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STABILIZATION OF FATS AND OILS WITH —CO—R DERIVATIVES OF 1,2,4-TRIHYDROXYBENZENE AND PREPARATION OF RELATED COMPOUNDS

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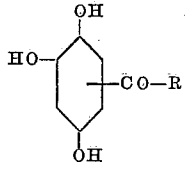
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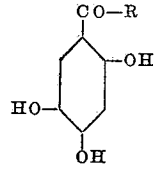
This invention relates to the stabilization of fats, oils and other organic materials subject to deterioration employing compounds as antioxidants which are —CO—R derivatives of 1,2,4-trihydroxybenzene wherein R represents an alkyl, alkenyl, aryl, substituted aryl, furyl, etc. radical, or an H atom.

It is an object of our invention to provide compounds which possess improved properties which are particularly useful in the stabilization of fats and oils. Another object is to provide antioxidant compositions containing the principal antioxidants of this invention admixed with a synergist. A further object of our invention is to provide antioxidant compositions of this nature dissolved in an inert organic solvent. An additional object is to provide stabilized fats and oils containing such antioxidant compositions. A still further object of our invention is to provide processes for preparing such stabilized fats and oils. Other objects will become apparent hereinafter.

In accordance with our invention, stabilized fats and oils can be prepared which contain from about 0.001 percent to about 1.0 percent by weight of an antioxidant selected from those having the following formula:



which can probably be more specifically written as follows:



wherein R represents a member selected from the group consisting of an H atom, an alkyl radical containing from 1 to 20 carbon atoms, an alkenyl radical containing from 1 to 10 carbon atoms, an aryl radical containing from 6 to 10 carbon atoms, and a furyl radical. The position of the substituent —CO—R on the benzene ring has not been definitely determined in every instance nor does it

appear to be critical. This is especially the case for the benzophenone derivatives where, in some instances, a mixture of isomers was prepared and in other instances pure isomers were obtained. In one case where a pure isomer was obtained, the isomer was different from the compound reported as an isomer of trihydroxybenzophenone by Bogert and Howells, J. A. C. S. 52, 845 (1930).

Examples of compounds which come within the scope of the above formula include 2,4,5-trihydroxyacetophenone, 2,4,5-trihydroxybutyrophenone, 2,4,5-trihydroxyvalerophenone, 2,4,5 - trihydroxybenzophenone, 2,4,5-trihydroxyphenyl furyl ketone, 2,4,5 - trihydroxycaprophenone, 2,4,5 - trihydroxynaphthophenone, 2,4,5 - trihydroxyphenyl tolyl ketone, 2,4,5-trihydroxyphenyl xylyl ketone, 2,4,5-trihydroxyphenyl octyl ketone, 2,4,5-trihydroxyphenyl propenyl ketone, 2,4,5 - trihydroxyphenyl allyl ketone, etc. Some of those compounds which can be advantageously employed are set forth in the table presented hereinbelow relating to the antioxidant properties of such compounds. The compound, 2,4,5-trihydroxybenzoic acid is described as an antioxidant and claimed in conjunction with certain processes and antioxidant compositions in a copending application, serial No. 302,413 filed on even date herewith.

It is known that 1,2,4-trihydroxybenzene can be employed for the stabilization of fats and vegetable oils. There is no suggestion, however, in the prior art that derivatives of this compound would also be useful as antioxidants for fats, vegetable oils and other organic materials subject to deterioration. The introduction of the group, —CO—R (wherein R is defined above) on the benezene ring of 1,2,4-trihydroxybenzene has been found to result in the formation of compounds which have excellent antioxidant properties. This was wholly unexpected and unpredictable especially since the introduction of —CO—R substituents on the nucleus of hydroquinone gives compounds with very little antioxidant value. The following table presents data relating to the effect of the introduction on the nucleus of hydroquinone of a —CO—R radical wherein the radical substituted is —$COCH_3$, —$CO(CH_2)_2CH_3$, and —COC_6H_5. This data is based on tests conducted under the active oxygen method (AOM) which is described hereinbelow. These tests were conducted employing lard as the substrate which had an AOM value of 4 hours (lard A) and 12.5 hours (lard B) when it contained no antioxidant. The concentration in each instance was 0.02 percent by weight of the antioxidant in the lard.

Antioxidant	AOM Value in Hours	
	Lard A	Lard B
Control (no antioxidant)	4.0	12.5
Hydroquinone	118.0	130.0
1,2,4-Trihydroxybenzene		135.0
2,5-Dihydroxyacetophenone	10	
2,4,5-Trihydroxyacetophenone		183
2,5-Dihydroxybutyrophenone	11	
2,4,5-Trihydroxybutyrophenone		160.0
2,5-Dihydroxybenzophenone	7.0	
2,4,5-Trihydroxybenzophenone		173.0

The difference between the dihydroxy and the trihydroxy derivatives containing a —CO—R radical is clearly evident, as indicated by the above table.

The introduction of the —CO—R substituent on to the nucleus of 1,2,4-trihydroxybenzene gives products which have many advantages as antioxidants over 1,2,4-trihydroxybenzene itself. Thus the compounds of antioxidant value described in this invention are stable to air, are less water-soluble and more fat-soluble and are generally more potent antioxidants than 1,2,4-trihydroxybenzene. All of these properties make them more useful as antioxidants for fats and oils. The compounds described as antioxidants in accordance with our invention can be employed for the stabilization of other organic compounds subject to deterioration in addition to fats and oils, e. g., carotene, plastic compositions, etc. The oils which can be stabilized include mineral oils as well as vegetable oils and can be extended to include paraffin and other organic compounds of similar characteristics.

When employed as antioxidants for fats, oils and the like, fractions of a percent of the compounds of this invention can be incorporated into such materials as lard, cottonseed oil, peanut oil, paraffin, etc., by admixing the antioxidant with the fat or oil whereby a solution of the antioxidant in the substrate is obtained. Alternatively, the antioxidant can be blended with suitable solvents to form an antioxidant solution. Examples of such solvents include glycerin, propylene glycol, hexane, etc., or other similar solvents which are inert insofar as concerns both the antioxidant and the other components of the ultimately prepared stabilized fat or oil. Such antioxidant solutions can be more readily dissolved in the fat or oil to be stabilized with less necessity for prolonged mixing of the fat or oil with the undissolved antioxidant. Similarly, synergists can be admixed with the fats or oils along with the dry antioxidant compounds of this invention or, in order to facilitate the incorporation of the antioxidant and the synergist into the fat or oil, they can both be dissolved in such solvents as described above. Examples of synergists which can be employed include citric acid, tartaric acid, phosphoric acid, ascorbic acid, propyl gallate, etc. In addition to the employment of a single antioxidant as described hereinbefore, mixtures of two or more such antioxidants together with one or more synergists can be employed. Moreover, other antioxidants which are known in the art can be added for their supplemental effects if such be desired.

In addition to the fats and oils mentioned above which can be stabilized by the antioxidants of this invention, other representative fats and oils include linseed oil, menhaden oil, cod liver oil, castor oil, olive oil, rape seed oil, coconut oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, butter fat, lard, beef tallow, etc., as well as hydrogenated oils and fats prepared from any of the foregoing. Furthermore, various other oils and fats may be similarly treated within the scope of this invention. In addition, the antioxidants of this invention can be employed in certain instances to stabilize fuels, plastic compositions, the carotene content of foods, mineral oils, paraffin, etc., as mentioned above.

The stabilized fats and oils provided by this invention contain from about 0.001% to about 1.0% by weight of an antioxidant comprising a —CO—R derivative of 1,2,4-trihydroxybenzene having the structural formula set forth hereinabove. This invention covers combinations of such antioxidants with other antioxidants as referred to hereinbefore, e. g. isomers of tert. butyl-p-hydroxyanisole, propyl gallate, etc., some of which combinations of antioxidants may be synergistic in nature. Accordingly, the invention covers fats and oils stabilized with from about 0.001% to about 1.0% by weight of an antioxidant defined by the depicted general formula admixed with from about 0.0005% to about 0.1% by weight of the fat or oil of a synergist, e. g. citric acid, tartaric acid, phosphoric acid, ascorbic acid, propyl gallate, etc. This invention also covers the processes involved in preparing such stabilized fats and oils.

A preferred procedure for preparing compounds of the type disclosed hereinabove as antioxidants is set forth in the examples which are given below. Some of the compounds coming within the scope of the above depicted general formula are well known, whereas others do not appear to have been previously described. The procedures set forth in the following examples can be readily adapted to prepare any of the compounds included in the general formula. Thiele and Jaeger, Ber. 34, 2840 (1901) describe a method for the preparation of 2,4,5-trihydroxybenzoic acid. This compound does not come within the scope of the instant application. Gatteman and Kobner, Ben. 32, 282 (1899) describe a method for the preparation of 2,4,5-trihydroxybenzaldehyde. Mauthner, J. Prakt. Chim., 136, 213 (1933) describes a method for the preparation of 2,4,5-trihydroxyacetophenone; however, the yields obtained were not very good. Healy and Robinson, J. Chem. Soc. 1628 (1934) also describe a method for preparing 2,4,5-trihydroxyacetophenone. An improved process for the preparation of this compound has been developed in conjunction with this invention and is described below in Example 1.

The following examples will serve to illustrate advantageous processes for the preparation of antioxidant compositions coming within the scope of this invention:

Example 1.—2,4,5-trihydroxyacetophenone

A mixture of 68 g. (0.5 mole) of freshly fused zinc chloride and 125 cc. of acetic acid was heated in an oil bath at 140° C. until solution resulted. The solution was cooled to 40–45° C. and while stirring 61 g. (0.6 mole) acetic anhydride was added, followed by the addition of 63 g. (0.5 mole) of powdered 1,2,4-trihydroxybenzene. The mixture was heated at 130°–135° C. for 45 minutes and then the solvent was stripped off under reduced pressure. The residue was treated with 300–350 cc. of hot water containing 5 cc. of concentrated hydrochloric acid and the mixture refluxed for 5–10 minutes. Then the mixture was cooled to 5° C. and the product which separated was filtered, washed with water, and dried at 110° C. The yield of product was 71 g. (84.5 per cent). It melted at 206–7° C.

Example 2.—2,4,5-trihydroxybutyrophenone

A Fries rearrangement was carried out with 1,2,4-tributyroxybenzene by gradually adding 26 g. (0.2 mole) of aluminum chloride to a solution of 67.2 g. (0.2 mole) of the tributyrate in 200 cc. of nitrobenzene. This mixture was left 16 hours at room temperature, poured into 150 cc. of 10 percent hydrochloric acid, and steam distilled to remove butyric acid and nitrobenzene. The residue in the pot was cooled to 5° C. and a yellow oil was extracted with ether. The ether extract was washed, dried, and then 100 cc. of methanol containing 5 g. of hydrogen chloride was added and the mixture was boiled for a few minutes. The methanol was distilled off and replaced with benzene. This was again distilled to remove the last traces of methanol. The benzene solution (150 cc.) was finally cooled and the solid which separated was recrystallized from hot water using charcoal to decolorize. The yield was 16 g. of a product which melted at 151–3° C. This compound, 2,4,5-trihydroxybutyrophenone, is not known to have been described in the prior art. The calculated analysis for this compound ($C_{10}H_{12}O_4$) is C, 61.21; H, 6.16; the actual analysis showed C, 61.31; H, 6.45.

1,2,4-tributyroxybenzene which is not known to have been described in the prior art and which was employed above was prepared by a Thiele reaction. Fifty-four grams (0.5 mole) of p-quinone was added portion-wise at 40–50° C. with stirring to 210 g. (1.4 moles) of n-

butyric anhydride containing 10 g. of concentrated sulfuric acid. After the addition of p-quinone was complete, the mixture was allowed to spontaneously cool to 25° C. and was then poured into water. The solution was extracted with ether. The extract was washed with water, then with dilute sodium carbonate solution, and finally with water again and distilled. The product distilled at 153–55° C. (0.08 mm.). The yield was 150 g. (90 per cent).

Example 3.—2,4,5-trihydroxybutyrophenone

The product of Example 2 was also prepared in the following manner: Thirty-three grams (0.25 mole) of aluminum chloride was added to a solution of 12.6 g. (0.1 mole) of 1,2,4-trihydroxybenzene in 200 cc. of nitrobenzene. The mixture was cooled at 25° C. and 16 g. (0.1 mole) of n-butyric anhydride added. The reaction mixture was then heated to 60° C. for 45 minutes. After cooling, 150 cc. of ice-cooled 10 percent hydrochloric acid was added and the mixture steam distilled to remove nitrobenzene. The pot residue, on cooling, deposited 12 g. (61 per cent) of pure 2,4,5-trihydroxybutyrophenone.

Example 4.—Trihydroxybenzophenone

Various trihydroxybenzophenone isomers were prepared by several methods which can be outlined as follows:

A. According to directions of Bogert and Howells, J. A. C. S., 52, 1845 (1930). This method gave a mixture of isomers, M. P. 111–119° C.

B. By a Hoesch reaction using 25 g. (0.2 mole) of 1,2,4-trihydroxybenzene, 21 g. (0.2 mole) of benzonitrile, 5 g. of freshly fused zinc chloride and 400 cc. of dry ether. The solution was saturated with dry HCl and left at 5° for 72 hours. The product was hydrolyzed and 8 g. of a product was obtained, M. P. 220–23° C. Anal. Calcd. for $C_{13}H_{10}O_4$ was—C, 67.8; H, 4.4; Found analysis was—C, 67.32; H, 4.55. This compound is probably pure 2,4,5-trihydroxybenzophenone.

C. By direct benzoylation of 25 g. (0.2 mole) of 1,2,4-trihydroxybenzene in 200 cc. of nitrobenzene using 28 g. (0.2 mole) of benzoyl chloride in the presence of 60 g. (0.45 mole) of aluminum chloride. The mixture was warmed at 80–90° for 3 hours, cooled, and decomposed with ice cold dilute hydrochloric acid. After steam distillation, the residue was worked up according to ordinary chemical procedures to give 8 g. of 2,4,5-trihydroxybenzophenone.

D. By rearrangement of 1,2,4-trihydroxybenzene monobenzoate. A mixture consisting of 12.6 g. (0.1 mole) of 1,2,4-trihydroxybenzene, 16 g. (0.12 mole) of $AlCl_3$ and 200 cc. of nitrobenzene were warmed at 60° C. for 5 minutes with 14 g. (0.1 mole) of benzoyl chloride. The mixture was immediately decomposed with ice cold dilute hydrochloric acid. After steam distillation to remove the nitrobenzene, the residue was cooled and 20 g. of 1,2,4-trihydroxybenzene monobenzoate crystallized. Yield was 20 g., M. P. 139–41° C. The antioxidant properties of this monobenzoate are covered in a copending application, Serial No. 302,411 filed on even date herewith by Bell and Knowles. The monobenzoate (13.5 g.; .059 mole) was intimately mixed with 25 g. (0.19 mole) of $AlCl_3$ and heated to 130° C. when reaction began. Over a 30-minute period the temperature was raised to 190° C. The mixture was cooled, decomposed with ice cold hydrochloric acid. The 2,4,5-trihydroxybenzophenone (12 g.) was recrystallized from dilute alcohol, M. P. 216°–218° C.

Example 5.—2,4,5-trihydroxyisobutyrophenone

A mixture of 300 ml. of nitrobenzene and 25.2 g. (0.2 mole) of 1,2,4-benzenetriol was gradually treated with 40 g. (0.3 mole) of anhydrous aluminum chloride. After evolution of hydrogen chloride ceased, the resulting solution was cooled to 25°, and 21 g. (0.2 mole) of isobutyryl chloride was added. The reaction mixture was allowed to stand for several hours and then warmed at 60–65° C. for one-half hour. After decomposing the complex with cold, dilute hydrochloric acid, the mixture was subjected to steam distillation to remove the nitrobenzene. When cooled, the residue crystallized. Recrystallization from ethylene dichloride gave a product light yellow in color and one which melted at 136–8° C. The yield was 12 g. (31%). This compound, 2,4,5-trihydroxyisobutyrophenone, is not known to have been described in the prior art.

Example 6.—2,4,5-trihydroxycaprylophenone

This compound was prepared as in Example 5 using 25.2 g. (0.2 mole) of 1,2,4-benzenetriol, 300 ml. of nitrobenzene, 40 g. (0.3 mole) of aluminum chloride, and 33 g. (0.2 mole) of n-caprylyl chloride. The crude product was recrystallized once from acetic acid-water and then from naphtha-butyl acetate; M. P. 113–114° C.; yield, 15 g. (30%). This compound, 2,4,5-trihydroxycaprylophenone, is not known to have been described in the prior art.

Example 7.—2,4,5-trihydroxystearophenone

This compound was prepared as in the preceding two examples (Examples 5 and 6) using identical molar ratios of reactants. The crude product was decolorized in ethanol solution then precipitated by adding a little water. Recrystallization from carbon tetrachloride and then from methanol gave a light yellow product which melted at 118–119° C. The yield was 39.2 g. (50%). This compound, 2,4,5-trihydroxystearophenone, is not known to have been described in the prior art.

Example 8.—2,4,5-trihydroxycrotophenone

This compound was prepared as in Example 5 using identical molecular proportions. The residue from steam distillation was blood red and crystallized to a mush only after standing at 10° C. for several hours. This mush was dissolved in methanol and the solution treated with charcoal; the product precipitated by the addition of water. Further purification was obtained by passing an acetone solution of the product through a short column of activated alumina (Al–0101–P). The acetone solution was concentrated and water then added caused a light brown, crystalline material to separate; M. P. 219–221° C.; yield 2 g. (5%). This compound, 2,4,5-trihydroxycrotophenone (2,4,5-trihydroxyphenyl propenyl ketone), is not known to have been described in the prior art.

Example 9.—2,4,5-trihydroxyphenyl furyl ketone

This product was prepared from the monofuroate in a similar manner to that described in Example 4, section D. The product, M. P. 209–211° C., bright orange crystals, was obtained in 20–30 percent yield. The antioxidant properties of 1,2,4-trihydroxybenzene monofuroate are covered in the copending application of Bell and Knowles, Serial No. 302,411, referred to above.

The above examples clearly indicate how the compounds of this invention can be prepared. By suitable modifications of the described procedures, any of the compounds coming within the scope of the above depicted formula can be similarly prepared.

The compounds prepared as described in the above examples can be employed as antioxidants in lard and in some vegetable oils. Tests according to the active oxygen method have shown the effectiveness of these antioxidants. The results of these tests are set forth in the following table. For comparison purposes, several commercial antioxidants and other compounds are also included. This table presents seventy seven examples of how the antioxidants of this invention (compounds numbered 6–14) can be employed as antioxidants in various pro-

portions, etc. These examples serve to further illustrate this invention.

Antioxidant		AOM Keeping Quality in Hours												
Compound	Percent Added	Lard B and C		Corn Oil			Cottonseed Oil A and B				Peanut Oil A and B			
		B 20	C 20	20	70	100	A 20	A 70	B 70	B 100	A 20	A 70	B 70	B 100
1. Control (no antioxidant)	0.00	12.5	3.5	2.5	6.0	8.5	5.5	11.0	11.0	13.5	5.0	12.0	20.0	21.5
2. BHA (viz. tert. butyl-p-hydroxyanisole)	0.01	26.5	17.0											
	0.02	32.0	23.0				4.5	9.0	10.5	12.0	4.0	12.0	22.0	25.0
3. Gallic acid	0.02	90.0												
4. Propyl gallate	0.02	86.0												
5. 1, 2, 4-Trihydroxybenzene	0.02	135.0	118.0											
6. 2, 4, 5-Trihydroxybenzaldehyde	0.01	96.												
	0.02	193.0		5.0	11.0	13.0	16.0	30.0			14.0	47.0		
7. 2, 4, 5-hydroxyacetophenone	0.005	88.0												
	0.01	122.0		5.5	10.5	12.5	13.0	22.0	19.5	23.0			50.0	52.0
	0.02	183.0		8.5	15.5	18.5	16.0	28.0	27.0	30.0			67.0	70.0
8. 2, 4, 5-Trihydroxybenzophenone	0.01	100.0												
	0.02	173.0		5.0	10.0	13.0	32.0	41.0			36.0	52.0		
9. 2, 4, 5-Trihydroxybutyrophenone	0.02	160.0												
10. 2, 4, 5-Trihydroxyphenyl furyl ketone	0.02	127.0												
11. 2, 4, 5-Trihydroxycaprylophenone	0.01								17.5	20.0			38.5	41.0
	0.02	153.0							20.0	24.0			52.0	54.0
12. 2, 4, 5-Trihydroxycrotophenone	0.01								15.0	18.0			33.5	35.0
	0.02	96.0							18.0	20.0			40.0	43.0
13. 2, 4, 5-Trihydroxyisobutyrophenone	0.01								18.0	20.0			31.5	42.5
	0.02	167.0							23.0	24.5			35.0	57.0
14. 2, 4, 5-Trihydroxystearophenone	0.01								14.0	17.0			34.5	36.5
	0.02	114.0							17.0	19.0			45.0	47.0

Inasmuch as it is well known in the art to employ antioxidants in the stabilization of fats and oils, it is not believed necessary to give numerous additional examples of how the antioxidants of this invention can be blended with fats or oils nor additional specific proportions which can be employed in the many possible examples which would come within the scope of the description hereinabove.

The data presented in the table above is based on tests conducted under equivalent conditions employing similar samples in each instance of corn oil, cottonseed oil, peanut oil and lard except as indicated. The AOM figures are in hours; the numbers beneath the name of the fat or oil are the peroxide values to which the sample was brought in order to determine the AOM value. The procedure employed under the AOM (active oxygen method) is well known in the antioxidant art and can be explained in this specification briefly as follows:

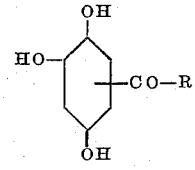
A weighed quantity (0.01–0.02 percent by weight) of the compound to be tested was dissolved in the lard or oil. The resulting solution was placed in a bath at 99° C. and air was then bubbled through at a rate of approximately 2.3 ml. per second. Periodically, a portion of the test solution was removed and the peroxide content quantitatively determined by iodometric titration, expressing the results as milliequivalents per kilogram of fat or oil. Experience has shown that initial rancidity in lard corresponds closely to a peroxide value of 20 and to 70 in oil such as cottonseed oil and peanut oil. The latter value has not been firmly established but is useful for comparative purposes. A control containing no additives was run simultaneously with the test compound to determine the induction period of the unstabilized materials. The final results are expressed in the number of hours required for rancidity to develop; i. e., an AOM value of 40 for a sample of lard means that 40 hours was required to form 20 milliequivalents of peroxide per kilogram of the lard.

A perusal of the data contained in the preceding table indicates that the antioxidants of this invention are, insofar as their stabilization characteristics are concerned, clearly superior to antioxidants which are commercially available such as tertiary butyl-p-hydroxy anisole and propyl gallate as well as other antioxidants known in the prior art such as gallic acid. Even where the superiority is not apparent from the point of view of the AOM keeping quality, the AOM value is clearly that of an excellent antioxidant and the other properties of the antioxidant render it superior to those known to the prior art, e. g. such properties as solubility in fats, freedom from discoloration, etc.

Other antioxidants coming within the scope of the above depicted general formula can be employed in a similar manner to obtain analogous advantageous results.

What we claim as our invention and desire to secure by Letters Patent of the United States is:

1. Stabilized fats and fatty oils containing from about 0.001 percent to about 0.1 percent by weight of a nuclearly substituted —CO—R derivative of 1,2,4 - trihydroxybenzene having the following formula:



wherein R represents a member selected from the group consisting of an H atom, an alkyl radical containing from 1 to 20 carbon atoms, an alkenyl radical containing from 1 to 10 carbon atoms, an aryl radical containing from 6 to 10 carbon atoms and a furyl radical.

2. Stabilized fats and fatty oils as defined in claim 1 wherein the antioxidant is 2,4,5 - trihydroxyacetophenone.

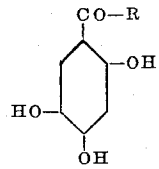
3. Stabilized fats and fatty oils as defined in claim 1 wherein the antioxidant is 2,4,5-trihydroxybenzaldehyde.

4. Stabilized fats and fatty oils as defined in claim 1 wherein the antioxidant is 2,4,5-trihydroxybenzophenone.

5. Stabilized fats and fatty oils as defined in claim 1 wherein the antioxidant is 2,4,5-trihydroxybutyrophenone.

6. Stabilized fats and fatty oils as defined in claim 1 wherein the antioxidant is 2,4,5-trihydroxyphenyl furyl ketone.

7. Stabilized fats and fatty oils containing from 0.0005 percent to about 0.1 percent by weight of a synergist selected from the group consisting of citric acid, tartaric acid, phosphoric acid, ascorbic acid and propyl gallate and from about 0.001 perent to about 0.1 percent by weight of an antioxidant selected from those having the following formula:



wherein R represents a member selected from the group consisting of an H atom, an alkyl radical containing from 1 to 20 carbon atoms, an alkenyl radical containing from

1 to 10 carbon atoms, an aryl radical containing from 6 to 10 carbon atoms and a furyl radical.

8. Stabilized fats and fatty oils containing from about 0.005 percent to about 0.5 percent by weight of citric acid and from about 0.001 percent to about 0.1 percent by weight of an antioxidant as defined in claim 1.

9. Stabilized lard containing from about 0.001% to about 0.1% by weight of an antioxidant as defined in claim 1.

10. Stabilized cottonseed oil containing from about 0.001% to about 0.1% by weight of an antioxidant as defined in claim 1.

11. Stabilized castor oil containing from about 0.001% to about 0.1% by weight of an antioxidant as defined in claim 1.

12. Stabilized tallow containing from about 0.001% to about 0.1% by weight of an antioxidant as defined in claim 1.

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