ANTIOXIDANT

Antioxidants

The chemical compounds which can delay the start or slow the rate of lipid oxidation reaction in food systems

Minimization of Lipid Oxidation

If a compound inhibits the formation of free alkyl radicals in the initiation step, or if the chemical compound interrupts the propagation of the free radical chain, the compound can delay the start or slow the chemical reaction rate of lipid oxidation.

The initiation of free radical formation can be delayed by the use of metal chelating agents, singlet oxygen inhibitors, and peroxide stabilizers.

The propagation of free radical chain reaction can be minimized by the donation of hydrogen from the antioxidants and the metal chelating agents.

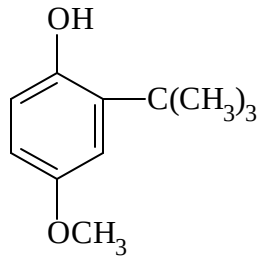
Characteristics of Antioxidants

The major antioxidants currently used in foods are monohydroxy or polyhydroxy phenol compounds with various ring substitutions. These compounds have low activation energy to donate hydrogen. The resulting antioxidant free radical does not initiate another free radical due to the stabilization of delocalization of radical electron.

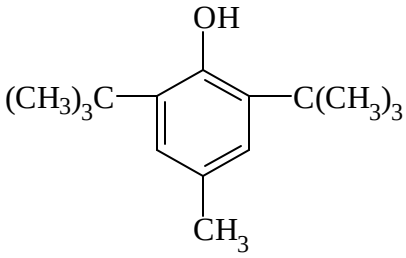
The resulting antioxidant free radical is not subject to rapid oxidation due to its stability.

The antioxidant free radicals can also react with lipid free radicals to form stable complex compounds.

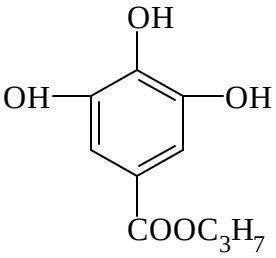
Antioxidants



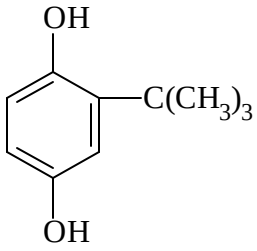
Butylated
Hydroxyanisole



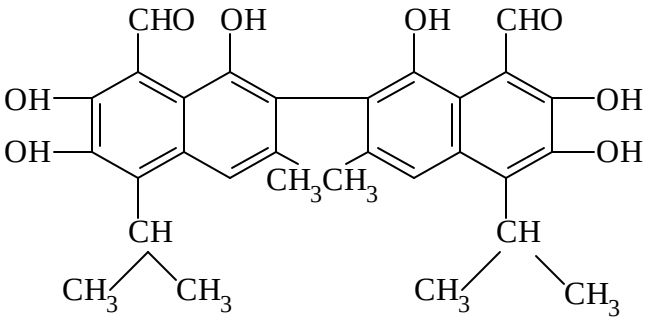
Butylated
Hydroxytoluene



Propyl Gallate



TBHQ



Gossypol

Mechanism of Antioxidants

Hydrogen donation to free radicals by antioxidants.

Formation of a complex between the lipid radical and the antioxidant radical (free radical acceptor).

Reaction of antioxidants with radicals:

$R\bullet + AH \longrightarrow RH + A\bullet$

$RO\bullet + AH \longrightarrow ROH + A\bullet$

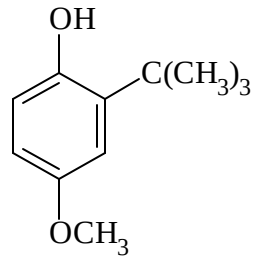
$ROO\bullet + AH \longrightarrow ROOH + A\bullet$

$R\bullet + A\bullet \longrightarrow RA$

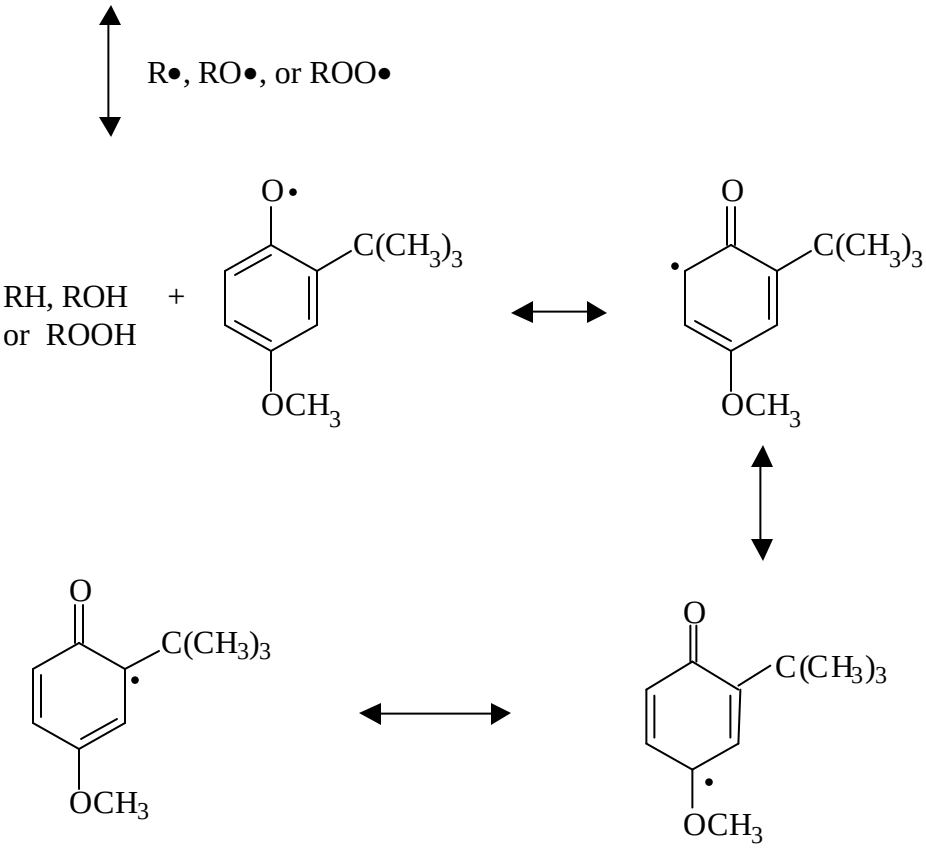
$RO\bullet + A\bullet \longrightarrow ROA$

$ROO\bullet + A\bullet \longrightarrow ROOA$

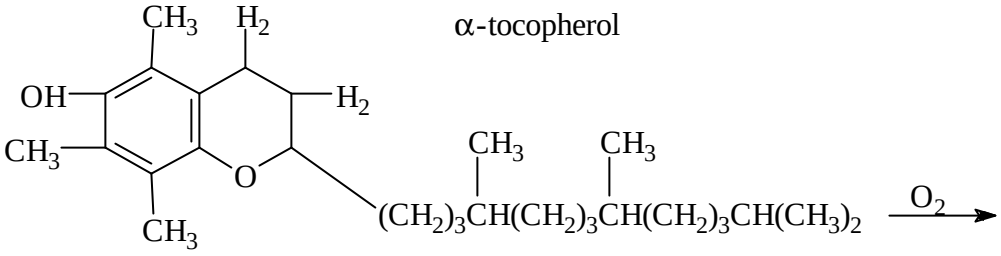
Antioxidant + O_2 $\longrightarrow$ Oxidized Antioxidant



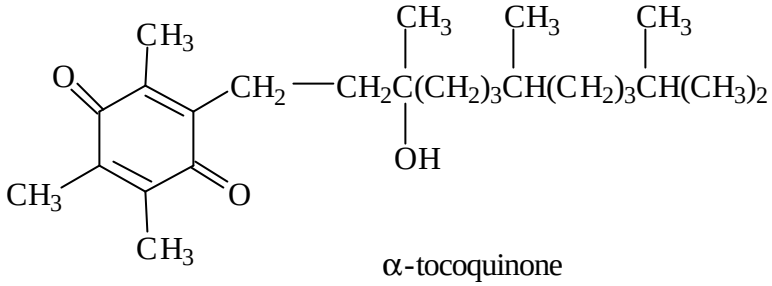
Butylated
Hydroxyanisole



Stable Resonance Forms of BHA



α-tocopherol



α-tocoquinone

Mechanisms of Metals in Accelerating Lipid Oxidation

Acceleration of hydroperoxide decomposition to form peroxy radical and alkoxy radical.

$$Fe^{3+} + ROOH \longrightarrow Fe^{2+} + ROO\bullet + H^{+}$$
$$Fe^{2+} + ROOH \longrightarrow Fe^{3+} + RO\bullet + OH^{-}$$

Formations of alkyl free radical by direct reaction with fats and oils.

$$Fe^{3+} + RH \longrightarrow Fe^{2+} + R\bullet + H^{+}$$

Activation of molecular oxygen for singlet oxygen formation.

$$Fe^{2+} + O_2 \longrightarrow Fe^{3+} + O^{-}_2 \longrightarrow {}^1O_2$$

Kinds of Antioxidants

Natural antioxidants:

1. Tocopherols (delta>gamma>beta>alpha)
2. Nordihydroguaretic Acid (NDGA)
3. Sesamol
4. Gossypol

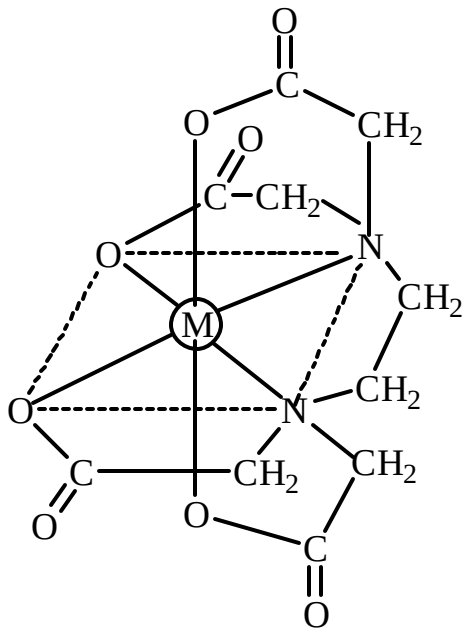
Synthetic antioxidants:

1. Butylated Hydroxy Anisole (BHA)
2. Butylated Hydroxy Toluene (BHT)
3. Propyl Gallate (PG)
4. Tertiary Butyl Hydroquinone (TBHQ)

Kinds of Metal Chelators

Metal chelators deactivate trace metals that are free or salts of fatty acids by the formation of complex ions or coordination compounds.

1. Phosphoric acid
2. Citric acid
3. Ascorbic acid
4. Ethylene-Diamine-Tetra-Acetate.(EDTA)



Metal Complex Ions

Synergism in Lipid Oxidation

Synergism occurs when mixtures of antioxidants produce a more pronounced activity than the sum of the activities of the individual antioxidants when used separately.

To have maximum efficiency, primary antioxidants are often used in combination with (1) other phenolic antioxidants, or with (2) various metal chelating agents.

Factors Affecting the Efficiency of Antioxidants

Activation energy of antioxidants.

Oxidation – Reduction potential.

Stability to pH and processing.

Solubility.

Choices of Antioxidants

Different antioxidants show substantially different antioxidant effectiveness in different fats and oils and food systems due to different molecular structures.

We should consider the following:

Safety
Antioxidant effectiveness
Off-odor
Off-color
Convenience of antioxidant incorporation to foods
Carry-through effect
Stability to pH and food processing
Availability
Cost
Non-adsorbable, if possible.

Antioxidants for Different Food Systems

A small surface-to-volume ratio – PG and TBHQ
A large surface-to-volume ratio – BHA and BHT

Application of Antioxidants to Foods

Direct addition of antioxidants to oil or melted fat.
Addition of antioxidants to the food after they are diluted in diluent.
Spraying antioxidant solution on the food or dipping food into antioxidant solution.

Antioxidant Safety

Food Additive Act, Meat Inspection Act, and Poultry Inspection Act.
Total concentration of authorized antioxidants added singly or in combination, must not exceed 200 parts per million by weight on the basis of fat content of the food.

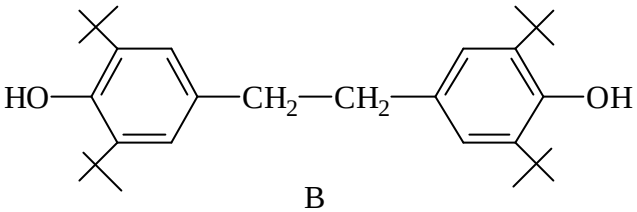
Possible Future Antioxidants

Polymeric antioxidant.
Antioxidant attached to the packaging materials.
Development of new, non-absorbable polymeric antioxidants for use in foods.

Possible Long-Term Safety of Monomeric Antioxidants

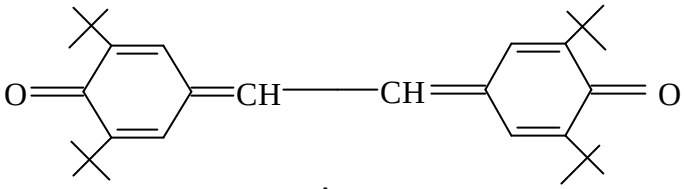
Pathological effect.
Carcinogenic potential
Interactions with enzymes
Effects of reproduction
The exact nature of the metabolism rate in man.

Isolation and Identification of Oxidation Product of 2,6-Di-(Tert-Butyl)-4-Methylphenol



B

3,3',5,5'-Tetra-Bis-(Tert-Butyl)-4,4'-Dihydoxyl-1,2-Diphenylethane



A

3,3',5,5'-Tetra-Bis-(Tert-Butyl)-Stillbenequinone

Ideal Antioxidants

No harmful physiological effects

Not contribute an objectionable flavor, odor, or color to the fat

Effective in low concentration

Fat-soluble

Carry-through effect → No destruction during processing

Readily-available

Economical

Not absorbable by the body

Biochemical Control of Lipid Oxidation in Mayonnaise

Composition of mayonnaise

INGREDIENT	COMPOSITION (%)
Soybean oil	77.0
Whole egg	7.0
Water	7.0
Vinegar	3.0
Egg yolk	2.0
Glucose	1.0
Fructose	1.0
Salt	0.9
Natural Flavor	0.1
	100%

From Weiss, 1980

Glucose oxidase/catalase reaction mechanism.

Glucose oxidase/catalase reaction:

$$2\ \text{Glucose} + 2O_2 + 2H_2O \xrightarrow{\text{Glucose Oxidase}} 2\ \text{Gluconic acid} + 2H_2O_2$$

$$2H_2O_2 \xrightarrow{\text{Catalase}} 2H_2O + O_2$$

The net chemical reaction is:

$$2\ \text{Glucose} + O2 \xrightarrow[\text{Catalase}]{\text{Glucose Oxidase}} 2\ \text{Gluconic acid}$$