A Preliminary Comparison of the Stabilizing Effect of Several Recently Proposed Antioxidants for Edible Fats and Oils

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Introduction

SINCE the original work of Moureau and Dufraisse (1) in 1922 many compounds have been studied as antioxidants in various fatty materials. The search for stabilizers suitable for use in edible products was accelerated by the necessity for retarding rancidity in the meat food fats. When these fats are subjected to the processing operations required to produce shortenings meeting modern standards of quality, varying proportions of the inhibitors naturally occurring in them are removed. The result is lowered keeping quality. The current necessity for conserving all edible fats and oils because of the shortage among the United Nations and the requirements of the Armed Forces for shortening products that will remain fresh over long periods of time under adverse conditions are factors which have stimulated considerable research recently.

The first material to be approved for use in lard by the Meat Inspection Division of the Bureau of Animal Industry was gum guaiac. This was in 1940. Later, lecithin was approved and during the last few months, nordihydroguairetic acid and tocopherols have appeared on the approved list. It is interesting to note that two of these materials, lecithin and tocopherols, occur in food products and the other two, although naturally occurring, are not found in common food materials.

An ideal antioxidant for fatty food products should possess the following characteristics:

(1) Exhibit effective inhibitory action. Products treated with it should show no traces of rancidity after storage for at least a year at 75 to 85°F. in unsealed containers.
(2) Be easily soluble in the fats.
(3) Impart no foreign flavor, odor or color even on long continued storage.
(4) Exhibit no harmful physiological effects.
(5) Exhibit no changes when heated.
(6) Possess the ability to retard rancidity in baked goods prepared from the fats treated with it.
(7) Be available in quantity, and economical.

Comparison of Antioxidants

THE present work is an attempt to evaluate, largely in a preliminary manner and from a practical standpoint, several antioxidants which have been recently proposed and which are attracting considerable attention. Some of them are in commercial use at present. Most of this work has been directed toward stabilizing bland meat fats and unhydrogenated vegetable oils. The antioxidants discussed are taken up in the order of their appearance in the literature.

The Swift stability test and incubation of the fats in loosely capped four-ounce glass jars at 140°F. were used as measures of keeping quality. Also the keeping time of soda crackers at 140°F. has been studied as this is an important measure of the effectiveness of a stabilizer.

Gum Guaiac. This material was proposed by Newton and Grettie (2) in 1933. It is the secretion of a tropical tree, *Guaiacum Officinalis,* which grows in the West Indies. Its stabilizing effect is shown in Table I.

TABLE I

Gum Guaiac

	Hours (AOM)	Days Before Rancid at 140°F.	Days Before Crackers Rancid at 140°F.
Prime Steam Lard	6	7	5
Prime Steam Lard + 0.01% Gum Guaiac	10	9	12
Prime Steam Lard + 0.05% Gum Guaiac	20	22	30
Prime Steam Lard + 0.10% Gum Guaiac	24	23	35
Refined and Bleached Cottonseed Oil	15	12	....
Refined and Bleached Cottonseed Oil + 0.10% Gum Guaiac	19	14	....
Refined and Bleached Soybean Oil	14	9	....
Refined and Bleached Soybean Oil + 0.10% Gum Guaiac	17	12	....

These results were obtained by incorporating gum guaiac into the deodorized fats by means of an acetic acid solution (3). It is an effective antioxidant for lard and the stability carries into the baked products. Extensive tests carried out by Professor Carlson (4) at the University of Chicago have proved it to be entirely innocuous physiologically. It is heat stable and adds no appreciable color.

A slight odor and flavor are imparted to the fats containing it, but these are easily removed by deodorization. Gum guaiac has been used for several years in a commercial lard.

TABLE II

Propyl Gallate

	Hours (AOM)	Days Before Rancid at 140°F.	Days Before Crackers Rancid at 140°F.
Prime Steam Lard	6	7	8
Prime Steam Lard + 0.01% Propyl Gallate	33	30	11
Prime Steam Lard +0.03% Propyl Gallate	50	60	12
Prime Steam Lard +0.05% Propyl Gallate	135	124	13
Prime Steam Lard +0.10% Propyl Gallate	145	135	14
Refined and Bleached Cottonseed Oil	12	10	....
Refined and Bleached Cottonseed Oil + 0.05% Propyl Gallate	45	35	....
Refined and Bleached Soybean Oil	18	14	....
Refined and Bleached Soybean Oil + 0.05% Propyl Gallate	54	45	....

Propyl Gallate. The antioxidant properties of gallic acid were described by Golumbic and Mattill (5) in 1942. They pointed out that this compound was effective in both meat fats and vegetable oils, and ascribed the results to the fact that it contains both the acidic and phenolic functions. A U. S. patent was issued to Sabalitschka and Boehm (6) covering lower alkyl esters of gallic acid as antioxidants. The esters are more fat-soluble than the acid. The properties and antioxidant effects of propyl gallate were described by Boehm and Williams (7) in 1943. At the present time, propyl gallate is commercially available. Table II shows the antioxidant properties of this compound.

The results were obtained by adding the easily soluble ester to the fats at 180°F. with stirring. Our results confirm those reported by Boehm and Williams. Its exceptional stabilizing action does not carry into the baked goods, due probably to its solubility in water. It is heat stable and deodorization does not lower the stability of fats containing it. The compound does not impart odors or flavors to the fats. Neither does it affect the color. Boehm and Williams reported preliminary tests which indicated it to be non-toxic. If the latter results are confirmed, this compound may prove quite valuable.

Tocopherols. In 1937 Olcott and Emerson (8) reported natural tocopherols to have marked antioxidant properties, especially for meat food fats. A British patent (9) was issued in 1939 to the Eastman Kodak Company covering the use of fractions rich in tocopherols distilled from vegetable oils. Later a U. S. patent (10) covering the use of hydrogenated tocopherols was granted. Table III gives results obtained with tocopherols.

TABLE III

Tocopherols

	Hours (AOM)	Days Before Rancid at 140°F.	Days Before Crackers Rancid at 140°F.
Prime Steam Lard	4	4	9
Prime Steam Lard + 0.01% tocopherols	8	13	10
Prime Steam Lard + 0.02% tocopherols	16	15	11
Prime Steam Lard + 0.10% tocopherols	23	18	12
Prime Steam Lard + 0.50% tocopherols	23	18	12
Refined and Bleached Cottonseed Oil	19	12	....
Refined and Bleached Cottonseed Oil + 0.01% tocopherols	19	12	....
Refined and Bleached Cottonseed Oil + 0.05% tocopherols	19	12	....
Refined and Bleached Soybean Oil	14	9	....
Refined and Bleached Soybean Oil + 0.01% tocopherols	19	11	....
Refined and Bleached Soybean Oil + 0.05% tocopherols	20	12	....

These results were obtained by adding the commercial concentrates obtained by molecular distillation. They are heat stable but do not impart their stabilizing effect to baked products. The concentrates carry a slight odor which is easily removed by deodorization, but this process does not affect the stabilizing action. Addition of the concentrates does not increase the color of the fats. At the present time they are available only in limited quantities. Being a natural constituent of vegetable oils there is little question concerning their physiological effects, and their use in lard has been approved by the Meat Inspection Division.

Wheat Germ Oil Derivative. Last year, Lips and McFarlane (11) reported that an ethylene dichloride extract of wheat germ oil combined with citric acid had slight antioxidant properties for lard and fair stabilizing action in certain blended shortenings. The process of manufacture was adapted to commercial practice and the product is now available. Table IV shows typical results obtained with this antioxidant.

TABLE IV

Wheat Germ Oil Derivative

	Hours (AOM)	Days Before Rancid at 140°F.	Days Before Crackers Rancid at 140°F.
Prime Steam Lard	5	5	6
Prime Steam Lard + 0.1% W.G.O. Derivative	8	6	6
Prime Steam Lard + 0.5% W.G.O. Derivative	10	6	6
Prime Steam Lard + 1.0% W.G.O. Derivative	13	7	7
Refined and Bleached Cottonseed Oil	19	12	....
Refined and Bleached Cottonseed Oil + 0.5% W.G.O. Derivative	21	15	....
Refined and Bleached Soybean Oil	14	9	....
Refined and Bleached Soybean Oil + 0.5% W.G.O. Derivative	21	14	....

THESE results were obtained by addition of the antioxidant, followed by deodorization. The material imparts a slight odor and color to products to which it is added. The odor is removed by deodorization, but a characteristic reverted odor appears during incubation. It is heat stable but baked products prepared from fats containing it are not improved.

N. D. G. A. Recently, Lundberg, Halvorson, and Burr (12) reported nordihydroguairetic acid, commonly referred to as N. D. G. A., obtained from a creosote bush *(Larrea divaricata)* to have exceptional stabilizing effects for lard. It is closely related chemically to guairetic acid, one of the active constituents of gum guaiac. The pure compound is a white crystalline solid, but products thus far available have varied in degree of purity. Only limited quantities are available but it is understood that a plant for commercial extraction is contemplated. It is not readily soluble in fats and an auxiliary solvent is required for optimum effect.

TABLE V

N. D. G. A.

	Hours (AOM)
Original Prime Steam Lard	5
Original Prime Steam Lard + 0.02% N.D.G.A. (deodorized 5 minutes at 350°F.)	28
Original Prime Steam Lard + 0.02% N.D.G.A. (deodorized 2 hours at 350°F.)	16
Original Prime Steam Lard + 0.02% N.D.G.A. (deodorized 5 minutes at 220°F.)	36
Original Prime Steam Lard + 0.02% N.D.G.A. (deodorized 2 hours at 220°F.)	33

Table V gives preliminary results obtained by adding N. D. G. A. to lard in an alcohol solution at the deodorization temperature. It is seen that high temperatures decrease the stabilizing effect.

Table VI gives typical results obtained by adding N. D. G. A. to lard and vegetable oil by means of an alcohol solution at 220°F.

It is more effective in lard than in the vegetable oils. This is to be expected from the phenolic nature of the compound. The stabilizing effect is imparted to a fair degree to baked goods. Since these results did not confirm the exceptionally long keeping qualities reported by Lundberg, *et al.* on lard, the addition

TABLE VI

N. D. G. A.

	Hours (AOM)	Days Before Rancid at 140°F.	Days Before Crackers Rancid at 140°F.
Refined Prime Steam Lard	5	6	11
Refined Prime Steam Lard + 0.01% N.D.G.A.	18	25	25
Refined Prime Steam Lard + 0.02% N.D.G.A.	35	32	32
Refined Prime Steam Lard + 0.05% N.D.G.A.	45	35	35
Refined and Bleached Cottonseed Oil	12	10	....
Refined and Bleached Cottonseed Oil + 0.02% N.D.G.A.	14	12	....
Refined and Bleached Soybean Oil	13	12	....
Refined and Bleached Soybean Oil + 0.02% N.D.G.A.	26	18	....

of the antioxidant at various stages of the processing was investigated. Table VII summarizes the results.

TABLE VII

	Hours (AOM)
Prime Steam Lard	6
Prime Steam Lard + 0.02% N.D.G.A. added in alcohol at 140°F.	50
Prime Steam Lard refined with alkali and 0.02% N.D.G.A. added at 140°F.	48
Prime Steam Lard refined with alkali, deodorized at 375°F. for 2 hours, cooled to 140°F. and 0.02% N.D.G.A. added in alcohol	42

As yet, we have been unable to confirm the reported results. The discrepancy might be due to difference in purity of the N. D. G. A. used. A further possibility is the method of handling samples prior to determination of the stability. All of our samples were filtered. It is likely that if solid particles of N. D. G. A. remained suspended in the fat greater stabilities would be obtained.

N. D. G. A. imparts no objectionable odor or flavor to freshly deodorized fats, but on standing or incubation a disagreeable metallic flavor is sometimes noted. The product has been shown to be harmless when administered in small amounts and has been approved at a 0.01% level for use in lard by the Meat Inspection Division (13).

Ascorbic Acid, Its Isomers and Derivatives. In 1939 ascorbic acid was proposed as an antioxidant for fatty emulsions (13). However, it is a very weak antioxidant for anhydrous fats, especially those of animal origin. This is due probably to its insolubility. Recently Riemenschneider, Turer, Wells, and Ault (14) proposed fat soluble derivatives of l-ascorbic and d-isoascorbic acid and reported data to show they were quite effective in lard and that their effect is markedly enhanced by combination with phospholipins and/or tocopherols.

TABLE VIII

D-isoascorbyl Palmitate, Lecithin and Tocopherols

	Hours (AOM)	Days Before Rancid at 140°F.	Days Before Crackers Rancid at 140°F.
Prime Steam Lard	4	7	12
Prime Steam Lard + 0.04% d-isoascorbyl palmitate, 0.04% lecithin, and 0.01% tocopherols	23	24	16
Prime Steam Lard + 0.04% d-isoascorbyl palmitate, 0.04% lecithin, and 0.01% tocopherols (deodorized)	63	21	18

Table VIII gives results obtained on lard, adding 0.04% d-isoascorbyl palmitate, 0.04% lecithin and 0.01% tocopherol to Prime Steam Lard and to deodorized Prime Steam Lard.

The isoascorbic acid ester is a white crystalline product easily soluble in fats. It imparts no objectionable odor or color. The combination with lecithin darkens slightly when heated to deep fat frying temperatures. Deodorization improves the stabilizing effect. The ester is not commercially available at the present time.

With the exception of gum guaiac, which has been successfully used in lard for a number of years, further work is necessary in order to evaluate the practical applicability of the antioxidants.

REFERENCES

(1) Moureau, C., and Dufraisse, C., Compt. rend. *174*, 258 (1922).
(2) Newton, R. C., and Grettie, D. P., U. S. Patent 1,903,126 (1933).
(3) Doegey, J. L., U. S. Patent 2,308,912 (1943).
(4) Carlson, A. J. *et al.*, Food Research *3*, 555 (1938).
(5) Golumbic, C., and Mattill, H. A., Oil & Soap *19*, 144 (1942).
(6) Sabalitschka, T., and Boehm, E., U. S. Patent 2,255,191 (1941).
(7) Boehm, E., and William, R., Quart. J. of Pharm. & Pharmacol. *16*, 232 (1943).
(8) Olcott, H. S., and Emerson, O. H., J. Am. Chem. Soc. *59*, 1008 (1937).
(9) British Patent 507,471 (1939).
(10) Taylor, A. E., and Jakobsen, J. L., U. S. Patent 2,267,224 (1941).
(11) Lips, A., and McFarlane, W. D., Oil & Soap *20*, 193 (1943).
(12) Lundberg, W. O., Halvorson, H. O., and Burr, G. O., Oil & Soap *21*, 33 (1944).
(13) Gray, P. P., and Stone, I., Food Ind. *11*, 626 (1939).
(14) Riemenschneider, R. W., Turer, J., Wells, P. A., and Ault, W. C., Oil & Soap *21*, 47 (1944).

Report of the Committee on Review of Scientific Literature of Fats, Oils and Soaps

THE tenth annual report of this committee has been completed and was published in two installments in the March and April numbers of *Oil and Soap.*

Material for this non-critical review was condensed from original sources where possible, and from Chemical Abstracts. This was classified and summarized as briefly as possible with no attempt to evaluate each contribution or to rate it by the consideration given it in the review.

The review should be a source of information on developments and should indicate the trend of scientific activities in the oil and fat field. We hope that the report will be of service to the members of the American Oil Chemists' Society and other readers of our official publication *Oil and Soap.*

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