cent.

8. A process for treating substantially dry fatty materials to retard oxidation and the consequent undesirable changes, without at the same time causing undesirable changes in color, odor and flavor, consisting in treating the said fatty material with a compound selected from the group consisting of phosphorous acid and its acid reacting derivatives, in quantity such that the phosphorous anhydride so introduced is equivalent to less than 0.01 per cent of phosphorous acid in the fatty material.

9. A process for treating substantially dry fatty materials to retard oxidation and the consequent undesirable changes, without at the same time causing undesirable changes in color, odor and flavor, consisting in treating the said fatty material with phosphorous acid in an amount less than .01 per cent.

10. A process for treating substantially dry fatty materials to retard oxidation and the consequent undesirable changes, without at the same time causing undesirable changes in color, odor and flavor, consisting in treating the said fatty material with an acid reacting phosphite in such an amount that the phosphorous anhydride in same is equivalent to less than .01 per cent of phosphorous acid.

11. Substantially dry fatty material stabilized against rancidity due to oxidation by the addition of a compound selected from the group consisting of phosphorous acid and its acid reacting derivatives, in quantity such that the phosphorous anhydride so introduced is equivalent to less than .01 per cent of phosphorous acid in the fatty material.

12. Substantially dry fatty material stabilized against rancidity due to oxidation by the addition of phosphorous acid in a quantity not exceeding 0.01 per cent.

13. Substantially dry fatty material stabilized against rancidity due to oxidation by the addition of an acid reacting phosphite in such an amount that the phosphorous anhydride in same is equivalent to less than .01 per cent of phosphorous acid.

14. Substantially dry salad oil stabilized against rancidity due to oxidation by the addition of phosphorous acid in an amount less than .01 per cent.

15. Substantially dry deodorized winterized cottonseed oil stabilized against rancidity due to oxidation by the addition of phosphorous acid in an amount less than .01 per cent.

ALBERT S. RICHARDSON.