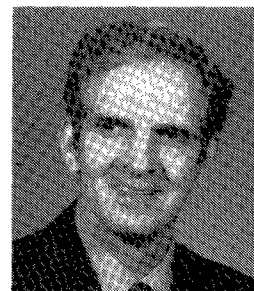


# Antioxidants for Vegetable Oils

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## ABSTRACT

Several chemical compounds having antioxidant efficacy in food fats and oils and cleared for food use by governmental regulatory agencies are available for such use by vegetable oil processors in many nations of the world. These antioxidants are reviewed with particular attention to major benefits and possible shortcomings they may afford when added to vegetable oils. Some guidelines in selecting antioxidants to achieve optimum results are offered. Also, precautions to be observed in adding antioxidants to fats and oils are discussed.

## INTRODUCTION

### Unsaturation and Oxidation in Vegetable Oils

An important feature common to most finished vegetable oils is the high percentages of unsaturated fatty acids in the triglyceride molecules (Table I). Perhaps an even more meaningful indicator of the total chemical unsaturation of a vegetable oil is its iodine value, and, as shown in Table I, typical iodine values for most vegetable oils are in excess of 75. Generally, it is conceded that the principal route of deterioration and possible economic loss of vegetable oils is through rancidity resulting from oxidation which takes place at the double bond (unsaturation) sites (Fig. 1) in the triglyceride molecules (1-6). In general, the higher the degree of unsaturation of a vegetable oil, as reflected by its content of unsaturated fatty acids or its iodine value, the more susceptible it is to oxidative deterioration.

The oxidation of vegetable oil takes place in a series of steps, as depicted in Figure 2, and is often referred to as a "free radical" type of oxidation because the first or initiating step is the formation of a fatty free radical. This occurs when hydrogen (or a proton) is lost from the  $\alpha$ -methylene carbon in the fatty acid group. The fatty free radical is readily susceptible to attack by atmospheric oxygen, result-

ing in the formation of peroxides and hydroperoxides. The free radicals formed in the glyceride oxidation act as strong initiators of further oxidation; hence, the oxidative degradation of a vegetable oil is often described as being an autocatalytic or an autoxidative process. As a final or terminating step in the autoxidation, hydroperoxides may split into smaller organic compounds, such as aldehydes, ketones, alcohols, and acids, which give the obnoxious odors and flavors characteristic of oxidative rancidity in vegetable oils.

Those oils containing substantial amounts of linolenic acid, or possibly other fatty acids with more than two double bonds in their molecular structures, present a unique form of oxidative degradation known as "flavor reversion." This seems to require a very much lower degree of oxidation than takes place when oxidative rancidity occurs. In commercial edible oils, the reversion problem is most likely encountered with soybean and rapeseed oils, which (Table I) have high levels of linolenic acid.

### TOCOPHEROLS IN VEGETABLE OILS

Over 40 years ago, distinct relationships were observed between Vitamin E (tocopherol) contents of vegetable oils and the resistance of such oils to development of oxidative rancidity. At least seven types of tocopherol, methyl-substituted forms of tocol (Fig. 3), have been isolated with the alpha, gamma, and delta homologs predominating in vegetable matter. Vitamin E activity is attributed mainly to  $\alpha$ -tocopherol, which also provides some oxidation inhibition (antioxidant) effect in oils, but the gamma and delta forms reportedly are more effective antioxidants and have no biologic effect. Generally, the order of antioxidant activity of these predominant tocopherols is found to be:  $\delta > \gamma > \alpha$ , but this order of antioxidant potency in vegetable oils may be influenced significantly by temperature and light conditions.

TABLE I  
Edible Vegetable Oils:  
Typical Unsaturated Fatty Acid Contents and Iodine Values

Vegetable oil	Unsaturated fatty acids in vegetable oils (percent on total fatty acid basis)				Total	Typical iodine value range
	Oleic	Linoleic	Linolenic	Misc. <sup>a</sup>		
Coconut	6.5	1.5	--	--	8.0	7-13
Palmkernel	13.7	2.0	--	--	15.7	14-24
Palm	38.8	9.4	0.3	--	48.5	45-56
Olive	71.1	10.0	0.6	1.2(16:1)	82.9	76-90
Peanut	46.5	31.4	--	1.4(20:1)	79.3	84-102
Safflowerseed (high oleic)	79.7	12.0	0.2	--	91.9	85-93
Rapeseed	23.8	14.6	7.3 <sup>b</sup>	12.1(20:1) 34.8(22:1)	92.6	97-110
Cottonseed	17.6	53.3	0.3	--	71.2	99-121
Sesameseed	41.2	43.2	0.2	--	84.6	104-118
Rapeseed (low erucic)	64.1	18.7	9.2 <sup>b</sup>	1.0(20:1)	93.0	110-115
Corn	27.5	57.0	0.9	--	85.4	110-128
Sunflowerseed	18.6	68.2	0.5	--	87.3	122-139
Soybean	23.4	53.2	7.8 <sup>b</sup>	--	84.4	125-138
Safflowerseed	13.1	77.7	--	--	90.8	138-151

<sup>a</sup>Significant unsaturated acids other than oleic, linoleic, and linolenic (carbons: no. of double bonds).

<sup>b</sup>High triene content (flavor reversion).

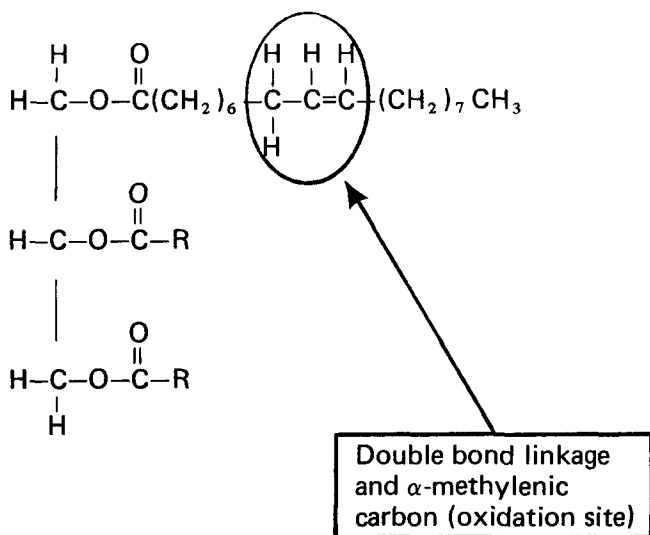


FIG. 1. Typical unsaturated triglyceride molecule with double bond (oxidation site). R = fatty acid group.

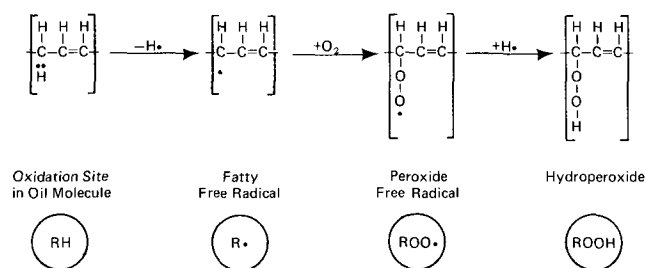


FIG. 2. Free radical oxidation of vegetable oil.

Not only are tocopherols widely distributed in vegetable matter from which edible oils of commerce are extracted, but it is very important to recognize that high proportions of these tocopherols survive oil processing steps and end up in finished vegetable oils, as indicated in Table II. These residual levels of tocopherol appear to be optimum for providing the oxidative stability which is inherent in most vegetable oils. If these residual tocopherols are stripped completely from vegetable oil by distillation or some other efficient method, it will be observed that the oxidative stability of the oil is reduced to an extremely low level. If tocopherols are added back to the stripped oil at levels normally present in refined vegetable oils, the oxidative stability of the oil will be restored to a level typical of normally processed vegetable oil. It is important to recognize and emphasize that these levels of tocopherols seem to be optimum for providing oxidative stability, and the addition of more tocopherol likely will provide no further increase in stability and, if added at high enough concentration, may even have a depressing effect on the oxidative stability of the oil.

### ANTIOXIDANT MECHANISM IN VEGETABLE OILS

Subsequent to the early observations that certain substances naturally present in vegetable oils substantially prolong the life of such oils until rancidity occurs, much work has been done to identify chemical structures providing this very desirable effect and to elucidate the mechanism of the oxidation inhibition or antioxidant action. From those studies and much practical experience, it may be concluded that the various substances which have been established as safe and effective for use as fat and oil "antioxidants" can and should logically be divided into two categories comprised or primary antioxidants and of synergists. This is especially helpful in considering the types of substances they are, their modes of action, and their effectiveness as

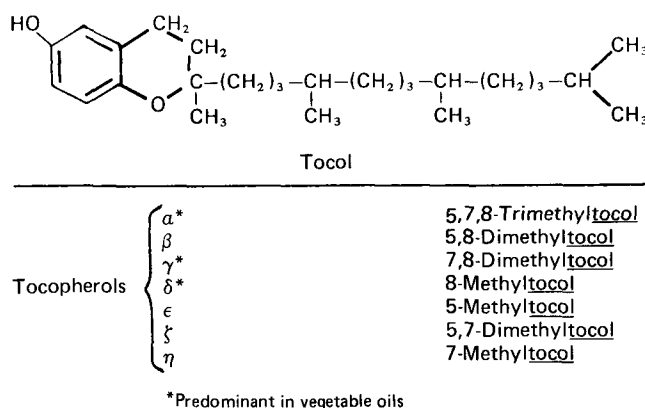


FIG. 3. Tocopherols found in vegetable matter.

TABLE II  
Concentrations of  
Tocopherols<sup>a</sup> in Vegetable Oils

Vegetable oil	Typical tocopherol contents of finished vegetable oils (ppm)
Coconut	83
Palm	560
Olive	30-300
Peanut	480
Rapeseed	580
Cottonseed	870-950
Sesameseed	180
Corn	900
Sunflowerseed	700
Soybean	940-1,000
Safflowerseed	800

<sup>a</sup>Mainly  $\alpha$ -,  $\gamma$ -, and  $\delta$ -tocopherols.

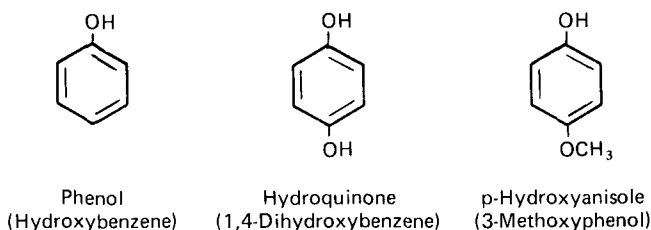


FIG. 4. Typical phenolic structures.

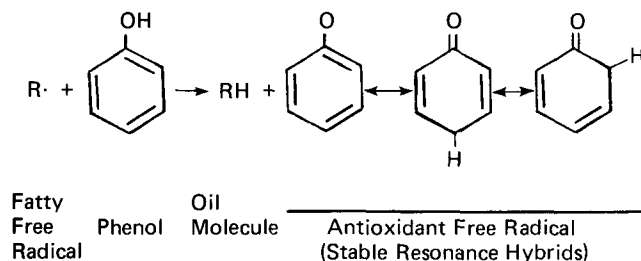


FIG. 5. Phenolic antioxidant mechanism in vegetable oil.

antioxidants in vegetable oils.

Primary antioxidants are those substances which function by inhibiting or interrupting the free radical mechanism of glyceride autoxidation. Their ability to do this is based on their phenolic structure (Fig. 4) or the phenolic configuration within their molecular structure. As depicted in Figure 5 in a very simplified fashion, the primary antioxidant or phenolic substance functions as a free radical acceptor, thus terminating the oxidation at the initiation step. As indicated, the antioxidant free radical which forms is stable and, most importantly, will not propagate further oxidation of the glyceride. Understanding this as the

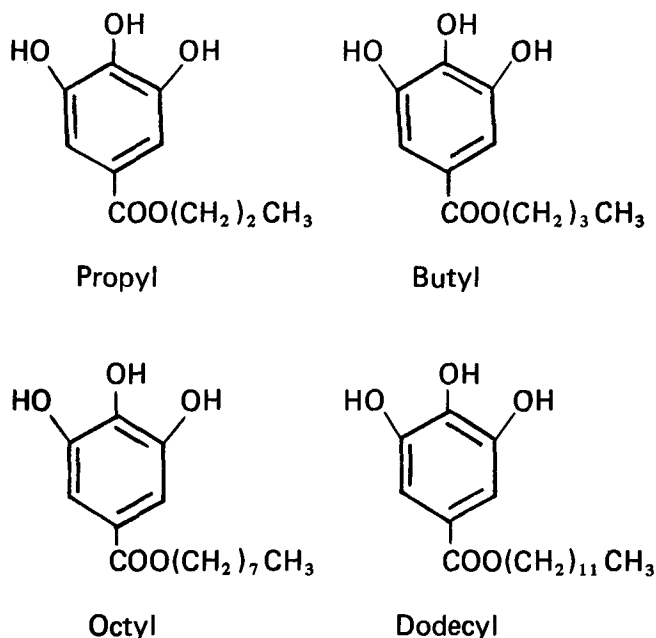


FIG. 6. Alkyl gallates.

mechanism of antioxidant action in vegetable oils, one should see that maximum efficiency of primary antioxidants can be achieved only if they are intimately mixed or dissolved in the oil and are added soon enough to inhibit or interrupt the free radical mechanism of vegetable oil autoxidation. If this is accomplished, there should be a significant delay in the onset of the final stages of autoxidation wherein the oxidation breakdown products responsible for rancidity are formed.

It has long been recognized that various acids (both organic and inorganic) and some of their derivatives provide apparent antioxidant effect when added to vegetable oils. These acid compounds often are included in general listings of antioxidants for food oils and may even be referred to as acid-type antioxidants. However, these acids, if added alone to oils known to contain no primary antioxidant, will exhibit virtually no effect on the oxidative stabilities of the oils. It is believed that the acids are not truly antioxidants but more likely function by enhancing, in some manner, the activity of primary antioxidants naturally present (such as tocopherols) in the oils or those antioxidants added by the processor. In view of this, these acids are commonly classified as synergists. The actual mechanism of acid synergism is not fully understood, but probably involves

1. Chelation or deactivation of prooxidant metals in the oil
2. Regeneration or sparing of primary antioxidants
3. Inhibition of peroxide decomposition, thus interrupting the autoxidation process

Flavor reversion has been mentioned as a type of oxidative degradation important in connection with vegetable oils with substantial linolenic acid content. Phenolic antioxidants are not effective in inhibiting this type of degradation of vegetable oil.

### PRIMARY ANTIOXIDANTS FOR VEGETABLE OILS IN VARIOUS COUNTRIES

A review of primary antioxidants, aside from tocopherols, authorized for use in edible vegetable oils in various countries logically should start with gum guaiac (sometimes called resin guaiac), a substance recognized in the early 1930s as having measurable antioxidant effectiveness, especially in animal fats. The United States Government cleared it in 1940 for meat fat applications, and, for some time, it was the only antioxidant available for that purpose. Gum guaiac is a resinous exudate from a type of tree found in the West Indies, and its antioxidant effectiveness stems from several phenolic compounds (ca. 10% guaiaretic and 70%  $\alpha$ - and  $\beta$ -guaiaconic acids) present in high proportions in the resin. Gum guaiac exhibits very little antioxidant effectiveness in vegetable oils—especially those with natural tocopherol content—and apparently is not being used to any significant extent in this application. It is a brown or reddish-brown solid sparingly soluble in oil, and it is reported to give color and flavor characteristics which may discourage its use.

Early in the 1940s, good antioxidant properties of several alkyl esters of gallic acid (Fig. 6) were reported, and they were shortly thereafter authorized for food use in a number of countries. As indicated in the description of the mechanism of phenolic antioxidants, the hydroxyl group plays a critical role in inhibiting free radical oxidation of unsaturated glyceride molecules. Based on the trihydroxyl structures of the gallates, they would be expected to have relatively high antioxidant potency in oils, and this is shown to be the case (Table III). Use of the higher gallates, octyl and dodecyl, serves to overcome solubility difficulties (high water and low oil solubility) which butyl and propyl esters may present, but the strong tendency of all gallate esters to complex with traces of iron to give a blue-black discoloration serves to minimize the use of these relatively potent antioxidant compounds in vegetable oils. In addition, the gallates are somewhat heat sensitive, especially under alkaline conditions, and are lost from cooking oils rather rapidly at high temperatures, especially those

TABLE III

Typical Antioxidant Effectiveness of  
Gallates, NDGA, THBP, and TBHQ in Vegetable Oils<sup>a</sup>

Antioxidant treatment of oil (% by wt)	AOM stability of vegetable oil (hr to 70 meq/kg peroxide content)			Oven storage life of vegetable oil (days at 63 C until rancid odor developed)		
	Cottonseed	Soybean	Palm	Cottonseed	Soybean	Palm
Propyl gallate (0.01)	19(9) <sup>b</sup>	21(11)	137(45)	13(9)	14(6)	75(45)
(0.02)	30(9)	26(11)	--	19(9)	22(6)	--
Octyl gallate (0.01)	11(8)	-- <sup>c</sup>	--	--	--	--
Dodecyl gallate (0.01)	10(8)	--	--	--	--	--
NDGA (0.02)	14(12)	26(13)	--	12(10)	18(12)	--
THBP (0.01)	13(10)	--	--	--	--	--
(0.02)	28(8)	--	--	--	--	--
TBHQ (0.01)	24(9)	29(11)	150(45)	15(9)	--	118(47)
(0.02)	34(9)	41(11)	--	23(9)	26(6)	--

<sup>a</sup>NDGA=nordihydroguaiaretic acid; THBP = 2,4,5-trihydroxybutyrophenone; TBHQ = tertiary butylhydroquinone; AOM = active oxygen method.

<sup>b</sup>Value in parentheses is for control oil without antioxidant treatment; value outside parentheses is for antioxidant-treated oil.

<sup>c</sup>Values not available.

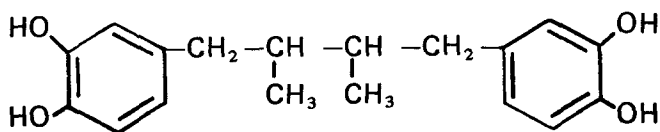
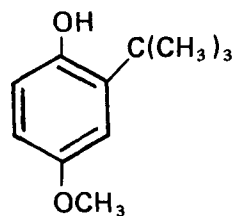
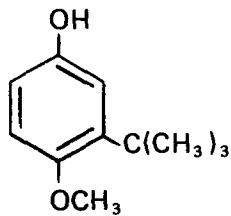


FIG. 7. NDGA (nordihydroguaiaretic acid).



2-Tertiarybutyl-4-Methoxyphenol  
(about 85%)



3-Tertiarybutyl-4-Methoxyphenol  
(about 15%)

FIG. 8. BHA (butylated hydroxyanisole).

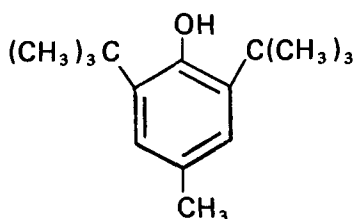


FIG. 9. BHT (butylated hydroxytoluene).

encountered in baking and in deep frying of foods.

In 1942, nordihydroguaiaretic acid (NDGA) (Fig. 7) was found to be extractable in substantial quantities from the creosote bush (a desert plant, *Larrea divaricata*). Shortly thereafter (1943), this compound was cleared in the U.S. for use as an antioxidant in meat fats and has been authorized in a number of countries for use in oils. As with the gallates, NDGA has the polyphenolic structure typical of primary antioxidants found to be particularly effective in vegetable oils, as indicated in Table III. NDGA is a white, crystalline solid with a slight water solubility and limited (0.5-1.0%) oil solubility. NDGA, like the gallates, causes discoloration in the presence of traces of iron and is readily inactivated as an antioxidant at food baking and frying temperatures, especially under alkaline conditions. NDGA is currently listed in some countries as an approved oil antioxidant, but it apparently has fallen into disuse primarily because of commercial nonavailability. A principal objection to NDGA has been its relatively high market price necessitated by the costly production techniques required in extracting it from its plant source.

Butylated hydroxyanisole (BHA), commercially available as a mixture of 2- and 3-isomers of tertiarybutyl-4-methoxy phenol (Fig. 8), was first approved in 1948 for food use in the U.S. and has since found widespread use in food fats and oils in many countries. Because of the tertiarybutyl group ortho- or meta- to the hydroxyl group, BHA is referred to as a hindered phenol. This steric hindrance is believed responsible for the relative ineffectiveness of BHA in vegetable oils because the tertiarybutyl group interferes with the antioxidant activity of the phenolic structure. On the other hand, however, this same steric hindrance also serves to protect the active hydroxyl group under some conditions and is probably responsible for the carry-through effect of BHA in fats and oils used in baked or fried foods. BHA is a white, waxy solid highly soluble in oil and insoluble in water. Although it is not a particularly effective antioxidant in vegetable oil, BHA is commonly used in combination with other primary antioxidants (such

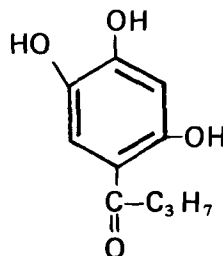


FIG. 10. THBP (2,4,5-trihydroxybutyrophenone).

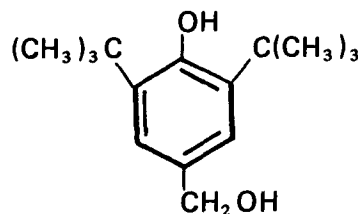


FIG. 11. 4-Hydroxy methyl-2,6-ditertiarybutylphenol.

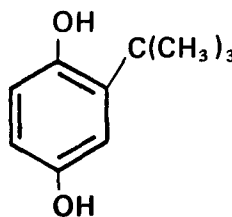


FIG. 12. TBHQ (tertiary butylhydroquinone).

as gallates) in order to take advantage of the synergistic effects observed when certain phenolic antioxidants are used together and also to benefit from the carry-through protection which BHA may afford. BHA has a strong phenolic odor which becomes particularly noticeable when an oil treated with it is subjected to high temperatures, such as in a baking or frying operation.

Another hindered phenol, 2,6-ditertiarybutyl-4-methylphenol (Fig. 9), had been in wide commercial use as an oxidation inhibitor in petroleum and rubber products for a number of years when, in 1954, it was cleared in the U.S. for use in food oils on the basis of favorable toxicity and potency test results showing it to be a safe and effective antioxidant in glycerides. As a food antioxidant, it has become known commonly as BHT (butylated hydroxytoluene), and, as might be expected from their similar molecular structures, BHT and BHA are similar in performance, including their relative weakness as antioxidants in vegetable oils. BHT is a white, crystalline solid with good oil solubility and insoluble in water. It provides relatively low antioxidant effectiveness in vegetable oils but, like BHA, is often used in combination with other primary antioxidants to take advantage of the carry-through protection it may afford in baked or fried foods.

In 1963, 2,4,5-trihydroxybutyrophenone (THBP) (Fig. 10) was cleared for use in food fats and oils in the U.S. on the basis of toxicity and potency test results (7,8) demonstrating the safety and effectiveness (Table III) of this compound. As may be expected on the basis of the similarity of their molecular structures, THBP and the gallates perform very similarly in vegetable oils. THBP is a light yellow, crystalline solid with slightly better oil solubility than propyl gallate. It presents much the same discoloration problem as the gallates in the presence of iron. THBP, although still cleared under U.S. Food Additives Regulations for vegetable oil use, has found no significant commercial usage in such food oils.

In 1967, a regulation was issued by the U.S. Food and

Drug Administration clearing 4-hydroxymethyl-2,6-ditertiarybutylphenol (Fig. 11) for use in edible oils. Substitution of a hydroxyl for one hydrogen in the methyl group of BHT provided this new compound which was believed to have reduced volatility as compared with BHT (9). However, this slight change in the BHT molecular structure did not affect any significant change in the antioxidant performance, and 4-hydroxymethyl-2,6-ditertiarybutylphenol apparently has found no significant commercial use in vegetable oils. It is a white, crystalline solid and appears to be essentially like BHT in most physical and chemical characteristics, including antioxidant activity.

Increased use in the past 15 years of highly oxidation-sensitive polyunsaturated vegetable oils in food processing and in the human diet gave rise to the need for more potent antioxidants (and possibly ones less troublesome to use than already available compounds, such as the gallates). Tertiary butylhydroquinone (TBHQ) (Fig. 12) was identified by extensive laboratory testing as a potential answer to this need (10,11) and, in 1972, was cleared by the U.S. Government for use in food fats and oils. Since then, the use of this compound to stabilize vegetable oils has been cleared in a number of other countries. As indicated in Table III, response of vegetable oils to treatment with TBHQ generally is found to be greater than with any of the other authorized primary antioxidants. Also, the laboratory tests and results of commercial experience indicate that the greater antioxidant performance of TBHQ in polyunsaturated oils may likely be achieved without certain problems (color and solubility, for instance) encountered with the use of other antioxidants. TBHQ is a white, crystalline solid with moderate oil solubility and very slight water solubility.

#### **SYNERGISTS USED WITH PRIMARY ANTIOXIDANTS IN VEGETABLE OILS**

Acids considered as synergists for primary antioxidants in vegetable oils and authorized for this use in many countries are citric, phosphoric, thiodipropionic, ascorbic, and tartaric.

However, insolubility of these acids in vegetable oils presents difficulties in their use as synergists along with primary antioxidants. As a step in overcoming this difficulty, certain derivatives of the acids have been proven effective and are also authorized. They are isopropyl citrate, didodecyl thiodipropionate, dilauryl thiodipropionate, dioctadecyl thiodipropionate, and ascorbyl palmitate. One other substance cleared in various countries for use as an antioxidant or synergist in vegetable oils is lecithin, a phospholipid or phosphatide, which may actually be looked upon as a triglyceride with one of its fatty acid groups replaced by phosphoric acid which in turn is esterified with choline. Lecithin is naturally present in many foods, where it may appear to exhibit antioxidant effect. However, this effect is likely due to the reinforcing or synergistic effect of the lecithin on the true antioxidant action of primary antioxidants which are naturally present or may be added.

#### **STATUS OF PRIMARY ANTIOXIDANTS AND SYNERGISTS FOR VEGETABLE OILS IN VARIOUS COUNTRIES**

It would be most difficult, or perhaps even impossible, to develop a totally up-to-date and complete listing of substances which may be used as primary antioxidants and synergists in vegetable oils in the many countries of the world. However, Table IV is offered as a very general summary of these oil additives, which may be cleared for use in various countries. For answers to specific questions about the regulatory status of any antioxidants or synergists, one should consult the full texts of pertinent regulations for the country of interest and seek the advice of legal counsel.

#### **IMPORTANT CONSIDERATIONS IN APPLYING ANTIOXIDANTS TO VEGETABLE OILS TO ACHIEVE OPTIMUM RESULTS**

In order that antioxidants may function with maximum efficiency in vegetable oils, not only must they be potent inhibitors of glyceride autoxidation, but they also must be properly incorporated into the oil. Improper application is the probable source of a majority of problems encountered with antioxidants used alone or in one or another of the various proprietary formulations which combine primary antioxidants with synergists for treatment of vegetable oils. The following is a brief review of the major types of problems related to putting antioxidants into vegetable oils.

##### **Incomplete Solution or Dispersion of Antioxidant in the Oil**

This may result from inadequate mixing equipment or techniques or from unwise or even unauthorized shortcuts being taken in procedures established for the proper application of antioxidants. For example, it is unlikely that a concentrated antioxidant solution or formulation just poured into a storage tank or shipping vessel as it is being filled with oil will dissolve and disperse properly in the oil. This can lead to serious stability deficiencies and other complications relative to insufficient antioxidant in the bulk of the oil and an unduly high concentration of antioxidant in the oil at the bottom of the vessel. The oil processor must recognize the absolute need for complete antioxidant solution in the oil being treated, and he must take steps necessary to ensure it.

##### **Improper Concentration of Antioxidant**

Maximum concentrations of antioxidants permitted in vegetable oils are defined by the regulations, and these levels generally are recognized as being optimum for achieving good stability results. The oil processor should be aware that the degree of effectiveness of antioxidants within the permitted concentration range is in fairly direct proportion to the concentration used. Accordingly, it may be a false economy to reduce treatment levels substantially below the permitted levels at the risk of producing an oil with inadequate storage life.

##### **Incompatibility of Antioxidant Formulations with Vegetable Oils**

Because of dissimilar solubility characteristics of primary antioxidants and synergists, solvents (propylene glycol, for example) necessary for preparing good antioxidant-synergist formulations are in some instances not very compatible with vegetable oils. In the use of certain antioxidant formulations, this factor must be fully recognized and proper application techniques employed to overcome solubility difficulties such formulations may offer.

##### **Changes in Antioxidant Formulations**

The many proprietary antioxidant-synergist formulations available to oil processors vary substantially in their complexity depending upon active ingredient contents and the solvent systems required to dissolve the ingredients and keep them in solution until the formulation is used. Users of these formulations must realize and be alert to the possibility that, under some storage or handling conditions, separation or crystallization or other changes may occur, necessitating some special handling of the formulation to ensure proper treatment of the vegetable oil.

##### **Use of Incorrect Type of Antioxidant or Formulation**

There are significant differences between antioxidants with regard to their performance characteristics in different types of oils and under different oil processing and handling conditions. The oil processor must give due consideration

TABLE IV  
Primary Antioxidants and Synergists for Vegetable Oils in Various Countries<sup>a</sup>

Countries	Primary Antioxidants											Synergists											
	Tocopherols	Gum guaiac	Propyl gallate	Butyl gallate	Octyl gallate	Dodecyl gallate	NDGA (nordihydroguaretic acid)	BHA (butylated hydroxyanisole)	BHT (butylated hydroxytoluene)	THBP (2,4,6-trihydroxybutyrophenone)	4-Hydroxy methyl-2,6-ditertiary butylphenol	TBHQ (tertiary butylhydroquinone)	Citric acid	Isopropyl citrate	Phosphoric acid	Thiodipropionic acid	Didodecyl thiodipropionate or didauryl thiodipropionate	Dioctadecyl thiodipropionate	Ascorbic acid	Ascorbyl palmitate	Tartaric acid	Lecithin	
Australia																							
Austria	X	X	X	X	X	X	X	X	X	X	X									X			
Belgium	X	X	X	X	X	X	X	X	X	X	X									X			
Brazil	X	X	X	X	X	X	X	X	X	X	X									X			
Canada	X	X	X	X	X	X	X	X	X	X	X									X			
Ceylon			X	X	X	X	X	X	X	X	X												
Czechoslovakia			X	X	X	X	X	X	X	X	X												
Denmark	X	X	X	X	X	X	X	X	X	X	X									X			
Finland	X	X	X	X	X	X	X	X	X	X	X								X				
France			X	X	X	X	X	X	X	X	X								X				
Britain			X	X	X	X	X	X	X	X	X												
Greece			X	X	X	X	X	X	X	X	X												
Haiti			X	X	X	X	X	X	X	X	X												
Hong Kong			X	X	X	X	X	X	X	X	X												
India	X	X	X	X	X	X	X	X	X	X	X								X				
Italy	X	X	X	X	X	X	X	X	X	X	X								X				
Jamaica			X	X	X	X	X	X	X	X	X												
Japan			X	X	X	X	X	X	X	X	X												
Korea			X	X	X	X	X	X	X	X	X												
Malaysia			X	X	X	X	X	X	X	X	X												
Mexico	X	X	X	X	X	X	X	X	X	X	X												
Morocco			X	X	X	X	X	X	X	X	X												
Netherlands	X	X	X	X	X	X	X	X	X	X	X									X			
New Zealand			X	X	X	X	X	X	X	X	X									X			
Nicaragua	X	X	X	X	X	X	X	X	X	X	X									X			
Norway	X	X	X	X	X	X	X	X	X	X	X									X			
Pakistan	X	X	X	X	X	X	X	X	X	X	X												
Peru			X	X	X	X	X	X	X	X	X												
Poland	X	X	X	X	X	X	X	X	X	X	X									X			
Republic of South Africa	X	X	X	X	X	X	X	X	X	X	X									X			
Rumania			X	X	X	X	X	X	X	X	X												
Spain			X	X	X	X	X	X	X	X	X												
Sweden	X	X	X	X	X	X	X	X	X	X	X												
Switzerland	X	X	X	X	X	X	X	X	X	X	X									X			
Turkey	X	X	X	X	X	X	X	X	X	X	X												
Taiwan			X	X	X	X	X	X	X	X	X												
USA	X	X	X	X	X	X	X	X	X	X	X									X			
USSR			X	X	X	X	X	X	X	X	X												
Wales			X	X	X	X	X	X	X	X	X												
Yugoslavia			X	X	X	X	X	X	X	X	X									X			

to this in making his selection of the type of antioxidant or formulation which will most likely fill his particular needs.

### **Antioxidants Added at Wrong Stage in Vegetable Oil Production**

Primary antioxidants are very effectively removed from vegetable oils during some steps in oil production, such as alkali refining, bleaching, and deodorization. While there may be special reasons to add antioxidants to vegetable oil at some early stage (to crude oil, for example), processors should recognize that a significant portion of the antioxidant likely will be lost and not end up in the finished oil which, because of low antioxidant content, may then have insufficient stability.

### **Failure to Add Antioxidant to Oil Soon Enough**

Since phenolic antioxidants function by inhibiting free radical formation, the initial step in oil oxidation, it is essential that they be added as soon as reasonably possible to the finished vegetable oil. Rancid oils cannot be rejuvenated by addition of antioxidants.

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