

**EASTMAN**

Eastman **TENOX™**  
antioxidants

**For cosmetics and  
personal care products**



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## Introduction

The fragrance or odor of a cosmetics or personal care product greatly affects consumer acceptance. Use of an appropriate antioxidant enhances the potential to supply consumers with fresh, stable products that are free from the ravages of oxidation.

Autoxidation (oxidation in air) can destroy the fragrance and/or cause an unpleasant odor and appearance in the product. Virtually any hydrocarbon can exhibit autoxidation, but the presence of unsaturation, such as in triglycerides, greatly increases the possibility of degradation in cosmetics products. Despite proper packaging and care during processing, oxidation can still occur in products containing oils, fats, and other natural ingredients.

Eastman has been producing antioxidants for more than 50 years and offers a dynamic line of synthetic antioxidants under the trademark Eastman Tenox™.

- Eastman Tenox™ TBHQ (tertiary butylhydroquinone)
- Eastman Tenox™ BHA (butylated hydroxyanisole)
- Eastman Tenox™ BHT (butylated hydroxytoluene)

Synergistic blends of these antioxidants with various oil vehicles are also available as Eastman Tenox™ antioxidant formulations. Tenox antioxidants are both kosher (manufactured under rabbinical supervision) and food grade.

For cosmetics and personal care products, the optimum level of antioxidant ranges from 0.02% to 0.1%. Levels of antioxidants listed in this publication's efficacy graphs are possible starting points. Careful evaluation is necessary to optimize the level of antioxidants for maximum effectiveness in your application. The Cosmetic Ingredient Review (CIR) Expert Panel has reviewed the safety of these antioxidants (see page 9). Prospective users of these antioxidants in cosmetics and personal care products should follow the guidelines or regulations that apply in their respective countries for use in the specific application.

## Function of antioxidants

Autoxidation is a process of lipid peroxidation during which lipid molecules, primarily unsaturated fatty acids, undergo a three-stage chain reaction.

1. Initiation — An oxygen free radical attacks a lipid molecule and forms a lipid radical. Metal ions, enzymes, heat, UV light, pigments and a high degree of unsaturation (double bonds) accelerate the formation of radicals.
2. Propagation — The lipid radicals react readily with oxygen to form peroxides. The peroxides react with other fatty acids to form hydroperoxides and new fatty acid radicals.
3. Termination — Peroxides combine to form stable products. Hydroperoxides decompose into aldehydes, ketones, alcohols and acids that produce offensive rancid odors and can have a negative effect on the overall appearance and feel of the product.

Antioxidants break the autoxidation chain reaction by donating a hydrogen atom to the lipid radical to form a stable product and an antioxidant free radical. The antioxidant free radical is adequately stable, so the autoxidation chain reaction is stopped. Refer to reaction below.

In natural oils, the rate of oxidation is primarily determined by the degree of unsaturation (or the number of double bonds in the fatty acids). The iodine value of a fat or oil is a measure of the unsaturation. Table 1 gives typical iodine values for various oils used in cosmetics products. Other unsaturated materials used in cosmetics applications can also benefit from the addition of an antioxidant. These include essential oils; fragrance oils; emulsifiers, such as unsaturated fatty esters and alcohols (including glyceryl esters, and ethoxylated esters and alcohols); and fat-soluble vitamins.

### Antioxidant Stops Autoxidation Chain Reaction

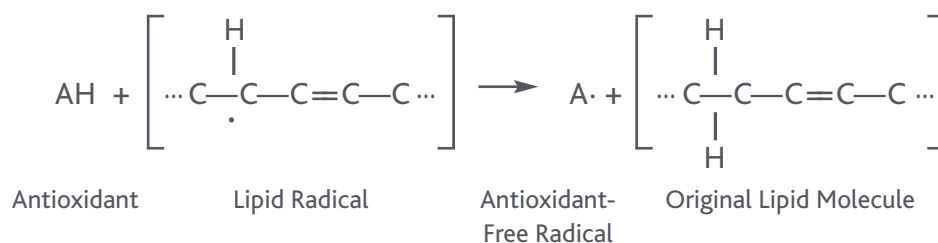
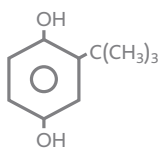
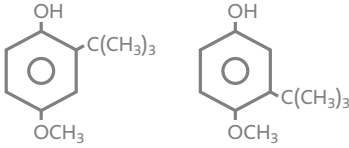
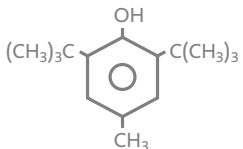


Table 1  
**Typical Iodine Values of Natural Cosmetic Oils**

Coconut	7–12	Cottonseed	97–112
Palm	48–56	Canola	100–120
Macadamia	70–81	Sesame	103–116
Joboba	79–89	Soybean	120–141
Castor	~85	Sunflower	125–140
Avocado	80–95	Wheat Germ	~130
High-Oleic Sunflower	83–97	Safflower	140–150
Almond	93–107		

An oxidative stability study conducted by Eastman showed that the higher the iodine value of the fat or oil, the more effective TBHQ is compared with BHA, BHT and propyl gallate. Therefore, TBHQ is the antioxidant of choice for most vegetable oils. The oxidative stability comparisons for many of the oils listed to the left are given on pages 4–8.

Table 2  
**Physical Properties**

	<b>Eastman Tenox™ TBHQ Antioxidant Tertiary Butylhydroquinone</b>   tertiary butylhydroquinone	<b>Eastman Tenox™ BHA Antioxidant Butylated Hydroxyanisole</b>   3-tert-butyl-4-hydroxyanisole      2-tert-butyl-4-hydroxyanisole	<b>Eastman Tenox™ BHT Antioxidant Butylated Hydroxytoluene</b>   3,5-di-tert-butyl-4-hydroxytoluene
INCI Name	TBHQ	BHA	BHT
Molecular Weight	166.22	180.25	220
Physical Appearance	White to light tan crystals	White to slightly yellow waxy flakes	White granular crystals
Boiling Point, 760 mm, °C	300	264–270	265
Melting Range, °C	126.5–128.5	48–63	69.7
Odor	Very slight	Slight	Very slight
<b>Solvent</b>	<b>Solubility, % (Approx.)</b>		
Water, 25°C	<1	<0.1	Insoluble
Glycerin, 25°C	23	1	Insoluble
Ethyl Alcohol, 25°C	60	50+	25
Ethyl Acetate, 25°C	60	ND <sup>a</sup>	ND <sup>a</sup>
Propylene Glycol, 25°C	30	50+	2
Cottonseed Oil, 25°C	6	40	30
Corn Oil, 25°C	6	32	27
Canola Oil, 25°C	6	30	26
Sunflower Oil, 25°C	6	30	32
Safflower Oil, 25°C	5	30	34
Soybean Oil, 25°C	6	30	26
Mineral Oil, 25°C	0.2	<1	5
Palm Oil, 50°C	10	65	55
Lard, 50°C	5	50	40
Glyceryl Monooleate, 50°C	22	75	45
Paraffin, 60°C	ND <sup>a</sup>	60+	60+

<sup>a</sup>ND = Not determined

Table 3  
Eastman Tenox™ Antioxidant Formulations

Antioxidant Formulation	Composition (Wt %) <sup>a</sup> Active Ingredients				Typical Properties <sup>b</sup>				
	BHA	BHT	TBHQ	Citric Acid	Color	Viscosity 25°C, cP <sup>c</sup>	Specific Gravity 20°/20°C	Solubility in Fats and Oils	Effectiveness in Vegetable Oils
Tenox™ 4	20	20	—	—	Light straw	61	0.942	Excellent	Good
Tenox™ 4B	20	—	—	—	Light straw	69	0.951	Excellent	Good
Tenox™ 8	—	20	—	—	Light straw to light amber	49	0.925	Excellent	Good
Tenox™ 20	—	—	20	10	Light amber to golden brown	235	1.087	Good	Excellent
Tenox™ 20A	—	—	20	3	Golden brown	369	0.998	Excellent	Excellent
Tenox™ 21	—	—	20	1	Golden brown	284	0.991	Excellent	Excellent
Tenox™ 25	—	10	10	3	Golden brown	190	0.938	Excellent	Excellent
Tenox™ R	20	—	—	20	Light straw	229	1.117	Good	Good

<sup>a</sup>Carriers used in solution formulations include vegetable oil, propylene glycol and/or mono- and diglycerides.

<sup>b</sup>Properties shown are typical of average lots. Eastman makes no representation that the material in any particular shipment will conform exactly to the values given. Availability of developmental products is limited and subject to substantial minimum order quantities.

<sup>c</sup>Brookfield Model RVT — spindle 2, speed 20 rpm

## Formulation and processing tips

- Protection of Fats and Oils — Select the antioxidant or antioxidant mixture that is most effective in the particular fat or oil being stabilized.
- Protection of Emulsifiers — Many cosmetic emulsifiers, especially those derived from unsaturated fats or oils, benefit from the addition of an antioxidant. Select the antioxidant that is most effective in the emulsifier being stabilized.
- Complete Dispersion — For maximum efficiency, choose an antioxidant system that can be easily dissolved or thoroughly dispersed in the fat or oil portion of the cosmetics product. To maximize ease of dispersion, consider using an Eastman Tenox™ antioxidant formulation.
- Discoloration Tendencies — Some discoloration may occur with TBHQ at an alkaline pH or in the presence of proteins and sodium salts. Specifically, TBHQ forms colored complexes with amines in fatty acid/amine emulsifier systems at alkaline pH. Therefore, when neutralizing acids with amines, neutralize to a pH of 7 or less.
- Antioxidant Stability — TBHQ, BHA and BHT are stable at typical processing temperatures for cosmetics products (<90°C). However, be aware that antioxidants will volatilize at higher temperatures.

## Methods of incorporation

### Direct method

The individual fat, oil, wax or emulsifier can be stabilized by heating to 60°C (140°F) minimum and agitating sufficiently to dissolve the antioxidant. The agitation should be continued for 20 minutes, and entrapment of air should be avoided.

### Antioxidant concentrate method

Concentrated solutions of antioxidants can be prepared by dissolving Eastman Tenox™ antioxidant in a small quantity of fat, oil or emulsifier heated to 93°–121°C (200°–250°F). The hot concentrate can be introduced into the main body of the fat. Agitation is required for thorough distribution.

## Antioxidant effectiveness

The effect of antioxidants on the oxidative stability of fats, oils or other natural products can be most realistically measured by subjecting samples to actual storage conditions and examining them periodically. This method of testing usually requires too much time to be practical. For this reason, accelerated tests conducted under controlled conditions are normally used to evaluate antioxidant performance.

If comparing data obtained by different methods, it is important to consider how the methods differ and what is actually being measured. For these reasons, direct data comparisons are not feasible if data is obtained by different methods or at different temperatures.

### Active oxygen method (AOM)

The Active Oxygen Method has been widely used for years on fats and oils that are liquid at the test temperature. It is not applicable to solid material. Air is bubbled through the heated test sample to speed oxidation and shorten testing time. Periodic analyses show when the peroxide value has reached the induction point. For vegetable fats and oils, the accepted industry standard is 70 meq peroxide/kg of fat or oil.

The AOM is labor-intensive and can take substantial time. Although some processors continue to use the AOM, many processors are replacing the AOM with the OSI method, which is more automated and precise.

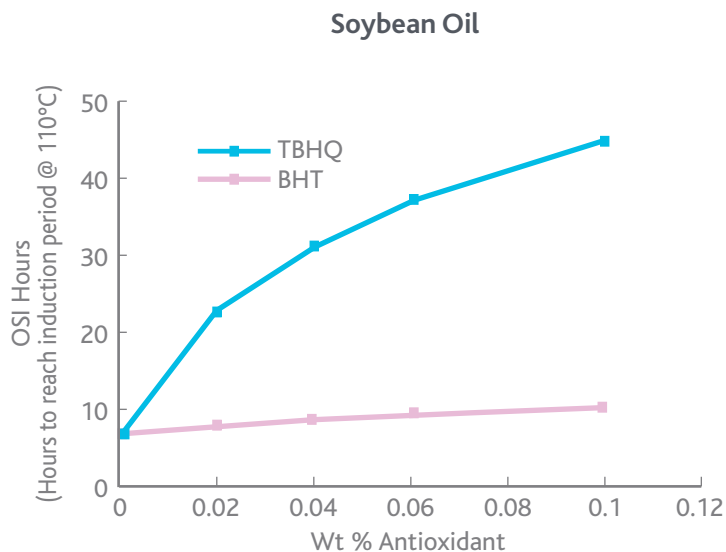
## Oil stability index (OSI)

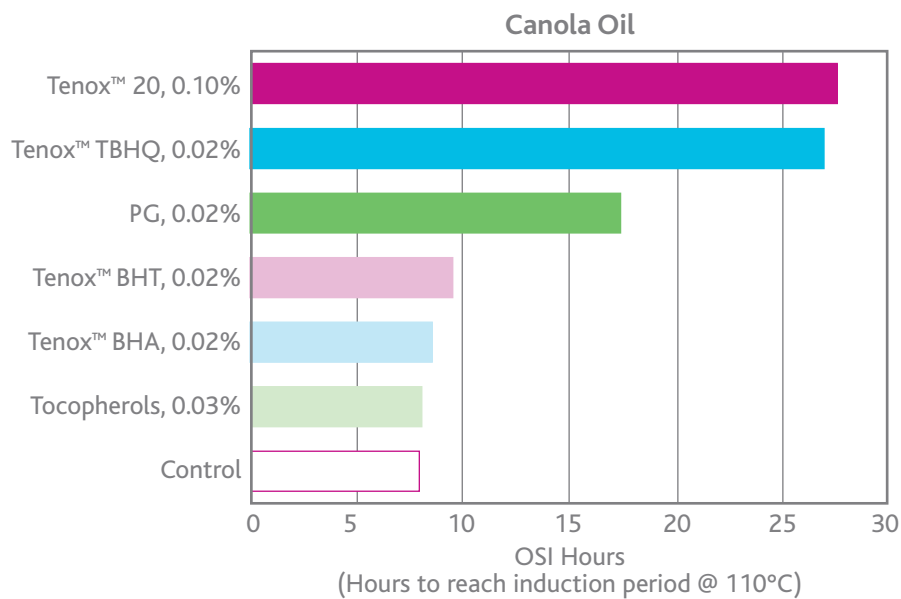
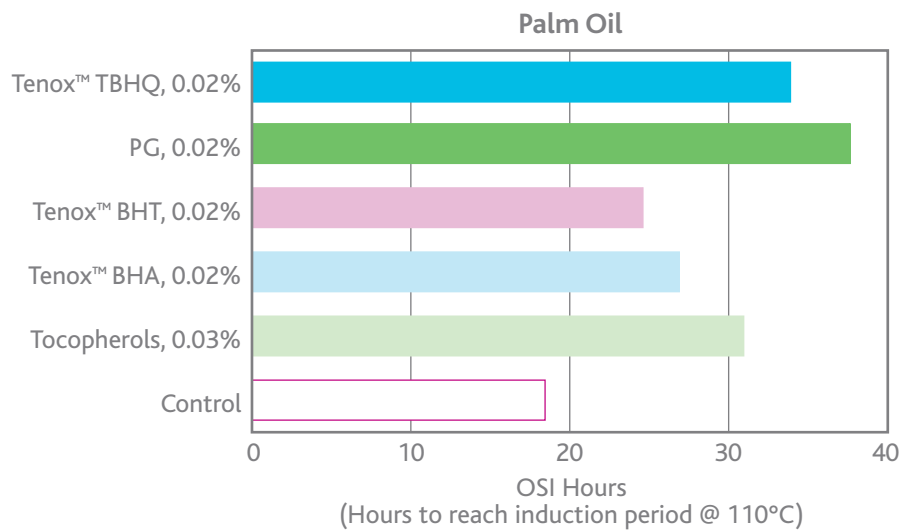
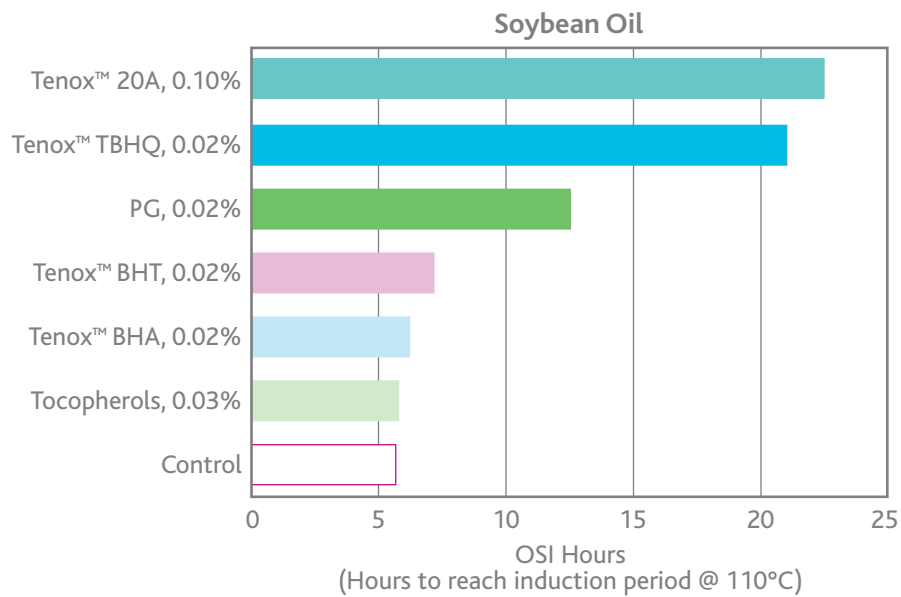
The Oil Stability Index is an automated, accelerated method of measuring stability of fats and oils. Fat or oil samples held at a constant temperature between 110° and 130°C are exposed to a stream of purified air. Over time the oil or fat begins to oxidize, giving rise to volatile organic acids. The volatile decomposition products, trapped in a measuring vessel filled with distilled water, are continuously monitored with a conductivity cell. The "induction period" is the period at which rapid acceleration of oxidation occurs and is recorded as number of hours.

### Oven storage tests

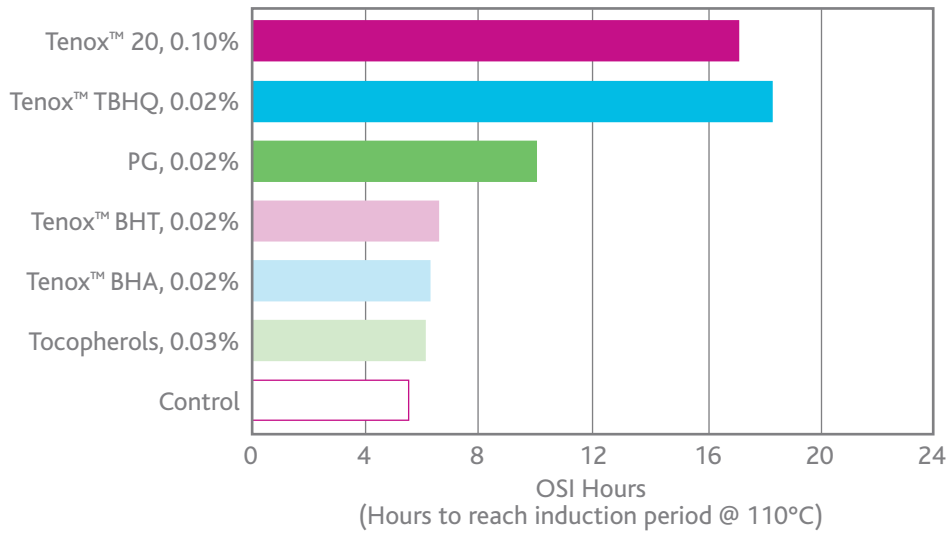
Higher temperatures will accelerate oxidation. Oven storage tests, such as the Schaal Oven Stability test, are simply shelf storage tests conducted at elevated temperatures to speed up the procedure. Periodic odor evaluations are commonly used, but chemical analyses (for example, peroxide value) may be used to determine rancidity development in the samples.

The preceding test methods were used to measure the relative effect of individual antioxidants on the oxidative stabilities of various fats and oils used in the cosmetics industry. The following data compare the effectiveness of Eastman Tenox™ antioxidants with propyl gallate (PG) and tocopherols under the conditions specified.

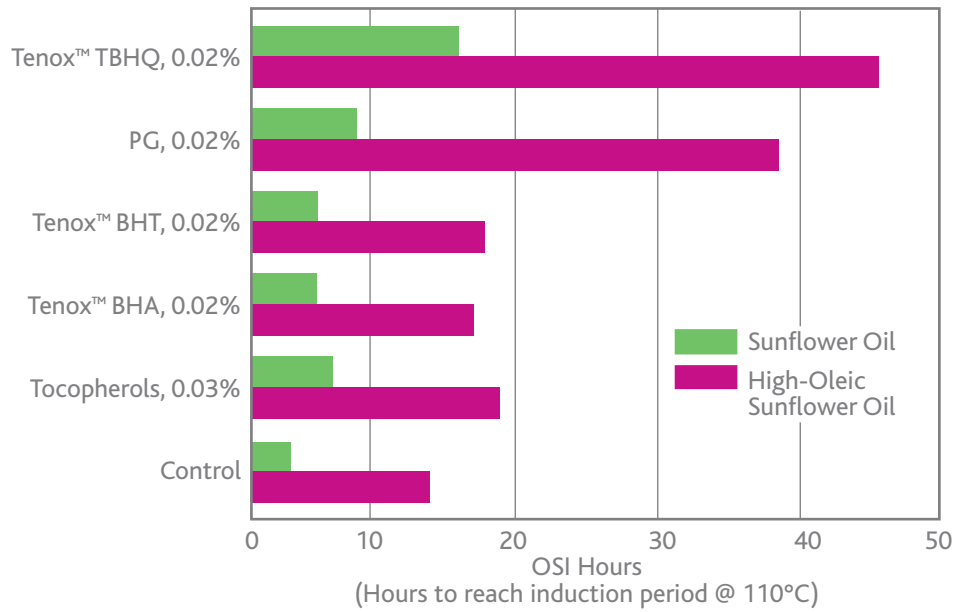




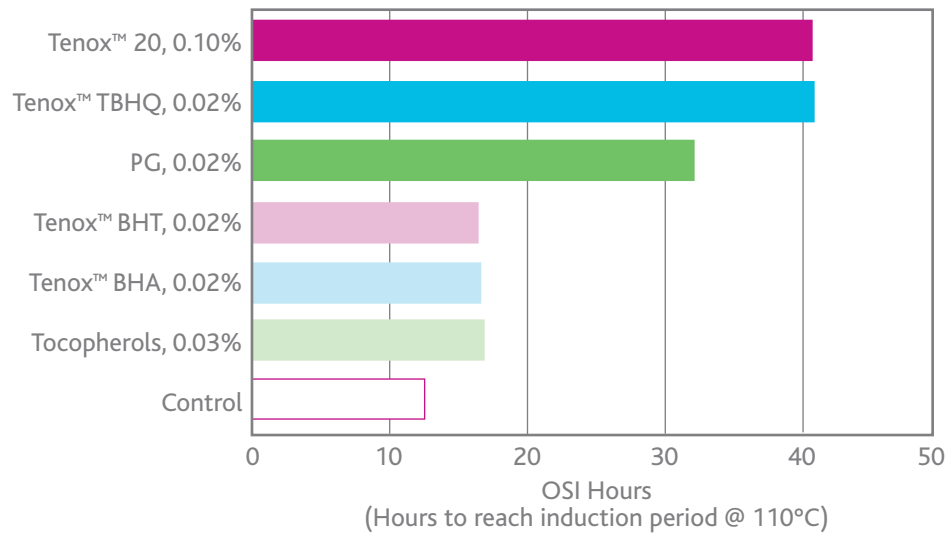
### Cottonseed Oil

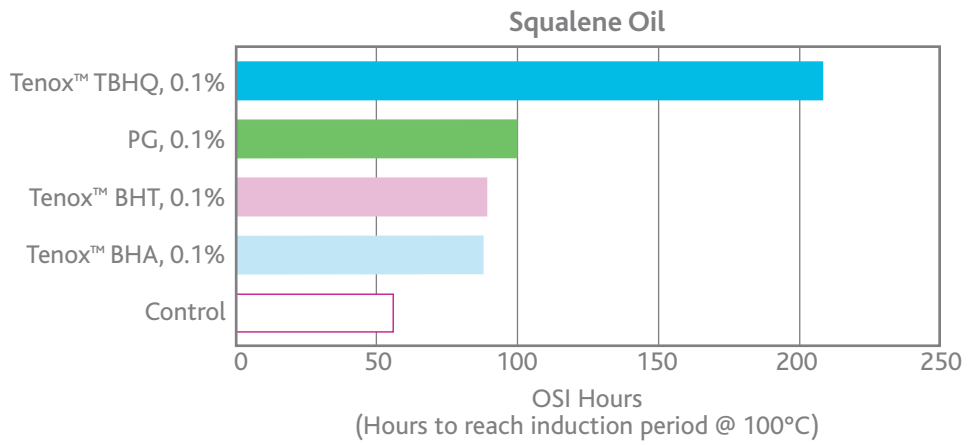
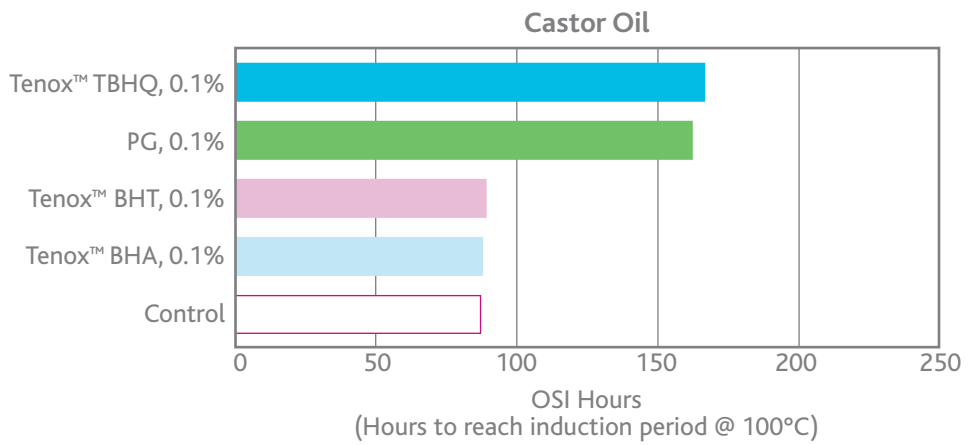
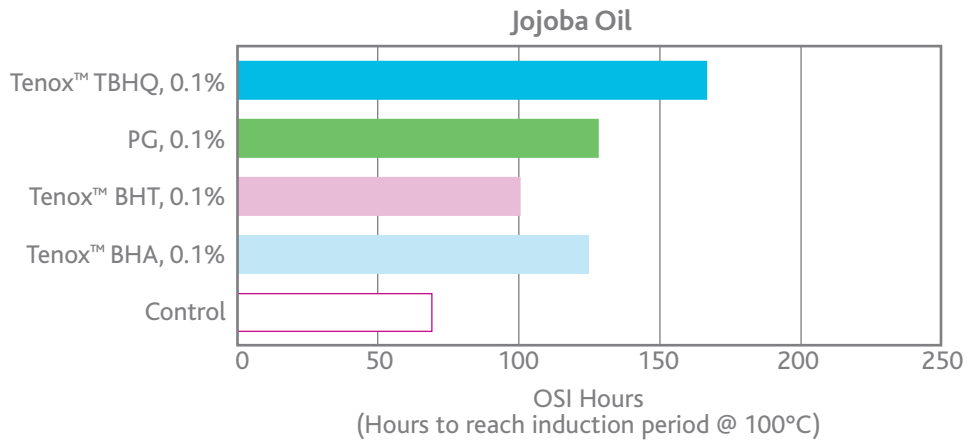


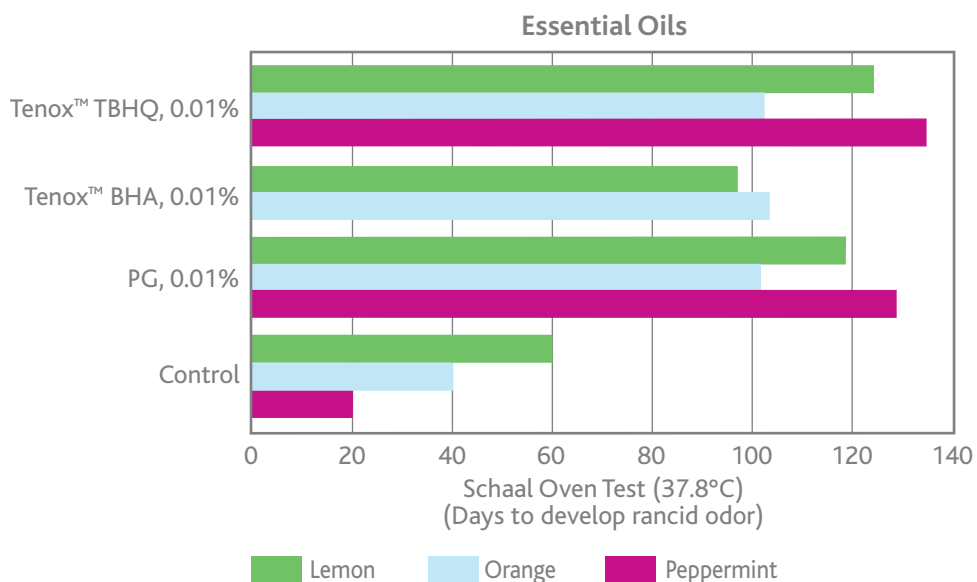
### Sunflower Oil and High-Oleic Sunflower Oil



### Safflower Oil







## Antimicrobial activity

In addition to their antioxidant effects, phenolic antioxidants have shown significant antimicrobial activity. While this activity has primarily been studied in foods, the benefits also apply to cosmetics products.<sup>1</sup>

Studies show that TBHQ and BHA are the most effective antimicrobials of the phenolic antioxidants. TBHQ at levels ranging from 100–500 ppm was found to inhibit or delay the growth of *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli* and several other bacteria.<sup>2</sup> BHA was found to inhibit *Staphylococcus aureus* at concentrations of 150 ppm, *E. Coli* at concentrations of 400 ppm and *salmonella typhimurium* at concentrations of 400 ppm.<sup>3</sup> BHT has shown little effectiveness except in combination with TBHQ. A 1:1 mixture of BHT/TBHQ inhibited 14 of 24 bacterial strains tested by Gailani and Fung.<sup>4</sup>

When used in combination with antimicrobial preservatives, TBHQ and BHA have shown an additive or synergistic effect. A study by Zeelie and McCarthy showed that typical antimicrobials, e.g., imidazolidinyl urea and DMDM hydantoin, are effective at lower levels when used in combination with TBHQ.<sup>5</sup> Several other studies have found a synergistic effect of both TBHQ and BHA with potassium sorbate against *Staphylococcus* species.<sup>6,7,8</sup>

Eastman has not conducted its own tests for antimicrobial activity for these antioxidants, and manufacturers must make their own determination of their safety, lawfulness and suitability as a cosmetic ingredient.

<sup>1</sup>Jon J. Kabara and Donald S. Orth, *Preservative-Free and Self-Preserving Cosmetics and Drugs, Principles and Practice*, Marcel Dekker, Inc., New York, 1997, pp. 160–164.

<sup>2</sup>P.M. Davidson and A. L. Branen, eds., *Antimicrobials in Foods*, 2nd ed. Marcel Dekker, Inc., New York, 1993, pp. 263–306.

<sup>3</sup>H. C. Chang and A.L. Branen, *J. Food Sci.* 40:349 (1975).

<sup>4</sup>M. B. Gailani and D. Y. C. Fung, *J. Food Prot.* 47:428 (1984).

<sup>5</sup>J. J. Zeelie and T. J. McCarthy, *Cosmetics & Toiletries*, Vol. 98, Dec. 1983, p. 51.

<sup>6</sup>C. Lahellec, D. Y. C. Fung and F. E. Cunningham, *J. Food Prot.* 44:531 (1981).

<sup>7</sup>P.M. Davidson, C. J. Brekke and A. L. Branen, *J. Food Sci.* 46:314 (1981).

<sup>8</sup>M. C. Robach and C. L. Stateler, *J. Food Prot.* 43:208 (1980).

## Regulations

### United States

Cosmetics and to a large extent most personal care products are regulated in the United States by the Food and Drug Administration. Unlike foods and drugs, however, the FDA has issued few regulations specifying, or approving, cosmetic ingredients. The industry instead is self-regulated through the Cosmetic Ingredient Review, an expert panel established by the Personal Care Products Council (PCPC — formerly called the Cosmetic, Toiletry, and Fragrance Association) to evaluate the safety of cosmetic ingredients and limit their concentrations in cosmetics when necessary. Commonly used cosmetic ingredients are cataloged in the *International Cosmetic Ingredient Dictionary and Handbook*, published by the PCPC.

Table 4  
Antioxidant Safety References

Antioxidant	CIR Cosmetic Ingredient Safety Assessment	Reference
TBHQ	Safe at concentrations not to exceed 0.1%	JACT 10(1) 1991
BHA	Safe in the present practices of use (Suggested level: $\leq 1\%$ )	JACT 3(5) 1984
BHT	Safe as used in cosmetic formulations (0.01 to 0.1%)	IJT 21 (Suppl. 2) 2002

JACT: *Journal of the American College of Toxicology*

IJT: *International Journal of Toxicology*

### California

The California Safe Drinking Water Act (Proposition 65) and the California Safe Cosmetics Act regulate the use of cosmetic ingredients. Proposition 65 lists BHA as a substance known to the state to cause cancer. Products containing BHA may be required under California law to carry a warning unless the product exposes the consumer to a level not exceeding the Proposition 65 No Significant Risk Level. It is the cosmetic product manufacturer's responsibility to determine the suitability, safety and lawfulness of a product for its intended use.

### Japan

As of April 1, 2001, premarket approval and licensing are no longer required for cosmetics products in Japan. Cosmetic product manufacturers need to provide notification of the product's trade name and comply with ingredient labeling requirements. The industry also requires the use of the International Nomenclature Cosmetic Ingredient (INCI) names as translated into Japanese by the Japan Cosmetic Industry Association (JCIA). The INCI names TBHQ, BHA and BHT have been translated and are available in Japanese.

### Europe

Antioxidants may be used in cosmetics in European Union member nations under the sixth amendment to the Directive on Cosmetics (93/35/EEC, 14 June 1993). The Directive does not directly address antioxidants, and they are not included in the Directive's positive or negative lists. Their use may be subject to a requirement for the cosmetic producer to complete a Product Information Package.

For additional information on cosmetic ingredient regulations in the United States or other countries, contact Eastman Technical Services at 1-800-EASTMAN.

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Material Safety Data Sheets providing safety precautions, that should be observed when handling and storing Eastman products, are available online or by request. You should obtain and review the available material safety information before handling any of these products. If any materials mentioned are not Eastman products, appropriate industrial hygiene and other safety precautions recommended by their manufacturers should be observed.

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