Vol 15 Issue 2 April 2023

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Published by: Aquafeed Media, S.L.U. www.aquafeed.com info@aquafeed.com

# Designing antioxidants: The effect of molecular structure

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Phenolic antioxidants are able to break down the oxidative degradation processes which affect different kinds of products and materials. These degradative processes result in the reduction of the lifespan of these products, as well as of economic, material and energy losses. For all these reasons, manufacturers of antioxidants have adapted their products to customers' needs, which have emerged from new regulations, and social and technological trends.

There are different types of antioxidants depending on how they act and protect materials against oxidation and whose mechanism of action is deeply related to their molecular structure. For instance, phenolic antioxidants deactivate free radicals by transferring their labile hydrogen atoms to them, thus transforming free radicals into non-reactive substances. The antioxidant, after losing its hydrogen, transforms into a radical (phenoxy radical) which is less reactive and does not participate in the oxidative degradation process. This is why it is said that the antioxidant is sacrificed because it is exposing itself to oxidation in order to prevent the oxidation of the components of the product.

Sterically hindered phenolic antioxidants are part of this phenolic family. These compounds are characterized by having voluminous functional groups in the ring, which provide them with interesting properties.

The molecular structure is paramount in dictating the effectiveness of hindered phenolic antioxidants in their role as antioxidants. Chemists carefully consider a range of critical parameters, including the arrangement of atoms, the nature of their interactions, and the distribution of electronic density within the molecule, when designing these compounds.

## The molecular structure

Chemical modification of phenols has made it possible to add or modulate their properties through specific structural changes.

For example, BHT, one of the most popular hindered phenolic antioxidants, is synthetically obtained. It can be described as a phenol with two tertbutyl groups on either side of the hydroxyl group, and a methyl group in front of them. These groups play different roles in the molecule. One is the stabilization of the phenoxyl radical formed after the transfer of the hydrogen atom to the free radical, which enhances its antioxidant activity. Another is the blocking of the reactive position of the ring, impeding secondary reactions.

In addition, these groups give BHT its apolar character, which is responsible for its low solubility in water, and its high solubility in oils and hydrocarbons. Thus, BHT is used to protect oils and fats, and other substances present in them.

Nutrition is one of the sectors where oils and fats are used extensively, so preventing their degradation is important to maintain the quality of many products. Antioxidants are added to food or packaging as

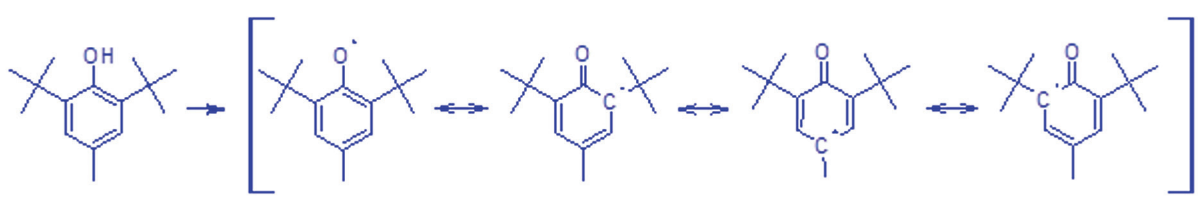

Figure 1. Aromatic ring stabilizing phenoxyl radical

technological additives to preserve them against oxidation. Antioxidants are also used during some industrial processes such as frying or rendering, which require high temperatures. Temperature, oxygen, metal ions and light are the main factors that promote the oxidation process.

The molecular structure is also related to other properties such as melting point, volatility, and optical properties. For instance, BHT is white because it does not have chromophore groups. It is therefore widely used to protect products where white color is a requirement, such as cosmetics or plastics. Moreover, BHT is practically odorless, so its addition to final products does not alter the user's final perception.

Figure 2. Left: crystalline BHT. Right: flakes BHT

Figure 3. Left: blend of BHT in sunflower.
Right: suspension of BHT in water

## Solid or liquid antioxidants?

Whatever the antioxidant and the type of application, the main requirement must be to ensure contact between the antioxidant and the substance to be protected. For this purpose, the nature of the antioxidant, its format and the carrier used to add it to the product are important.

### *Solid antioxidants*

Solid antioxidants are very useful when solid products, such as vitamin premixes, need to be protected. Because the amount of antioxidants required is usually very small, antioxidants can be mixed with inert solids, such as silica or calcium carbonate, which facilitates dosage.

In all these cases, particle size is an important parameter. The evidence shows the smaller the particle size, the better the protection. However, other aspects, such as cost and others associated with solids handling, must be considered.

BHT is a molecule that can be obtained by different industrial chemical processes. Depending on the purification process, BHT can be an amorphous powder, a crystalline solid or flakes, and each of them has its own advantages.

### *Liquid formats*

BHT is one of the fewer examples of antioxidants with a low boiling point, 70°C. Thus, is relatively easy to melt and add as a liquid without adding any other solvent.

However, antioxidants are often dissolved in liquid carriers, such as vegetable oils, propylene glycols, water or acids. These carriers facilitate addition, dosage and mixing with the product.

Vegetable oils are possibly the most widely used carrier of BHT in nutrition applications, due both to their safety for humans and animals and to the solubility of BHT in oils.

In liquid blends, the maximum concentration of BHT depends mainly on two parameters: the type of oils and the solubility of BHT in them; the temperature changes during production, transport, and storage which may lead to precipitation of BHT.

However, it is possible to prepare stable mixtures using solvents in which BHT is not soluble such as water. In these cases, it is necessary to stabilize the antioxidant with some substances to prevent precipitation.
Some of these substances are:

- Wetting agents that coat the solid particles and promote their interaction with the liquid phase.
- Surfactants that prevent the agglomeration and sedimentation of particles keeping the particles separated.
- Thickeners that increase the viscosity of the mixture by creating a three-dimensional net which keeps the dispersive phase stable.

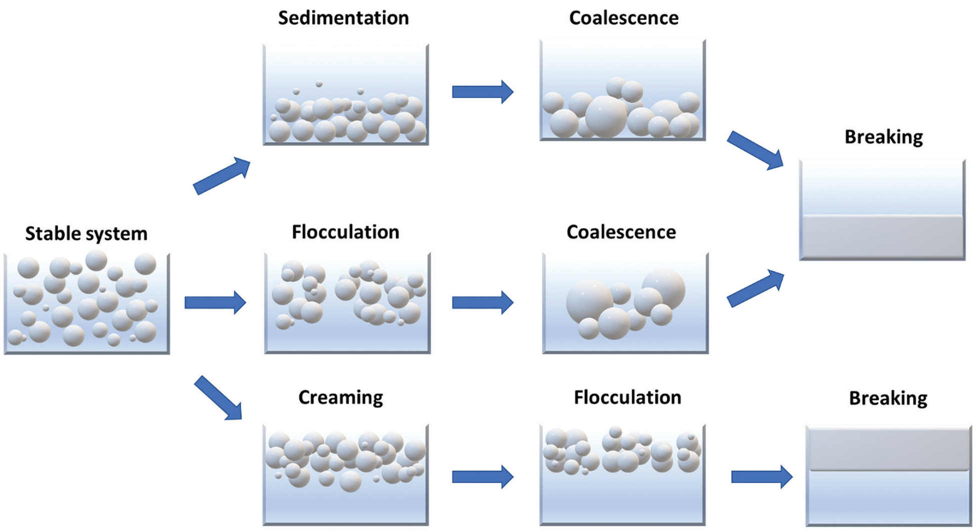


Figure 4. Different types of physical instability of a suspension

- Preservatives that prevent the growth of micro-organisms in the medium.

Suspensions, like other dispersions, tend to break down over time, so it is important to ensure microbiological, chemical and physical stability for as long as possible.

Some of the strategies to increase the stability of a suspension are:

- Reduce particle size by micronization.
- Ensure the separation of particles with the best selection and proportion of surfactants.
- Increase the viscosity to prevent the particles get together.
- Avoid sudden temperature and pH changes which can break the interactions formed.

In conclusion, the selection of the best antioxidant, and the best way to use, is an important decision that requires technical expertise. A seemingly simple change in the format of the antioxidant or the carrier used can greatly improve the results in protecting products against oxidation.

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