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PRESERVING MATERIALS

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This invention relates to preserving materials; and it comprises a method of preserving materials which are subject to autoxidation with the formation of peroxides, such as fats, fatty oils, fatty acids, ether, ascorbic acid and the like; said process comprising adding to the material to be preserved a small amount, usually not exceeding 1 per cent by weight, of a methyl, ethyl, propyl or butyl ester of gallic acid; all as more fully hereinafter set forth and as claimed.

Fats, oils and many other materials undergo autoxidation when exposed to air or to light and air, which more or less reduces or destroys their utility. For example fats upon oxidation assume an unpleasant rancid odor and taste which render them unsuitable for human consumption. For the prevention of these difficulties numerous methods have already been proposed, for example, inorganic acids, unsaturated polybasic aliphatic acids, amino acids, aryl amines and phenols have been suggested for use as anti-oxidants. The application of these compounds is, however, very limited. Some of them effect an injurious discoloration of the material to be protected, some cause injury from the point of view of odor and taste and some are unsuitable for health reasons and so cannot be used for the preservation of foodstuffs and the like.

In particular the proposed phenols, on account of their poisonous nature, are unsuitable for the protection of foodstuffs, medicines and the like against autoxidation, as is also the case with the previously proposed hydroquinone; cf. H. Oettel, Archiv. F. exper. Pathologie u. Pharmakologie, vol. 183, page 319, 1936.

It has now been found that the low molecular alcohol esters of gallic acid are antioxidant agents of high activity and quite non-injurious to health. The addition of a small amount of one of these esters retards or prevents the autoxidation of oils and fats and also the oxidation of organic compounds in general which undergo autoxidation with the formation of peroxides in the presence of oxygen, for example, ethers, ascorbic acid and oleic acid.

The gallic acid esters used in accordance with the present invention are, from a pharmacological point of view, similar to gallic acid, which is completely non-poisonous, that is, it is physiologically inert. It is assimilable even in very large doses; cf. Beilsteins Handbuch der organischen Chemie, vol. 10, page 476, 1927.

The suitability of such esters for the prevention of the autoxidation of fats and oils is shown by the following tables which contain the results of tests upon peroxide formation in various test samples. As is known, the production of peroxides induces the autoxidation of the fats. In these tests the gallic acid esters were dissolved in the fats in the specified concentrations, the

test portions being kept in open vessels in a thin layer with a large surface exposed to the air. In the case of the cod liver oil, the test specimen was kept at room temperature in diffused light, while in the case of arachis oil the specimen was held at 42° C. in the dark. These specimens were tested for peroxide, in the case of cod liver oil, after 10 days and 40 days; in the case of arachis oil, after 10 days. The peroxide content was ascertained in the following manner. A 0.5 cc. sample of the oil was taken and dissolved in 10 ccs. of a mixture of 2 parts of glacial acetic acid and 1 part chloroform. 1 cc. of saturated aqueous potassium iodide solution was then admixed. The mixture was kept for 3 minutes in the dark, then immediately treated with 10 ccs. of water and the separated iodine was titrated with N/500 sodium thiosulphate solution. In the same manner the peroxide content of the oil was determined before the experiment. The consumption in each case of N/500 sodium thiosulphate solution is designated in the following tables, as the peroxide number.

TABLE I

Experiments with cod liver oil

(Peroxide number at the commencement of the experiment 6.7)

Peroxide number after the addition of—	10 days standing	40 days standing
0.05% gallic acid propyl ester.....	8.0	8.0
0.1% gallic acid propyl ester.....	8.0	8.0
0.15% gallic acid propyl ester.....	7.8	7.8
0.2% gallic acid propyl ester.....	7.7	7.7
0.00% gallic acid propyl ester.....	24.4	100

It will be seen from the above table that, whereas without ester addition, the peroxide number rose 17.7 units in 10 days and 93 units in 40 days upon the addition of only 0.05 per cent ester, it rose only 1.3 units in 10 days and 2.2 units in 40 days.

TABLE II

Experiment with arachis oil

[Peroxide number at the commencement of the experiment 1.5]

Peroxide number after the addition of—	10 days standing
0.01% gallic acid methyl ester.....	2.0
0.025% gallic acid methyl ester.....	1.9
0.05% gallic acid methyl ester.....	1.8
0.1% gallic acid methyl ester.....	1.7
0.00% gallic acid methyl ester.....	5.9

The above table shows that, whereas without ester addition, the peroxide number rose 4.4 units in 10 days, upon the addition of only 0.01 per cent ester, under the same experimental condi-

tions, it rose only 0.5 unit, and after the addition of 0.1 per cent ester only 0.2 unit.

Similar results were given by experiments with other alcohol esters of gallic acid and other oils. It has been found that oils which are strongly inclined to autoxidation, that is, oils with high iodine numbers, require somewhat higher ester additions than oils which are less inclined to autoxidation, that is with smaller iodine numbers.

Tests similar to those outlined above have also been made on several materials of widely divergent character but having the common property of being subject to autoxidation with the formation of peroxides. In one of these tests pure peroxide-free ether in a half-filled colorless flask was allowed to stand at room temperature in a north-lighted window. After 20 days the ether contained a considerable quantity of peroxide as was shown by testing for peroxide with potassium iodide solution and vanadium-sulphuric acid in accordance with the method outlined in the German Pharmaceutical Codex, 6th edition. These results were checked by the titanium sulphate method according to L. Brandt, *Chemiker-Zeitung*, vol. 51, page 983, 1927. In contrast it was found that, if 0.01 per cent or 0.025 per cent gallic acid methyl ester or gallic acid propyl ester was added to samples of the ether, even after 100 days standing under otherwise the same conditions, all tests were negative, showing that the ether was free from peroxide.

Two test samples of a sterilized 0.1 per cent solution of ascorbic acid in tap water were kept, one without addition and the second with the addition of 0.5 per cent gallic acid propyl ester, in half-filled colorless flasks at room temperature in diffused daylight. These samples were tested 1, 2, 3 and 5 days later for their content of ascorbic acid by titration with 2,6-dichlorophenolindophenol according to the method of Tillmans. In these tests in each case two similar solutions, designated as (a) and (b) in the following table, were employed. Table III gives the quantity of ascorbic acid found after the time periods designated in per cent of the amount originally present.

TABLE III

Ascorbic acid still present	Without addition sol.		With addition of 0.5 per cent ester sol.	
	(a)	(b)	(a)	(b)
	Per cent	Per cent	Per cent	Per cent
After 1 day.....	83.0	84.7	100	100
After 2 days.....	52.5	49.4	93.8	93.6
After 3 days.....	29.4	24.7	85.5	88.0
After 5 days.....	10.8	6.2	64.2	64.1

It is seen from the above table that, after five days standing, the solution without the addition of ester only contained on the average about 8 per cent ascorbic acid while the solution with 0.5 per cent ester addition still contained 64 per cent of the ascorbic acid originally present. An addition of 0.5 per cent gallic acid propyl ester thus strongly prevents the autoxidation of the ascorbic acid.

The autoxidation of oleic acid was also measured by the determination of the peroxide produced, as described above, by titrimetric estimation of the iodine separated by the action of hydriodic acid, with N/500 sodium thiosulphate solution. 0.5 gram of the oleic acid employed in these

tests liberated, before the tests, a quantity of iodine corresponding to 2.5 ccs. of N/500 sodium thiosulphate solution. The number of cubic centimeters of N/500 thiosulphate solution required for 0.5 gram sample in each case is designated in Table IV as the peroxide number. The oleic acid samples, with the addition of 0.00-0.075% gallic acid propyl ester, were poured into open vessels in a thin layer with large surface and introduced into a heated oven at 40° C. These samples were allowed to stand in the dark for 10 days and then their percentages of peroxide were determined. The values found are shown in Table IV.

TABLE IV

Quantity of ester added	Peroxide number after 10 days
0.000%.....	23.4
0.025%.....	6.0
0.050%.....	5.0
0.075%.....	2.6

It is seen from this table that the addition of only 0.025 per cent of the ester reduces the peroxide formation substantially while the addition of 0.075 per cent prevents it completely.

The methyl, ethyl, propyl and butyl esters of gallic acid are thus broadly suited to the prevention of the autoxidation of all organic substances which oxidize in the presence of oxygen with the formation of peroxides.

The following examples illustrate practical embodiments of the invention:

Example 1

In order to protect arachis oil from autoxidation 0.025 per cent of gallic acid ethyl ester is dissolved therein.

Example 2

In order to protect lard against autoxidation it is treated with 0.05 per cent of a mixture of equal parts by weight of gallic acid methyl ester and gallic acid butyl ester.

Example 3

In order to protect cod liver oil from autoxidation there is dissolved therein 0.15 per cent of gallic acid propyl ester.

Example 4

In order to protect ethyl ether from autoxidation there is dissolved therein 0.01 per cent gallic acid ethyl ester.

Example 5

In order to retard the oxidation of ascorbic acid in aqueous liquids, the aqueous liquids are treated with 0.05 per cent gallic acid propyl ester.

Example 6

In order to protect oleic acid from autoxidation there is dissolved therein 0.1 per cent of a mixture of 30 per cent gallic acid methyl ester and 70 per cent gallic acid propyl ester.

The quantity of ester necessary for satisfactory protection against autoxidation depends upon the composition of the organic materials treated, the conditions of storage and the period of storage. Suitable proportions range from about 0.01 to 1.0 per cent by weight. The high capacity of the gallic acid esters for preventing the autoxidation of oils and the like is closely connected with the structure of these esters. The esters of the pro-

tocatechuic acid, containing 1 hydroxyl group less, exhibit a considerably lower capacity for prevention, while the esters of the isomeric gantisic acid show a still less capacity. Also it has been found that etherification of the phenolic hydroxyl groups of the gallic acid esters leads to compounds with lower capacity for preventing the autoxidation of the oils.

While we have described what we consider to be the best embodiments of our process it is evident that various modifications may be made in the specific procedures set forth without departing from the purview of our invention. It is evident, for example, that the gallic acid esters can be employed alone or in admixture. They can also be mixed with other compatible antioxidants. While our process is particularly adapted to the stabilization of fatty oils, including animal, vegetable and fish oils within this term, it can be employed for the stabilization of all manner of products of the types previously defined, both alone and in admixture, for example, in emulsions, creams and the like. The products so stabilized can be used for all purposes for which they may be suited; even as foodstuffs. The content of gallic acid ester required for stabilization is usually so minute that it cannot be detected without an accurate chemical analysis and only in very exceptional cases does the presence of such a small quantity of stabilizing agent restrict or interfere with the normal uses of the products so stabilized. Other modifications of this invention which fall within the scope of the following claims will be immediately evident to those skilled in this art.

What we claim is:

1. In the stabilization of high-molecular fatty acids, animal and vegetable fats and oils and fish oils subject to autoxidation with the formation of peroxides, the process which comprises adding to such a material, in a quantity sufficient to pre-

vent oxidation thereof, at least one low molecular ester of gallic acid selected from a group consisting of the methyl, ethyl, propyl and butyl esters of gallic acid.

2. The process of claim 1 wherein said ester is added in proportions ranging from about 0.01 to 1.0 per cent by weight.

3. In the stabilization of high-molecular fatty acids, animal and vegetable fats and oils and fish oils subject to autoxidation with the formation of peroxides, the process which comprises adding to such a material a small quantity, not substantially exceeding 1 per cent by weight, of a low molecular ester of gallic acid selected from a group consisting of the methyl, ethyl, propyl and butyl esters of gallic acid.

4. The process of stabilizing fatty oils which comprises adding to such an oil in a quantity sufficient to prevent oxidation thereof, a low molecular ester of gallic acid selected from a group consisting of the methyl, ethyl, propyl and butyl esters of gallic acid.

5. The process of stabilizing ethyl ether which comprises adding thereto, in a quantity sufficient to prevent oxidation thereof, a low molecular ester of gallic acid selected from a group consisting of the methyl, ethyl, propyl and butyl esters of gallic acid.

6. The process of stabilizing high-molecular fatty acids which comprises adding to such an acid thereto a small quantity of a low molecular ester of gallic acid selected from a group consisting of the methyl, ethyl, propyl and butyl esters of gallic acid.

7. The process of preserving high-molecular fatty acids, animal and vegetable fats and oils and fish oils which comprises adding to such a material, in quantity sufficient to prevent oxidation thereof, the propyl ester of gallic acid.

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