Antioxidants for Food Fats and Oils[1]

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ABSTRACT

Types of antioxidants currently available for food fats and oils are listed, and theoretical and practical aspects of selecting the proper ones for various food uses are reviewed. Consideration is given to relative potencies, modes of application, regulations governing use, and some of the more prominent problems encountered in their commercial applications. A brief look is taken into future needs and possible developments with fat and oil antioxidants.

INTRODUCTION

Oxidative rancidity in fatty foods was probably observed by people in ancient times, and for hundreds of years various substances have been added to foods for the purpose of delaying the onset of such rancidity. Only in relatively recent years, however, have the reasons for the oxidative changes and the effects of the added substances been made clear. Antioxidant technology related to food fats and oils probably had its real beginning in the late 1940's when studies on butylated hydroxyanisole (BHA) revealed this phenolic substance to have outstanding antioxidant properties in various fatty materials and to be safe for use in foods. Also, in the early 1940's, results of studies with alkyl esters of gallic acid were published, revealing these esters to have considerable potential as antioxidants in food fats and oils.

Based on the earlier findings with gallate esters (especially *n*-propyl) and the subsequent development of BHA, it became apparent that combinations of these two antioxidant compounds might be used to great advantage in food fats and oils. These combinations would take advantage of the heat stability or carry-through effect of BHA and the outstanding effectiveness of the gallate ester in providing improved shelf life to fats and, especially, to vegetable oils. In early attempts to use these antioxidant formulations, it was soon recognized that some agent was needed to counteract the harmful effects of metallic ions commonly encountered in most food fats and oils. These metals, such as iron and copper, were recognized as powerful catalysts of fat oxidation and also were found to "react" with antioxidant compounds to cause color problems. Citric acid was selected to fill this need for a "metal deactivator" because it was found to chelate trace metals and minimize problems relative to their interaction with antioxidants. Evidence also was developed indicating a possible synergism of the acid with antioxidant compounds. A problem arising from the different solubility characteristics of BHA, propyl gallate and citric acid was overcome when it was found that propylene glycol could be used as a solvent for many possible combinations of these three additives.

Various combinations of BHA, propyl gallate and citric acid dominated the food fat and oil antioxidant scene until 1954, when another phenolic substance, butylated hydroxytoluene (BHT), was cleared for food use. Laboratory studies and commercial experience revealed BHT to have certain characteristics making desirable its use in the already existing combinations of BHA, propyl gallate and citric acid. A major difficulty with including BHT in these combinations arose, however, because of BHT's insolubility in propylene glycol. A solvent system was needed to permit the use of BHT in these antioxidant formulations. This need was filled by the development of vegetable oil-monoglyceride-propylene glycol systems in which the four active ingredients BHA, BHT, propyl gallate and citric acid could be dissolved in various required proportions.

In this review of fat and oil antioxidants, mention should be made of another polyphenolic compound which, in the early 1940's, was revealed to have outstanding antioxidant potency in food fats and oils and which, in 1943, was cleared for use in edible animal fats. This compound, nordihydroguaiaretic acid (NDGA), obtained by extraction from the leaves and twigs of a desert creosote bush, has been rather widely used as an antioxidant in some fairly specialized applications and has also been included with other antioxidants in some solution formulations. Because of problems encountered with its production and marketing, NDGA has been removed from the market and is not presently being used in food fats and oils.

Many dozens of compounds, both naturally occurring and synthetic, have been investigated in the past 20 years as oxidation inhibitors in food fats and oils. The majority of these have found little or no commercial use, and today most needs for antioxidants in food fats and oils are filled with BHA, BHT and propyl gallate used individually or in various combinations, sometimes combined with a chelate or acid synergist such as citric acid.

During the 20 or more years which have elapsed since our present fat and oil antioxidants had their beginning, much effort has been expended in laboratories of food and chemical companies, colleges and universities, and other institutions to elucidate the oxidative rancidity problem in food fats and oils; to understand how certain compounds or substances work in inhibiting oxidation; and to develop new inhibitors or new techniques for use in overcoming the problem. These studies are described in depth in a number of published articles (1-7). Details of autoxidation and antioxidants as related to food fats and oils may be had by referring to these publications. Meanwhile, this presentation is intended to focus briefly on some important considerations in achieving the most effective and trouble-free use of currently available antioxidants. Also, a brief look will be taken into future needs and possible new developments with fat and oil antioxidants.

ANTIOXIDANTS CLEARED FOR USE IN FOOD FATS AND OILS IN THE U.S.

Food products in interstate commerce in the U.S. are subject to regulations under the Food, Drug and Cosmetic Act, the Meat Inspection Act and the Poultry Inspection Act. These regulations establish limitations on the use of antioxidants and other food additives; hence the selection of antioxidants for use in food products is limited primarily to those cleared by appropriate regulations. Presently, antioxidants cleared under these regulations for addition to food fats and oils are: BHA (butylated hydroxyanisole or 2- and 3-isomers of tertiary butyl-4-hydroxyanisole); BHT (butylated hydroxytoluene or 2,6-ditertiary butyl-4-methyl phenol); propyl gallate (*n*-propyl ester of gallic acid); dilauryl thiodipropionate; thiodipropionic acid (3,3′-thiodipropionic acid); gum guaiac; lecithin; tocopherols (tocopherols concentrate, mixed; vitamin E); THBP (2,4,5-trihydroxybutyrophenone); ethoxyquin (1,2-dihydro-6-ethoxy-2,2,4-trimethylquinoline); 4-hydroxymethyl-2,6-di-tert-butylphenol; and glycine. Of these, BHA, BHT and propyl

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gallate are the most widely used. The others are generally quite limited in their usage because of certain technological problems or because of certain restrictions imposed by the regulations.

OXIDATION OF FOOD FATS AND OILS

Most evidence developed in recent years on oxidation mechanisms in organic matter supports the theory (8-10) that oxidation of fatty substances is an autocatalytic "chain" reaction based on formation of free radicals which serve to perpetuate the oxidation reaction. Oxidation of fatty substances is believed to take place in three stages.

a) Initiation: This probably corresponds to the oxidation induction period of a fat or oil, and during this stage fat or oil molecules convert to unstable fatty free radicals which can catalyze further free radical formation in the substrate. This may be depicted as:

$$\underset{\text{(fat molecule)}}{RH} \xrightarrow{\text{Initiator(s)}} \underset{\text{(fatty free radical)}}{R\cdot} + H\cdot$$

Various agents such as light (especially in the UV region), heat and heavy metals (particularly copper and iron) are principal initiators of autoxidation.

b) Propagation: Fatty free radicals which have formed can combine with molecular (atmospheric) oxygen to form peroxide free radicals which can react with the substrate to form more fatty free radicals and hydroperoxides. This "chain" reaction may be depicted as:

$$\begin{gathered} R\cdot + O_2 \longrightarrow \underset{\text{(peroxide free radical)}}{ROO\cdot} \\ ROO\cdot + RH \longrightarrow \underset{\text{(hydroperoxide)}}{ROOH} + R\cdot \\ ROOH \longrightarrow RO\cdot + \cdot OH \\ \cdot OH + RH \longrightarrow R\cdot + H_2O, \\ \text{etc.} \end{gathered}$$

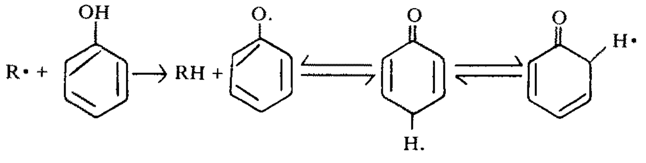
During propagation, especially in the presence of catalytic agents, decomposition of the hydroperoxides leads to formation of a wide variety of aldehydes, ketones, acids, etc., responsible for the obnoxious odor and flavor characteristics of rancid food fats and oils.

c) Termination: Termination of the oxidation chain reaction occurs when the free radicals (autocatalysts) are deactivated or destroyed. This may occur in various ways, such as:

$$\begin{gathered} R\cdot + R\cdot \longrightarrow RR \\ R\cdot + ROO\cdot \longrightarrow ROOR, \\ \text{etc.} \end{gathered}$$

FUNCTION OF FAT AND OIL ANTIOXIDANTS

Since the "chain" reaction of fat and oil autoxidation is initiated and propagated by the formation of free radicals, removal or deactivation of the free radicals should terminate the autoxidation in early stages before the end products responsible for organoleptically detectable rancidity can form. Fat and oil antioxidants are substances which can react with the initiating and propagating radicals to give harmless products (11,12) and extend the shelf life of the substrate until autoxidation takes place. This reaction is often depicted as follows, where AH is the antioxidant molecule: $R\cdot + AH \longrightarrow RH + A\cdot$ It is essential that the antioxidant free radical (A·), thus formed, not have capability of initiating or propagating the oxidation reaction. This is the case with phenolic compounds, since the resultant phenoxy radical is a "stable resonance hybrid" (13).



Pheno' Stable Resonance Hybrid

In other words antioxidants *do not* function by competing with the substrate for oxygen. Antioxidants *are not* "oxygen absorbers." Fat and oil antioxidants *are* free radical inhibitors and function by interfering with the free radical mechanism which is fundamental to autoxidation.

In selecting antioxidants it is helpful to recognize that phenolic compounds function differently as antioxidants depending upon the types and positions of groups affixed to the benzene ring nucleus of the compound. Not only is the antioxidant potency affected, but other physical and chemical characteristics having a bearing on antioxidant efficacy are also affected. For example, tertiary butyl groups on BHA and BHT molecules provide steric hindrance which will render the antioxidant free radical even less likely to serve as an initiator or propagator of autoxidation. On the other hand, this steric hindrance may also cause the compound to be somewhat less active as an antioxidant, since its electron releasing mechanism may be suppressed. Propyl gallate is generally found to be a much more effective free radical inhibitor than BHA or BHT, and this high degree of effectiveness is probably due to its polyhydroxyl configuration. However this same polyhydroxyl structure gives propyl gallate water solubility which can interfere with the optimum use of propyl gallate as an antioxidant in some fat-water systems.

Since fat and oil antioxidants function by interfering with the autoxidation "chain" reaction mechanism, it is essential that they be added as early as possible in the processing of food fats and oils. Also, it should be recognized that oxidized fat or oil cannot be restored by the addition of antioxidants. In addition, since heavy metals such as copper and iron play such an important role in initiating or propagating autoxidation, one can realize the values of minimizing their presence in fats and oils and using chelates along with antioxidants to inactivate the prooxidant effects of such metals. Citric acid is commonly used for this purpose, but monoisopropyl citrate, phosphoric acid and monoglyceride citrate are also used as chelates or synergists with fat and oil antioxidants (14).

SOME MAJOR CONSIDERATIONS IN SELECTING ANTIOXIDANTS FOR FOOD FATS AND OILS

Antioxidant formulations containing various combinations of different antioxidants and chelating agents are generally used, rather than individual antioxidant compounds, in most food applications. Not only does the use of such formulations provide a convenience, in that it is easier to handle the diluted antioxidants, but it permits advantage to be taken of different properties of the antioxidant compounds. One or another of the numerous antioxidant formulations available on the market will usually fill a given need, but there are still some instances where special formulations must be developed to fill particular requirements. In selecting the best antioxidant compound or antioxidant formulation or in devising a new formulation, the conditions surrounding manufacture, handling and use of the food product to be treated should be examined closely. These conditions must then be matched with the characteristics of the antioxidant compounds available for use. Some outstanding considerations in making the best match of antioxidant with food fat or oil are listed in the following paragraphs.

Potency of the Antioxidant

As already mentioned, the various compounds available for use as food fat and oil antioxidants differ in their degrees of antioxidant potency. These differences can be attributed to differences in their molecular structure. For example, propyl gallate is an extremely effective antioxidant from the standpoint of its ability to improve shelf life of vegetable oils, whereas BHA and BHT are not particularly effective in this type of application. The three hydroxyl groups in the propyl gallate molecule, with essentially no steric hindrance, are responsible for this effectiveness. On the other hand, BHA and BHT both have a single hydroxyl group in their molecules, and they are sterically hindered phenols with tertiary butyl groups positioned ortho to the hydroxyl groups. BHT is hindered somewhat more than BHA, and this no doubt accounts for some differences in potency between these two antioxidant compounds. As another example of the relationship of structure to potency, NDGA is an effective antioxidant in vegetable oils; and an examination of its structure reveals multiple hydroxyl groups and no steric hindrance, much like propyl gallate.

There is considerable evidence that phenolic antioxidants, such as BHA and BHT, will act synergistically when used together. That is, the combined effect of the two antioxidants is greater than the sum of the individual effects obtained when they are used alone. Also, it is recognized that a similar synergistic effect exists when phenolic antioxidants are used with certain acids, such as citric acid. This is often referred to as "acid synergism." These synergistic effects are often important considerations in the selection of antioxidant formulations.

Antioxidant Solubility or Dispersibility

Basically, the antioxidants available for food fats and oils are reasonably soluble and present no particular problems when added directly to fats and oils, but there are some solubility problems which may occasionally present difficulties. A particular problem exists with propyl gallate which has significant water solubility. In water-fat systems, there is a strong tendency for propyl gallate to be leeched from the fat into the water phase. Not only does this cause significant reduction in antioxidant effectiveness of propyl gallate in such a system, it also brings the antioxidant into more intimate contact with other components in the water phase. Traces of iron in the water can complex with propyl gallate to cause iron-gallate discoloration.

In contrast with propyl gallate, BHA and BHT are extremely soluble in food fats and oils and have practically no water solubility. This is quite desirable where these two antioxidants are added directly to pure fats and oils; however, where they are to be added to more complex food systems containing moisture, this may give rise to the need for development of emulsions or other types of antioxidant solutions which are more compatible with the food product and which will serve to carry the BHA or BHT into the food. A high percentage of problems encountered in day-to-day commercial use of fat and oil antioxidants can be attributed to poor solution or dispersion of the antioxidant.

Discoloration Tendencies

Color problems with antioxidants in food fats and oils generally stem from two sources. First, antioxidant compounds may interact with certain components of the food to provide reaction products having unacceptable color characteristics. Second, antioxidant compounds themselves may change, oxidatively or otherwise, to form end products having unacceptable color characteristics. Use of propyl gallate in some applications is discouraged or precluded by the tendency of this antioxidant to complex with traces of metallic iron to give a blue-black product. In some foods, even the presence of a chelate such as citric acid will not prevent such a discoloration from occurring. Also, the trace of iron present inherently in certain foods, i.e., iron-containing proteins, can be sufficient to cause this iron-gallate complex to form. The darkening of scrambled eggs prepared with a propyl gallate-treated shortening exemplifies this color potential.

While some discoloration can occur with BHA and BHT, especially the latter, in the presence of iron, the degree of this discoloration is generally not very serious, particularly in food fats and oils with significant inherent color characteristics. Possibly of more concern is a pink color which can occur when BHA comes into contact with fairly high concentrations of alkaline metal ions, such as sodium or potassium. This may occur, for example, in refined lard which has not been adequately washed after refining to remove soaps and excess caustic.

Consideration should also be given to color changes which can occur in antioxidants prior to their actual use in food fats and oils. On aging, especially if exposed to light and high temperatures, phenolic antioxidants will tend to darken, but the slight increase in color which occurs usually does not preclude their satisfactory use. Propyl gallate-containing formulations can present discoloration problems if packaged in metal containers or when brought into contact with metallic processing equipment. Even though specially lined drums may be used to ship such formulations, breaks in the lining may occur, exposing the concentrated solution to the bare metal of the container. This can happen when the drum is damaged in shipment or when the formulation is allowed to remain in contact with the bare metal threads of the bung hole. This problem can be avoided through careful handling of the drums and by avoiding prolonged contact of concentrated solutions with metal containers and equipment.

Acidity or Alkalinity of Food

Phenolic antioxidants tend to be acidic; hence they are probably most compatible with acidic substrates. Propyl gallate may be inactivated readily in alkaline systems, particularly at elevated temperatures. An example of this is encountered with antioxidant-treated shortenings used in baked products which are alkaline in nature. During baking, propyl gallate in the shortening will be inactivated and will not appear as an antioxidant in the finished baked food product. BHA and BHT, on the other hand, are noted for their ability to survive conditions such as these and "carry through" into baked products.

Of considerable concern to fat, oil and food processors is hydrolytic decomposition of fats and oils. This decomposition is measured by analyzing for free fatty acids, and it is important to recognize that antioxidants and antioxidant formulations, especially those containing acid-type chelates, will contribute significant "apparent" fatty acid to food fats and oils. The method to measure free fatty acids does not distinguish between acidity contributed by free fatty acids and that contributed by other acid-type materials.

Type of Processing of Food Products

Fat and oil antioxidants can survive, in varying degrees, many different conditions to which foods are subjected during their manufacture. Possibly one of the greatest challenges to the effective use of antioxidants is in deep-fat frying because of the relatively high temperatures involved and the large quantities of moisture usually driven off. BHA and BHT, which are steam distillable, and propyl gallate, which tends to decompose at high temperatures, are rather readily depleted from frying fats. The food processor must recognize this and take steps to maintain an adequate level of antioxidant during the frying operation so that the finished food product will have sufficient antioxidant protection. Loss of antioxidants through steam distillation can occur under even less strenuous processing conditions, such as in spray- or freeze-drying of food products.

Odor and Flavor of Antioxidants

Fat and oil antioxidants in their pure form do possess certain odor and flavor characteristics. Ordinarily at the low levels normally used in food fats and oils, the presence of antioxidants cannot be detected by odor or flavor. There may be an exception to this in some food products having extremely low levels of odor and flavor themselves.

Modes of Antioxidant Application

In many instances, the type of antioxidant to be used may be dictated by the techniques which can be considered for applying it to the food fat or oil. Basic methods for applying antioxidants are as follows.

a) *Direct addition* to food fat or oil as an antioxidant formulation or as a concentrate of the antioxidant in some of the fat or oil itself is the most simple means of application. Available antioxidants and formulations usually lend themselves quite readily to this type of application.

b) *Spray treatment* may be attractive in the case of fatty food products where oxidation tends to be a surface phenomenon on irregularly shaped articles of varying size. Nut meats exemplify food products which may be treated in this manner. A prime objective is to apply the minimum of spray needed to accomplish the protective effect without altering the appearance or texture of the food. In accomplishing this, BHA and BHT are probably the most desirable of the antioxidants, since highly concentrated spray solutions can be made with them and there will be the least amount of potential discoloration problem when the solution contacts metal portions of the spraying equipment.

c) *Antioxidant-treated spices and seasonings*: In some instances it is practical to use one of the components of a food product as a carrier for antioxidants. Antioxidant-treated salt may be used in preparing salted snack foods, for example, while spices and seasonings serve as good carriers for antioxidants to treat sausage products.

d) *Antioxidant-treated packaging materials*: Various types of food products benefit from being packaged in containers which have been treated with antioxidants. This benefit is derived from migration of the antioxidant from the package into the food product or, where there is transfer of fat or oil from the food product to the packaging material, from inhibition of oxidation on the inner surface of the food package itself.

FUTURE TRENDS WITH FAT AND OIL ANTIOXIDANTS

Much progress has been made in food antioxidant technology during the past two decades when most of the theories of autoxidation and antioxidant mechanisms as we know them were developed. Many problems with practical use of antioxidants have been solved and a variety of new applications and some new antioxidant compounds have been developed benefiting both food processors and consumers. However there are still outstanding needs associated with the use of currently available food antioxidants and for new types of antioxidants for food fats and oils.

Problems with Currently Available Antioxidants

Frequently, unsatisfactory performance of antioxidants in foods may be traced back to inadequacy of the application technique. Dispersing an additive in a food at a concentration of 100 or 200 ppm is a challenge even under the best of conditions. There are still instances of food products which could benefit significantly from antioxidant treatment if suitable application techniques were devised to meet commercial needs. In other instances antioxidants are being used in some applications without maximum benefit, because the application techniques are not adequate to bring the antioxidant into good enough contact with oxidizable portions of the food product. In some applications antioxidants thoroughly dispersed in a food product during processing do not carry through into the finished food, which is then left with insufficient protection. New techniques are needed for adding antioxidants to some foods.

New Types of Food Products

The trend in recent years toward the use of more highly unsaturated fats and oils in the diet has led to changes in susceptibility of certain foods to oxidative degradation. It appears this trend will continue, and new, more potent antioxidants will be needed for these more highly oxidation-sensitive food fats and oils. Tertiary butyl hydroquinone (TBHQ) (15) still seems to be a candidate to fill this need and is currently the subject of a petition to the U.S. Food and Drug Administration seeking clearance of its use in edible fats and oils.

New Types of Inhibitors

Increasing concern over the use of "chemical additives" in foods is giving rise to an interest in replacing "synthetic" additives with additives deemed to be more "natural" in origin. In the case of fat and oil antioxidants, it is conceivable that, to satisfy this desire, there will be some instances where natural-type antioxidants, i.e., tocopherols, may be developed to replace synthetic materials. Considerable work will need to be done to overcome certain color, odor, cost and potency problems inherent in the use of so-called "natural" antioxidant materials. Demands by consumers may put increasing emphasis on these efforts.

New Types of Chelates or Synergists

Many oxidation problems still being encountered with food fats and oils may be attributed to prooxidant effects of metals (16), which are present naturally in foods or which may be added (intentionally or otherwise) during processing. It still appears that a chief factor in the oxidative deterioration of meat products is the heme-catalyzed oxidation of the lipid fraction. Further efforts will be made to elucidate this problem and to overcome the catalytic effects of the pigments so that antioxidants may function more effectively in such foods.

New Applications for Free Radical Inhibitors Related to Human Health and Nutrition

In recent months there has been mounting evidence that free radical autoxidation occurring in cellular tissue plays a vital role in the aging process (17-19). Also, there have been reports (20,21) that free radical inhibitors may function as anticancer compounds or may serve to overcome other physiological problems related to the human body. It remains to be determined whether or not such benefits may be achieved with inhibitors added to food fats and oils.

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