Inhibiting Rancidity in Soaps & Cosmetics

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Population today has increased manifold, with a high rise of urban settlements in different parts of India. Soaps and cosmetic products, produced in one part of our nation are sent to areas located far away that have, varying environmental and climatic differences from the place of its origin. Soaps and cosmetic formulation today, significantly comprise of fats and oils derived from natural plants. Lipids extracted from vegetable sources have limited stability upon storage. Fats start detoriating from the very moment; it is extracted from the vegetable or plant source. Soaps and cosmetics that are made out of these naturally occurring lipids are susceptible to degradation in the same manner as the original oil or fat, and so have to be preserved in the same manner. The preservation of fat or oil based products, has been a challenge to people for a long time now. The fatty acid components of toilet soaps and cosmetics, is such, that they can readily undergo auto-oxidation due to atmospheric oxygen. This auto-oxidation is greatly favoured by heat, light and is strongly catalysed by heavy metals, particularly copper or iron, causing product discoloration and formation of objectionable degradation products of unpleasant odour. This oxidised condition is called "rancidity." Our sensory characters of taste and smell readily notice rancidity. Rancidity may be due to oxidation either by bacterial action & enzyme-induced hydrolysis or by atmospheric oxygen (auto-oxidation). The development of rancidity, cause colours and texture changes, reduce shelf life and impair the quality of the product.

Auto-oxidation is difficult to prevent as this chemical reaction has very low activation energy. Oxidation of oil and fats depends on the number of double bonds present and their inherent arrangement. The oxidation also depends on the pro-oxidants or substances that favour oxidation present either inherently or added accidentally and inhibitors (anti-oxidants) that is substances that inhibit oxidation and are present naturally in fats and oils. Naturally, occurring fats and oils contain characteristic antioxidants to protect the oil from detoriation during the normal life of the plant seed or fruit. Antioxidants are present in all higher plants in their wood, bark, stems, leaves, flowers, seed, fruit, even pods and pollens. Chemically these natural antioxidants are phenolic or poly phenolic compounds. Some common antioxidants found in nature include tocopherols, flavanoids, cinnamic acid derivatives, gallic acid and phosphotides. It is noteworthy that even at low concentrations, proportional to the content present, these natural antioxidants are effective to keep the oil or fat stable during its lifetime. Rancidity develops in a very characteristic fashion comprising of two stages.

- First inductions stage wherein decomposition is slow, and the rate varying. Decomposition is directly dependent on the presence of naturally occurring in-hibitors of oxidation or on the presence of pro-oxidant substances.

- The second stage where the reaction rate increases logarithmically.

Enzymes, present in the oxidisable portion of the material or in microorganisms that have gained entry may cause rancidity. Some of these enzymes attack saturated fatty acids at their β carbon atom to produce ketonic acid and methyl ketones.

$$CH_2CH_2COOH \rightarrow -\underset{\underset{O}{||}}{C}CH_2COOH \rightarrow -\underset{\underset{O}{||}}{C}CH3$$

This is referred to as "ketone rancidity" and is different from "oxidative rancidity" that is caused due to atmospheric oxygen. Where microorganisms are involved, sterilisation techniques, aseptic processing, good and proper cold storage, packaging and transportation employed can usually solve the problem largely. If it is practically difficult to follow all the above methods then antiseptic preservatives may also be used at optimum levels to over come the situation.

The decomposition of oil or fat based soaps and cosmetics' products, by oxidation may be kept in check by use of chemical additives that prevent or diminish oxidation and subsequent degradation of the product. Antioxidants are chemical additives that are effective against oxidation by atmospheric oxygen. Product protecting agents like antioxidants and chelates or sequestering agents (synergists) are usually used in a combination as stabilisers system in cosmetic products to retain the pleasant appearance (e.g., colour, odour, etc.) and to ensure stability and efficacy of incorporated active ingredients (e.g., fragrances). Modern day cosmetic products also contain UV-filters to prevent photo-labile ingredients like fragrances, colorants, etc., which are affected by photolytic deterioration.

The selection of the appropriate product protection system, depends on

- the different ingredients used in the product that have to be protected
- Type of product, viz., emulsion, gels, non-aqueous formulation, etc.
- Type of packaging, viz., opaque, transparent, glass or plastic, etc.

To fully understand and appreciate the usage of these additives, let us understand in brief, how an antioxidant functions.

Rancidity is very readily noticed by smell, but detected chemically in lipids by the presence of hydroperoxides. Hydroperoxides further degrade, producing aldehydes and esters that are characteristic of rancidity. Many theories have been postulated to explain the autooxidation of oils and fats and the role of antioxidants in its prevention. However, no mechanism is universally accepted, to explain how small amounts of foreign additives are able to control and prevent this natural phenomenon of degradation by autooxidation. In fact, if the chain life of auto-oxidation is long then even trace amount of antioxidants is sufficient to prolong the stability of oils and fats by greatly reducing the rate of atmospheric oxidation.

It is believed that antioxidant act at the very beginning or at the starting stage of oxidation, by effectively preventing the formation of peroxides that are the first detectable products of rancidity. Moreover, as only small amounts of antioxidants are required to fulfil this role, it can be assumed that, they are very different from reducing agents that become oxidised, and are used up comparatively faster. The most acceptable theory to explain this phenomenon suggests the interference with the chain reaction due to formation of free radical mechanism.

A free radical is formed by the loss of hydrogen atom from the methylene group next to a double bond. The formation of a free radical is triggered by agents such as heat, light, trace metal impurities like copper, nickel, iron or manganese or any other pro-oxidant present in oils and fats.

$$R'CH_2CH = CHCH_2R'' \rightarrow R'\underset{\displaystyle *}{\underset{|}{C}}HCH = CHCH_2R''$$

Atmospheric oxygen then converts this free radical formed into peroxide, this is also a free radical.

$$R'\underset{\displaystyle *}{\underset{|}{C}}HCH = CHCH_2R'' + O_2 \rightarrow R'\underset{\displaystyle OO - *}{\underset{|}{C}}HCH = CHCH_2R''$$

The peroxide radical now reacts with an other molecule of the original oxidisable substance to produce a hydroperoxide and another free radical.

$$R'\underset{\displaystyle OO - *}{\underset{|}{C}}HCH = CHCH_2R'' + R'CH_2CH = CHCH_2R'' \rightarrow$$

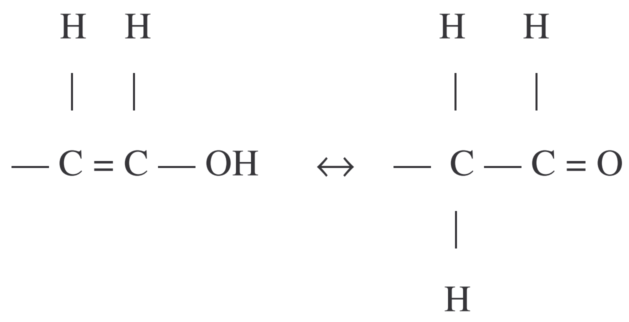
$$R'\underset{\displaystyle OOH}{\underset{|}{C}}HCH = CHCH_2R'' \rightarrow R'\underset{\displaystyle *}{\underset{|}{C}}HCH = CHCH_2R''$$

The free radical, thus produced, then takes up oxygen and starts all again as before. Thus proceeds the continuous chain reaction, with the hydroperoxides decomposing to culminate in the formation of undesirable aldehydes and esters.

Antioxidants it is believed act, by stopping the chain reaction at its very beginning by supplying a hydrogen atom thus destroying the free radical produced, and preventing it from being converted to peroxide.

$$R'\underset{\substack{|\\ *}}{C}HCH = CHCH_2R'' + H \rightarrow R'CH_2CH = CHCH_2R''$$

This theory is supported by the fact that ortho and para derivatives of dihydric and polyhydric phenols are among the most effective antioxidants they being capable to donate a hydrogen atom, by undergoing keto-enol tautomerism.



(Enol Structure) (Keto Structure)

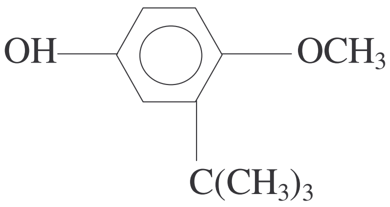
Keto - enol tautomerism

BASIC REQUIREMENTS FOR AN IDEAL ANTIOXIDANT IN SOAPS AND COSMETICS.

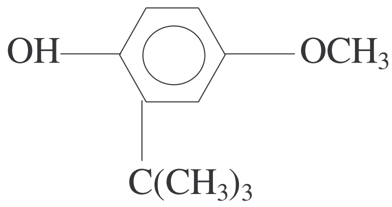
- It should be effective in providing sufficient degree of protection at low concentration levels.
- Antioxidants should be compatible to different ingredients or components used in the manufacture of Soaps and Cosmetics.
- It should be easily and readily soluble or dispersible in the medium and easy for application.
- It should be stable to pH variations /changes and under process conditions. The stability should carry throughout the shelf life /storage of the product.
- It should be free from objectionable odour and colour.
- It must be non-toxic and non-irritant forming, no harmful oxidation products during its lifetime and should have no physiological activity.
- It should not constitute a safety risk to consumers and there should be sufficient Toxicological Support for use in Soaps and Cosmetics.
- It should be inexpensive, easily affordable, and readily available.

Various classifications have been suggested. However, considerable confusion persists in its classification. The most important classes of antioxidants that are relevant to soap and cosmetics are the Primary antioxidants and synergists. Sequestrants and chelating agents are also listed as synergist due theirs marked synergism with the primary antioxidants. **Synergist** are compounds that which increase the effectiveness or the activity of primary antioxidants and **Chelating agents,** complex metallic ions, primarily copper, iron and nickel that act as catalyst in lipid oxidation. Synergists by themselves have very little or no effect on lipid oxidation but generally act by enhancing the effect of antioxidant. A significant synergistic effect that occurs between a primary antioxidant and a synergist result in increased hydrogen donation that is greater than one can expect from the sum of two antioxidants. Their method of action is not always clear, but they are said to help in some cases, due to their sequestering of metallic ions that are known pro-oxidants. Synergist may also function as regenerating agents of primary antioxidants, as hydroperoxide decomposers and by other means of sparing primary antioxidants. The use of synergist is of particular value in emulsified fats and oils. Many of the synergists are water soluble like, EDTA, ascorbic acid, citric acid, tartaric acid, phosphoric acid, etc., while some are oil soluble viz., ascorbyl palmitate, etc. In an emulsified lipid medium, the entrained air present in the medium and the larger surface area that is exposed to air makes the oil more susceptible to oxidation. The reaction of the aqueous phase is also very important and in this connection, the water-soluble acid synergists are very valuable. Oil soluble synergists are effective in acidic but not in alkaline emulsions. EDTA salts (Ethylenediaminetetraacetic acid as di & tetra sodium salt), Citric acid, Tartaric acid, Phosphoric acid, EHDP (Ethane hydroxy 1,1 diphosphonic acid), Magnesium Silicate, are perhaps most commonly used as sequestrants. EDTA chelates copper, EHDP, Citric acid, Tartaric acid, Phosphoric acid and Magnesium silicate chelate iron. Citric acid, Tartaric acid and Phosphoric acid are said to prevent metal ion induced degradation that usually occurs at higher pH.

Of the hundreds of compounds, proposed to inhibit oxidation and prevent detoriation of oxidisable substance only a few of them are popular. Primary Antioxidants are compounds that eliminate free radicals' chains in a typical auto-oxidation. BHT, BHA, TBHQ and Gallic acid esters (propyl gallate) are popular antioxidants commonly used in soaps and cosmetics.



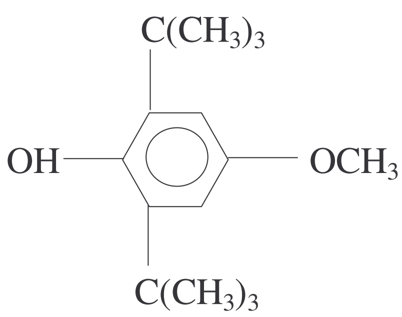
3 - tert - butyl - 4 - methoxyphenol



2 - tert - butyl - 4 - methoxyphenol

Butyalated Hydroxy Anisole (BHA)

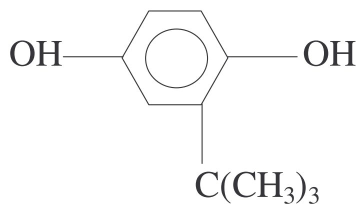
Butyalated Hydroxy Anisole: - 3 - tertiary - butyl - 4 hydroxyanisole, 2 - tertiary - butyl - 4 - hydroxyanisole**,** is a mixture of two isomers (85% of 2 - tert - butyl - 4 - methoxyphenol and 15% of 3 - tert - butyl - 4 - methoxyphenol), is commercially available as white waxy flakes or tablets with a faint characteristic phenolic odour and a melting point in the range of 48° to 63°C. It has a molecular weight of 180.25, and is highly soluble in oil and alcohol but insoluble in water. BHA is more effective in inhibiting oxidation in animal fats than vegetable fats. BHA is particularly useful in protecting the colour and flavour of essential oils and short chain fatty acids as those contained in Coconut and Palm kernel oils typically used in soap, shampoo and cosmetics. Fat solubility is increased by the tertiary butyl side chain in the ortho and meta position to the Hydroxy group ensuring a good carry through protection. BHA is stable under mild basic conditions but has a somewhat objectionable odour at elevated temperatures.



Butyalated Hydroxy Toluene (BHT)

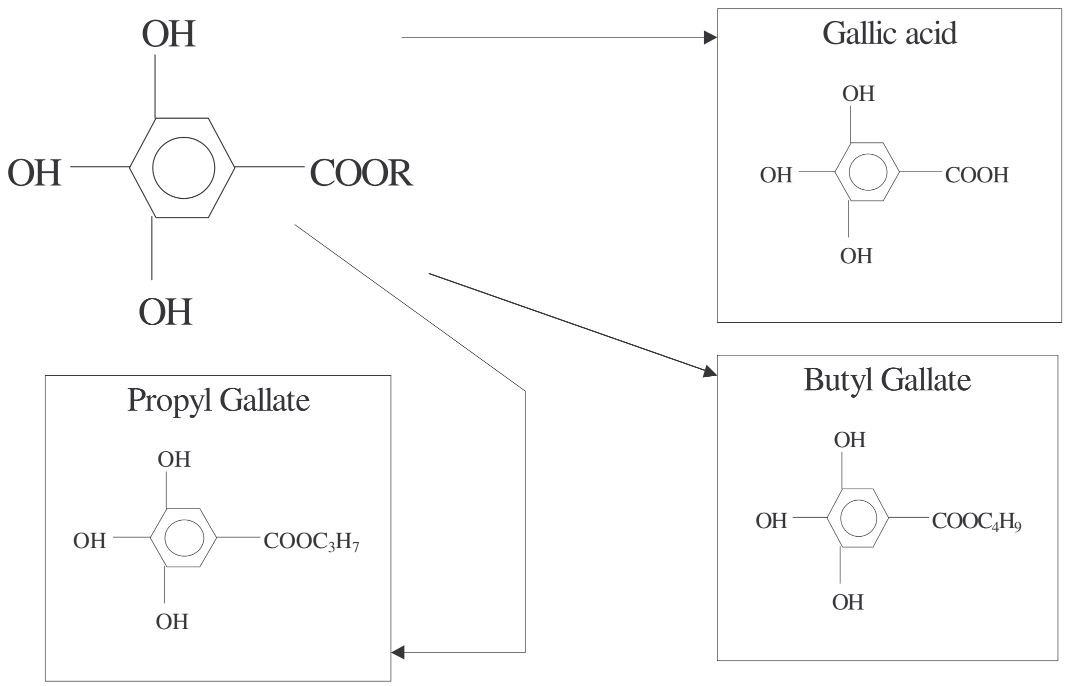
Butyalated Hydroxy Toluene (BHT): - 2, 6, - ditertiary butyl - 4 - menthyl phenol, **or** 2,4, -di-tetra-butyl-4-methylphenol like BHA is a hindered phenol. It is relatively weak when used alone in vegetable oils but more effective when combined with other antioxidants or synergist. It is a white crystalline solid with a molecular weight of 220 and a melting point of 69.7°C. Its properties are very similar to BHA in action but have the advantage, that at raised temperature it is odourless unlike BHA that has a disagreeable odour at elevated temperatures.

Tertiary butyl hydroquinone (TBHQ) is a white or beige coloured crystals, moderately soluble in oil / fats and slightly soluble in water. TBHQ has a molecular weight of 166.22 and melts at a temperature range of 126.5 to 128.5°C. TBHQ is regarded as the best antioxidant when compared with others due to its several advantages. It is more potent and resistant to heat and does not cause discoloration, as it does not complex with copper or iron.



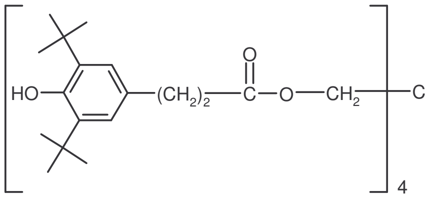
Tertiary butyl hydroquinone (TBHQ)

Gallic acid (3, 4, 5, trihydroxy benzoic acid) esters like propyl gallate, butyl gallate, octyl and dodecyl gallate that are highly potent antioxidants due to their trihydroxy structures are also used as antioxidants for fats and oils. Propyl gallate of molecular weight 212.2, the more commonly used gallic acid ester, is a white to creamy-white crystalline powder. It has a slight odour with a melting point of 146° to 150°C. Lower gallates as propyl and butyl gallate are slightly soluble in water and fats, but increased solubility is observed in case of higher gallates like octyl and dodecyl gallates. The various gallates have approximately equal antioxidant activities at equimolar concentrations. Although the gallates are effective, antioxidants with lower volatility that BHT and BHA their use is relatively less due to their tendency to form coloured complexes with the non chelated metal ions of iron and copper.



Gallic Acid Esters

Tinogard™ TT that was recently introduced to the soaps, detergent and cosmetic industry is a sterically hindered phenolic antioxidant. It is claimed to be a highly effective, **non-discolouring** stabiliser to prevent deterioration of soaps, fatty acids and surfactants, protecting bar / liquid soaps and other rinse-off products efficiently against thermo-oxidative degradation. Chemically it is Pentaerythritol Tetrakis (3 - (3, 5 - di - tert - butyl - 4 - hydroxyphenyl) propionate), having a molecular weight of 1178, and melting point between 110° to 125°C. It is a white free flowing odourless and tasteless powder, compatible in soap - type formulations. Exhibiting solubility characteristics, very similar to BHT, its effectiveness is enhanced by using a combination system alongwith chelate - type synergists.



Tinogard™ TT

Antioxidants are usually used as a combination in a liquid formulation system in fats and oils. The different antioxidants are selected to take advantage of the various potent properties of the individual compounds. It is also dependent on the type of product and its needs or requirements. Combining different antioxidants into a liquid formulation system has many advantages. It is convenient and helps one to have a better control / accuracy in applications, and ensure a complete distribution of the antioxidant in oils and fats. Antioxidants in formulation system with metal chelating agents help take benefit of the synergistic properties of the antioxidant and acid combinations and minimise the discoloration problems that are associated with it.

In soap cakes the concentration levels for antioxidants range between 0.01% to 0.05% w/w of the formulation. In liquid soaps and other liquid formulations (e.g., shampoos) concentration between 0.005% to 0.03% w/w is sufficient. Actual incorporation levels however depend on the formulation its ingredients, processing conditions and long-term stability requirements. Optimum levels have, therefore to be standardised, specific for an application.

It is very important that the antioxidant is thoroughly blended into the oil or lipid phase on incorporation in any product. Although the method of addition is influenced on the type of product, the processing equipment's and conditions, it is added directly as a concentrate solution in oil, fat, through a solvent like fragrance or in an emulsified form. It can be sprayed or added along with other ingredients. In case of soaps and soap products, the antioxidant and synergist are added to the oil / fatty acid blends used during manufacture. The incorporation of additives is carried out early in the process. Sometimes it is also incorporated into the formulation through fragrance, as most of the antioxidants used are soluble in aroma chemicals.

Product protecting agents like antioxidants and chelates (synergists) are necessary as stabilisers in cosmetic products, to retain a pleasant appearance and to ensure stability and efficacy of incorporated active ingredients. It is also equally important that the absence of yellow discoloration to soap & cosmetics, caused by the antioxidants itself, is confirmed by stability studies before the product is put for sale in the market.