EASTMAN

Eastman TENOX™
antioxidants

for cosmetics and personal care

Contents

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, which 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 the following reaction.

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

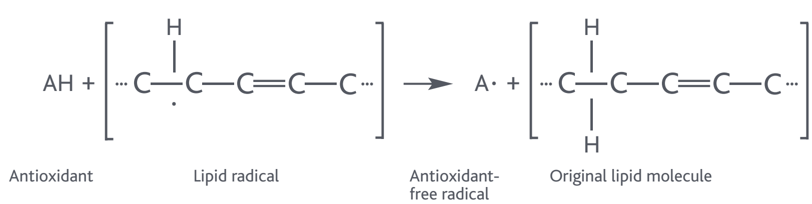
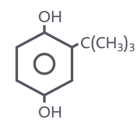


Table 1 **Typical iodine values of natural cosmetic oils**

Product	Iodine value	Product	Iodine value
Coconut	7–12	Cottonseed	97–112
Palm	48–56	Canola	100–120
Macadamia	70–81	Sesame	103–116
Jojoba	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		

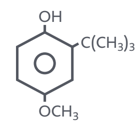
An oxidative stability study conducted by Eastman showed that the higher the iodine value of the fat or oil, the more effective TBHQ is compared with BHA, BHT, and propyl gallate. Therefore, TBHQ is the antioxidant of choice for most vegetable oils. The oxidative stability comparisons for many of the oils listed to the left are given on pages 6–10.

Eastman Tenox™ TBHQ antioxidant

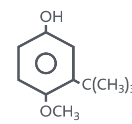


tertiary butylhydroquinone

Eastman Tenox™ BHA antioxidant

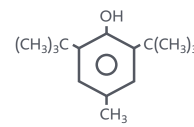


3-tertiarybutyl-4-hydroxyanisole



2-tertiarybutyl-4-hydroxyanisole

Eastman Tenox™ BHT antioxidant



3,5-di-tert-butyl-4-hydroxytoluene

Table 2 **Physical properties**

	Eastman Tenox™ TBHQ antioxidant, tertiary butylhydroquinone	Eastman Tenox™ BHA antioxidant, butylated hydroxyanisole	Eastman Tenox™ BHT antioxidant, butylated 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
Solvent		**Solubility, % (Approx.)**	
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[a]	ND[a]
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[a]	60+	60+
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[a]	60+	60+

[a]*ND = Not determined*

Table 3 **Eastman Tenox antioxidant formulations**

Antioxidant formulation	Composition (Wt%)[a] active ingredients				Typical properties[b]				
	BHA	BHT	TBHQ	Citric acid	Color	Viscosity 25°C, cP[c]	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

[a]*Carriers used in solution formulations include vegetable oil, propylene glycol, and/or mono- and diglycerides.*

[b]*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.*

[c]*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)

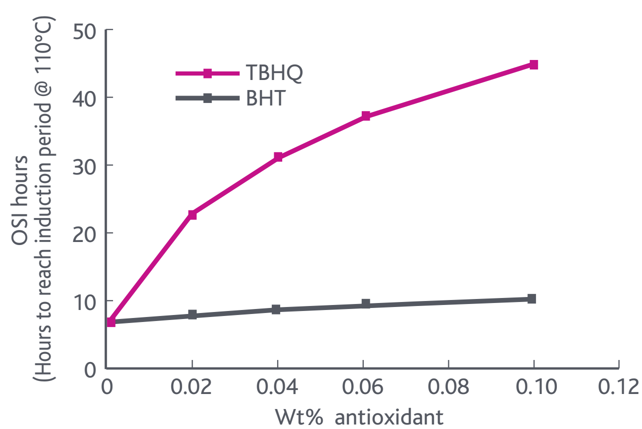
The Oil Stability Index is an automated, accelerated method of measuring stability of fats and oils. Fat or oil samples held at a constant temperature between 110° and 130°C are exposed to a stream of purified air. Over time the oil or fat begins to oxidize, giving rise to volatile organic acids. The 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.

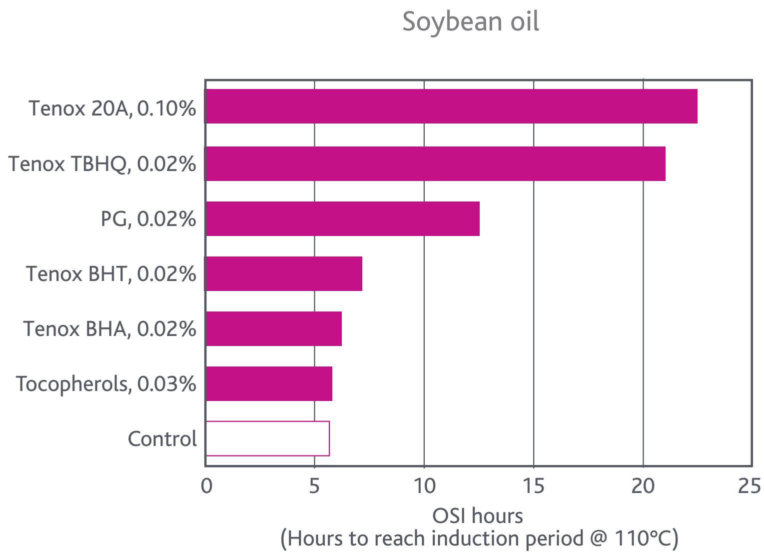
Oven storage tests

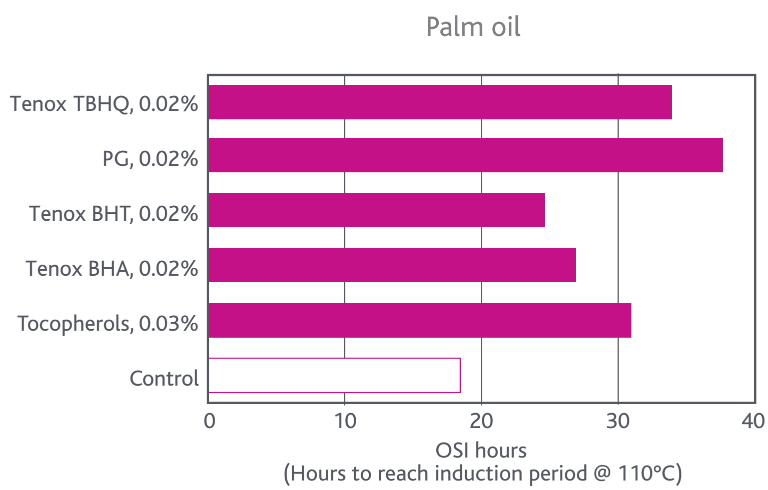
Higher temperatures will accelerate oxidation. Oven storage tests, such as the Schaal Oven Stability test, are simply shelf storage tests conducted at elevated temperatures to speed up the procedure. Periodic odor evaluations are commonly used, but chemical analyses (for example, peroxide value) may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

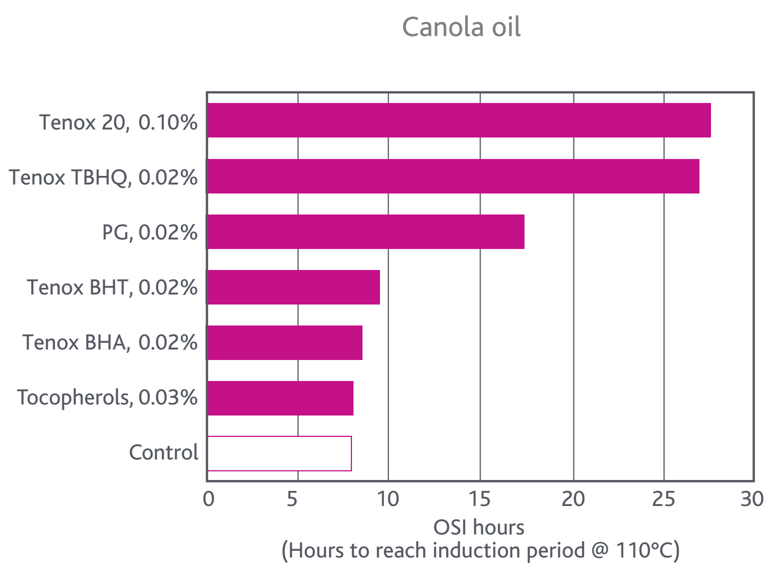
The preceding test methods were used to measure the relative effect of individual antioxidants on the oxidative stabilities of various fats and oils used in the cosmetics industry. The following data compare the effectiveness of Eastman Tenox™ antioxidants with propyl gallate (PG) and tocopherols under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

Soybean oil

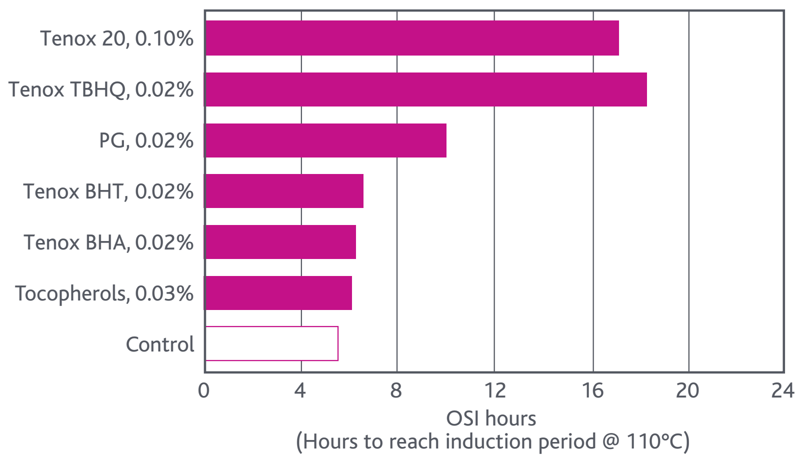



Soybean oil
Tenox 20A, 0.10%
Tenox TBHQ, 0.02%
PG, 0.02%
Tenox BHT, 0.02%
Tenox BHA, 0.02%
Tocopherols, 0.03%
Control
0
5
10
15
20
25
OSI hours
(Hours to reach induction period @ 110°C)

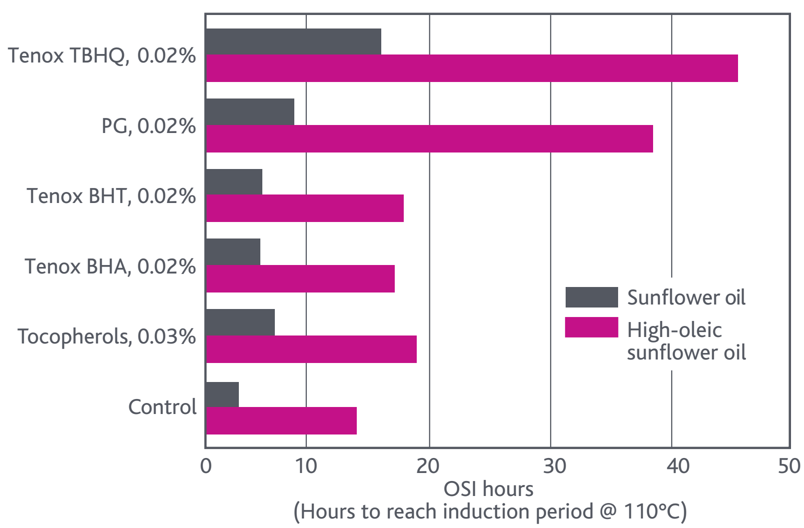

Palm oil
Tenox TBHQ, 0.02%
PG, 0.02%
Tenox BHT, 0.02%
Tenox BHA, 0.02%
Tocopherols, 0.03%
Control
0
10
20
30
40
OSI hours
(Hours to reach induction period @ 110°C)


Canola oil
Tenox 20, 0.10%
Tenox TBHQ, 0.02%
PG, 0.02%
Tenox BHT, 0.02%
Tenox BHA, 0.02%
Tocopherols, 0.03%
Control
0
5
10
15
20
25
30
OSI hours
(Hours to reach induction period @ 110°C)

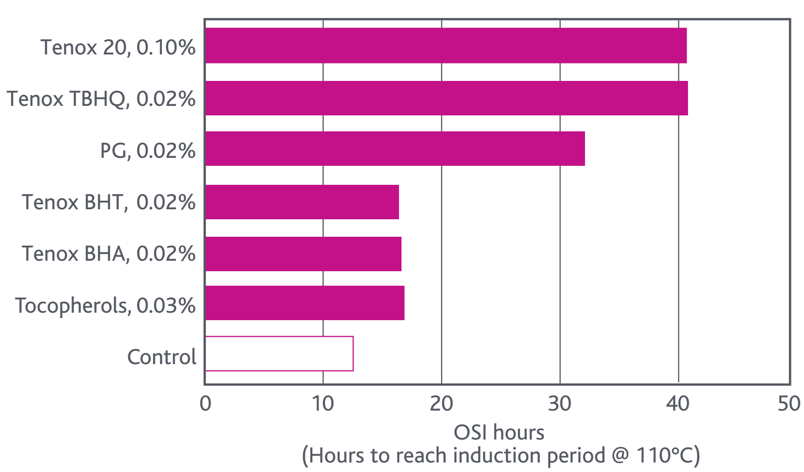
Cottonseed oil



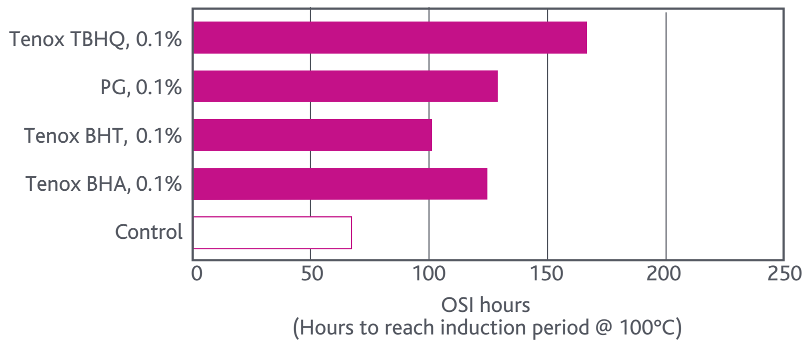
Sunflower oil and high-oleic sunflower oil



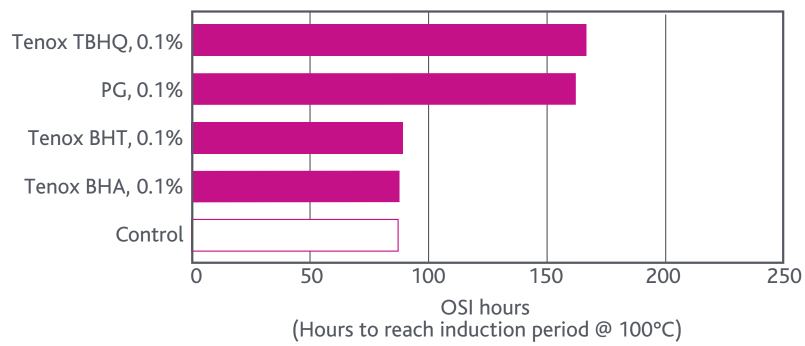
Safflower oil



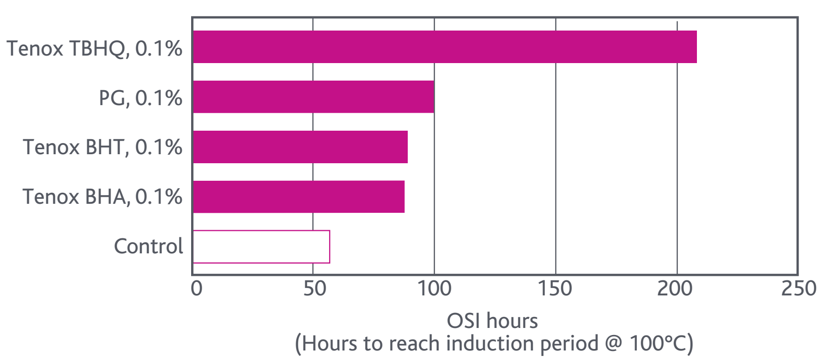
Jojoba oil

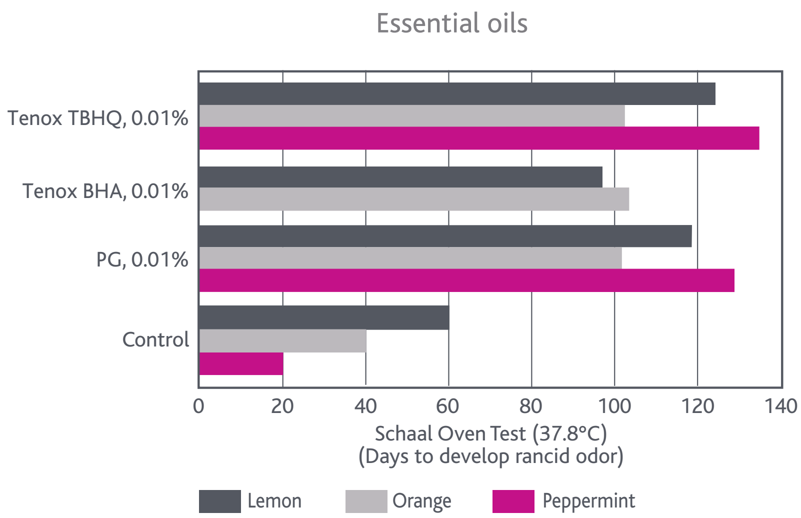


Castor oil



Squalene 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.[1]

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.[2] BHA was found to inhibit *Staphylococcus aureus* at concentrations of 150 ppm, *E. coli* at concentrations of 400 ppm, and *Salmonella typimurium* at concentrations of 400 ppm.[3] 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.[4]

[1]*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.*

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

[3]*H. C. Chang and A. L. Branen, J. Food Sci. 40:349 (1975).*

[4]*M. B. Gailani and D. Y. C. Fung, J. Food Prot. 47:428 (1984).*

[5]*J. J. Zeelie and T. J. McCarthy, Cosmetics &Toiletries, Vol. 98, Dec. 1983, p. 51.*

[6]*C. Lahellec, D. Y. C. Fung, and F. E. Cunningham, J. Food Prot. 44:531 (1981).*

[7]*P. M. Davidson, C. J. Brekke, and A. L. Branen, J. Food Sci. 46:314 (1981).*

[8]*M. C. Robach and C. L. Stateler, J. Food Prot. 43:208 (1980).*

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.[5] Several other studies have found a synergistic effect of both TBHQ and BHA with potassium sorbate against *Staphylococcus* species.[6,7,8]

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.

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: ≤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

Regulations

Customers should contact their Eastman representative at 1-800-EASTMAN and request a Product Regulatory Information Sheet for the most current regulatory information on specific Eastman products. The following provides general information related to the regulation of cosmetics and personal care ingredients.

United States

Cosmetics and most personal care products are regulated in the United States by the Food and Drug Administration (FDA). 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) 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 HandbookC*.

California

The California Safe Drinking Water and Toxic Enforcement Act (Proposition 65) and the California Safe Cosmetics Act (SB 484) may impact the use of some cosmetic ingredients. It is the cosmetics product manufacturer's responsibility to determine the suitability, safety, and lawfulness of a product for its intended use.

China

In China, new cosmetic ingredients to be used for cosmetics production must be approved by Chinese food and drug administration authorities. If an ingredient is not included on the revised version of the Inventory of Existing Cosmetic Ingredients in China (IECIC 2012), it must be registered with the authorities prior to use in cosmetics. Guidelines have been published to assist with the registration and technical review of new ingredients. This is usually accomplished by the appointment of an agent in China. Also, the Hygienic Standard for Cosmetics published by the Ministry of Health banned or restricted many substances in cosmetics (chemicals/preservatives/colorants/sunblock agents/dyes). Before applying for hygiene license or record-keeping certificate for finished cosmetics, companies must ensure that their product meets the requirements of this hygienic standard.

In addition cosmetic ingredients must be listed on the Inventory of Existing Chemical Substances Produced or Imported in China (IECSC).

Japan

Cosmetics product manufacturers must provide notification of the final cosmetics product's trade name and comply with ingredient labeling requirements. International Nomenclature Cosmetic Ingredient (INCI) names must be translated into Japanese by the Japan Cosmetic Industry Association. The INCI names for Eastman antioxidants have been translated and are available on request.

Europe

The Cosmetic Products Regulation (EU Regulation 1223/2009) requires the following for the final cosmetics product: (1) A product safety report must be submitted prior to placing a product on the market, which includes an expert scientific safety assessment. (2) Only cosmetics products for which a legal or natural person is designated within the EU as "responsible person" can be placed on the market and outlines the obligations. (3) The centralized Cosmetic Products Notification Portal will be used for notification of cosmetics products. (4) Serious undesirable effects must be reported to national authorities. (5) Rules for the use of nanomaterials in cosmetics products were introduced. (6) The Regulation sets out common criteria for cosmetic claims. (7) Annex II provides a list of substances prohibited for use in cosmetics. Annex III provides a list of substances which cosmetics products must not contain except subject to stated restrictions. Annex IV, V, and VI are lists of colorants, preservatives, and UV filters allowed in cosmetics products. (8) Animal testing must be replaced by alternative methods. The Regulation prohibits the performance of animal testing in the European Union for finished products or ingredients or combinations of ingredients. The Regulation also prohibits the placing on the European Union market of products where the final formulation has been the subject of animal testing; or products containing ingredients or combinations of ingredients which have been the subject of animal testing for the sole purpose of their usage in cosmetics products.

EASTMAN
The results of insight™

Eastman Chemical Company
Corporate Headquarters
P.O. Box 431
Kingsport, TN 37662-5280 U.S.A.

Telephone:
U.S.A. and Canada, 800-EASTMAN (800-327-8626)
Other Locations, (1) 423-229-2000
Fax: (1) 423-229-1193

Eastman Chemical Latin America
9155 South Dadeland Blvd.
Suite 1116
Miami, FL 33156 U.S.A.

Telephone: (1) 305-671-2800
Fax: (1) 305-671-2805

Eastman Chemical B.V.
Fascinatio Boulevard 602-614
2909 VA Capelle aan den IJssel
The Netherlands

Telephone: (31) 10 2402 111
Fax: (31) 10 2402 100

Eastman (Shanghai) Chemical
Commercial Company, Ltd. Jingan Branch
1206, CITIC Square
No. 1168 Nanjing Road (W)
Shanghai 200041, P.R. China

Telephone: (86) 21 6120-8700
Fax: (86) 21 5213-5255

Eastman Chemical Japan Ltd.
MetLife Aoyama Building 5F
2-11-16 Minami Aoyama
Minato-ku, Tokyo 107-0062 Japan

Telephone: (81) 3-3475-9510
Fax: (81) 3-3475-9515

Eastman Chemical Asia Pacific Pte. Ltd.
#05-04 Winsland House
3 Killiney Road
Singapore 239519

Telephone: (65) 6831-3100
Fax: (65) 6732-4930

www.eastman.com

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