

Transformation of Hindered Phenolic Antioxidants

The expression less is more and more is less becomes more applicable to discoloration and stabilization today than previously in terms of our historical understanding.

What happens during thermal processing of a polymer with a hindered phenolic antioxidant often depends more with the purity of the additive than its known structure. We spend too much time focusing on the existing structure and assume this is 100% pure. This assumption is false and clearly not in line with known problems and realities of all organic synthesis. Purity determines performance with a phenolic antioxidant. As purity goes down relative to the known pure standard discoloration reactions' increase faster over time. Discoloration being visual is our first and fastest indication of performance while this degree of discoloration may not be reflected in the rheology of the

product. In the normal course of performance hindered phenolic antioxidant will undergo in-situ transformation as part of its known mechanism but the degree of discoloration does not have to be intense and can be controlled to limit the level of discoloration.

Furthermore, discoloration does not have to be a indication of poor thermo-oxidative stability.

Discoloration is more an indication of in-situ reaction chemistry in a solid that leads to ever changing color being manifested initially during processing, on long term storage in a clean environment and a hostile environment having prompt oxides of nitrogen or from lignin reactions in cardboard storage gaylords. Discoloration is more a nuisance and not to be confused with stabilization of the matrix.

The challenge has been to limit or eliminate the discoloration initially and during storage of the pelletized product and after fabrication and storage. However, this is not always the case when designing product. The focus is always on good color during manufacturing of the pelletized product not downstream end use applications.

This mistake in ignoring a total systems approach to product design has its negative consequences.

Polyolefins are either designed for a preferred end use application on density or melt flow (melt index). This is followed by the targeted end use requirements for stabilization and finally the economics or cost of the product versus the competition. This philosophy differs from manufacturer to manufacturer and has its own internal limits based on the chemical engineering of manufacturing the polyolefin and treatments during isolation of the resin and catalyst.

Over, the decades we have seen many novel phenolic antioxidant chemistries introduced into the market that unfortunately were before their time or showed deficiencies based on the immediate paradigms and wants of the moment.

Rarely were the true needs of the product fully understood or the chemistries understood as test methods were being developed and changing as fast as the catalyst systems for making the resins.

The consequences of these changes resulted in a few inexpensive phenolic antioxidants dominating the landscape in polyolefins. In addition, as patents on the additive ended their life cycle more additive manufacturers making the same additive increased and purity decreased as competition for lower prices became the dominant motivation.

However, the problem of discoloration never went away but only got more complicated as less technical expertise in the market dropped and a historical understanding of the products became distorted by those less informed.

One example of this has been a reversal in the perception of phenolic antioxidant to secondary antioxidant. The historical literature from the biggest vendors of additives showed a connection between ratio of primary to secondary antioxidant and affects on melt flow or rheological control. This ratio depended on polyolefin but was consistent with polypropylene being 1:1 to 1:2 primary to secondary and in polyethylene from 1:1 to 1:4 depending on hydroperoxides and control of crosslinking and gels. This was especially noteworthy for linear low density polyethylene when it was first introduced prior to metallocene LLDPE. Today this ratio has been distorted to mean 2:1, 3:1 or 4:1 by compounders and those

designing new systems. The claim being it has always been this way!

This same trend can be seen with other ratios used for thermo-oxidative stability with thioesters.

Therefore, new realities have entered in the stream of knowledge that conflict with a historical perspective based on the science.

Regardless, discoloration has not been altered but control of other properties like melt rheology and more die drip and additive migration and black specks have increased.

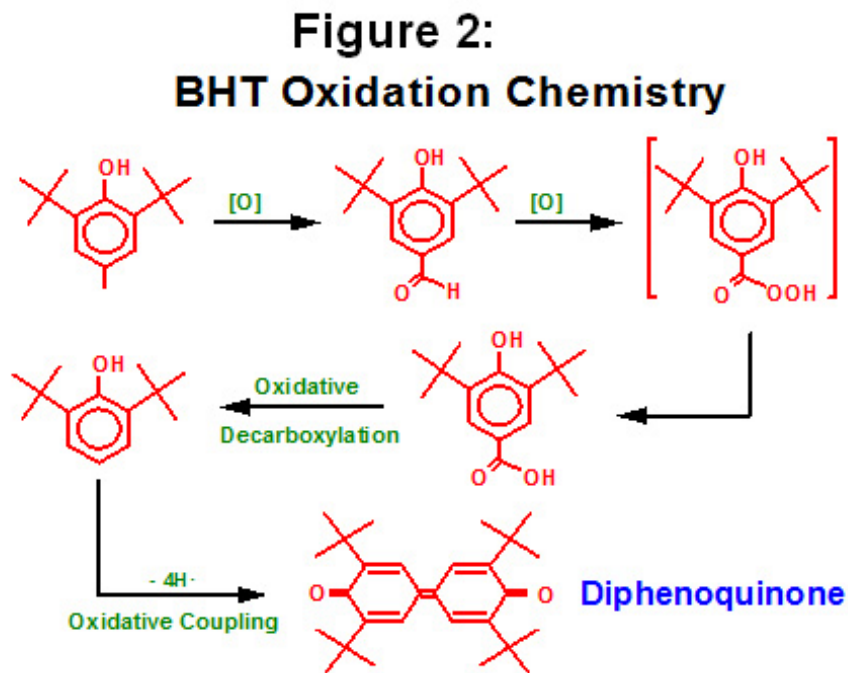
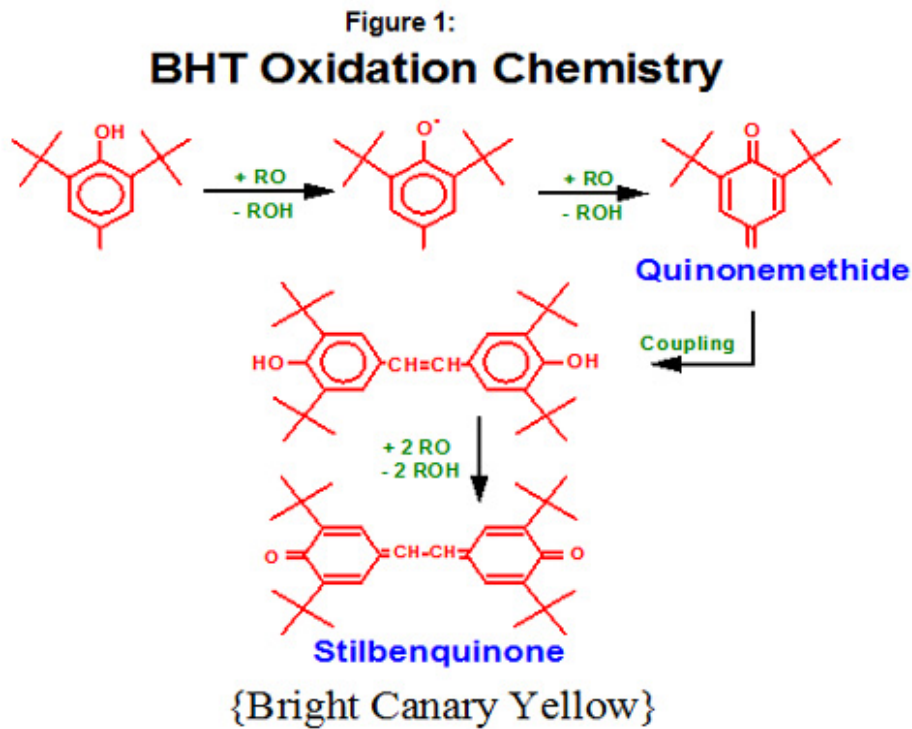
Today we appear to have three dominant primary hindered phenolics that are used globally to stabilize polyolefins. There are exceptions to this rule and these exceptions are not covered in this bulletin at this time.

These three include Pentaerythritol Tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione.

The last mentioned phenolic 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione is more commonly found in polypropylene than in polyethylene resins.

The first two on the list are dominant in both polypropylene and polyethylene and in many cases combined with a secondary antioxidant to enhance synergism especially melt flow control. Their known utility and long-term use and cost are the driving force for their use along with comfort levels among the less informed.

The mechanism of action is typically shown by many authors in the literature as Figure 1 and 2.



Others report the mechanism as Figure 3 and 4.

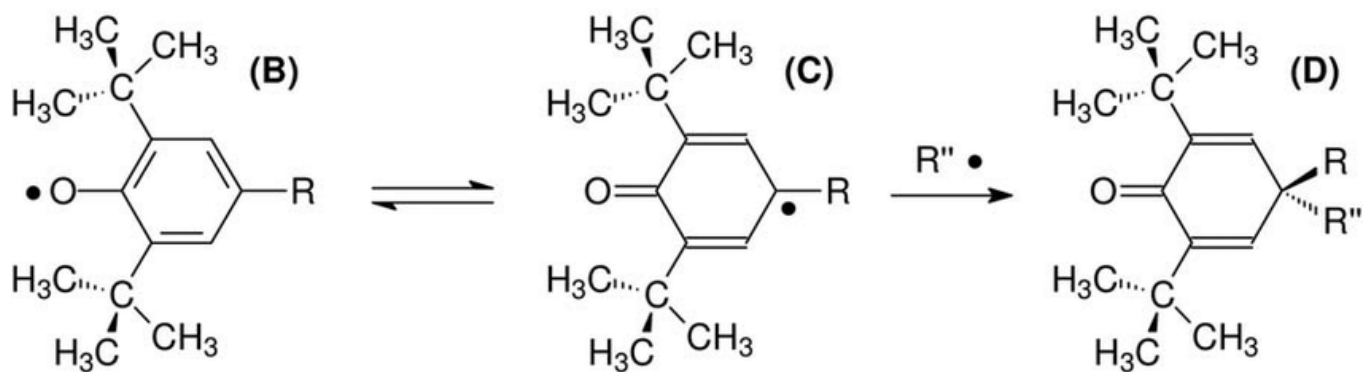
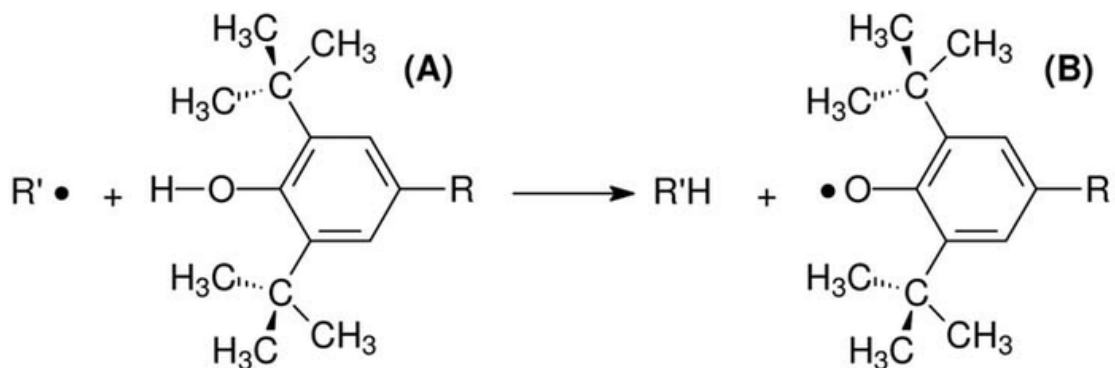
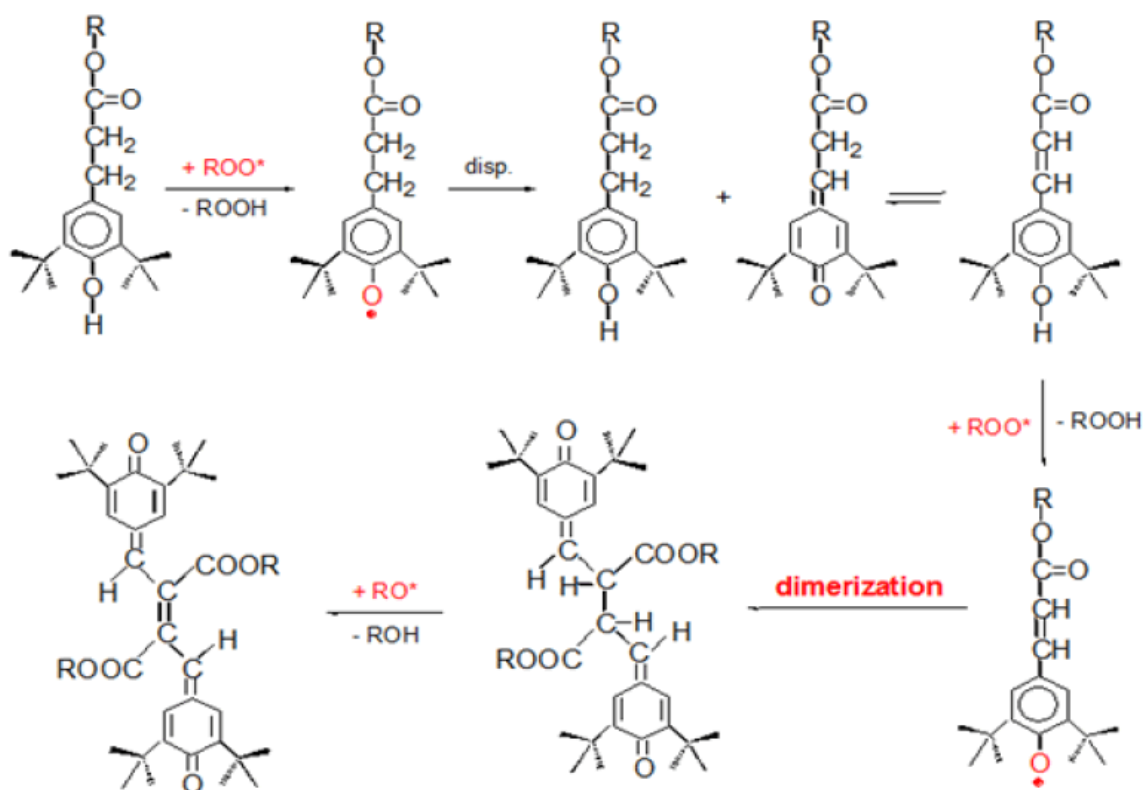
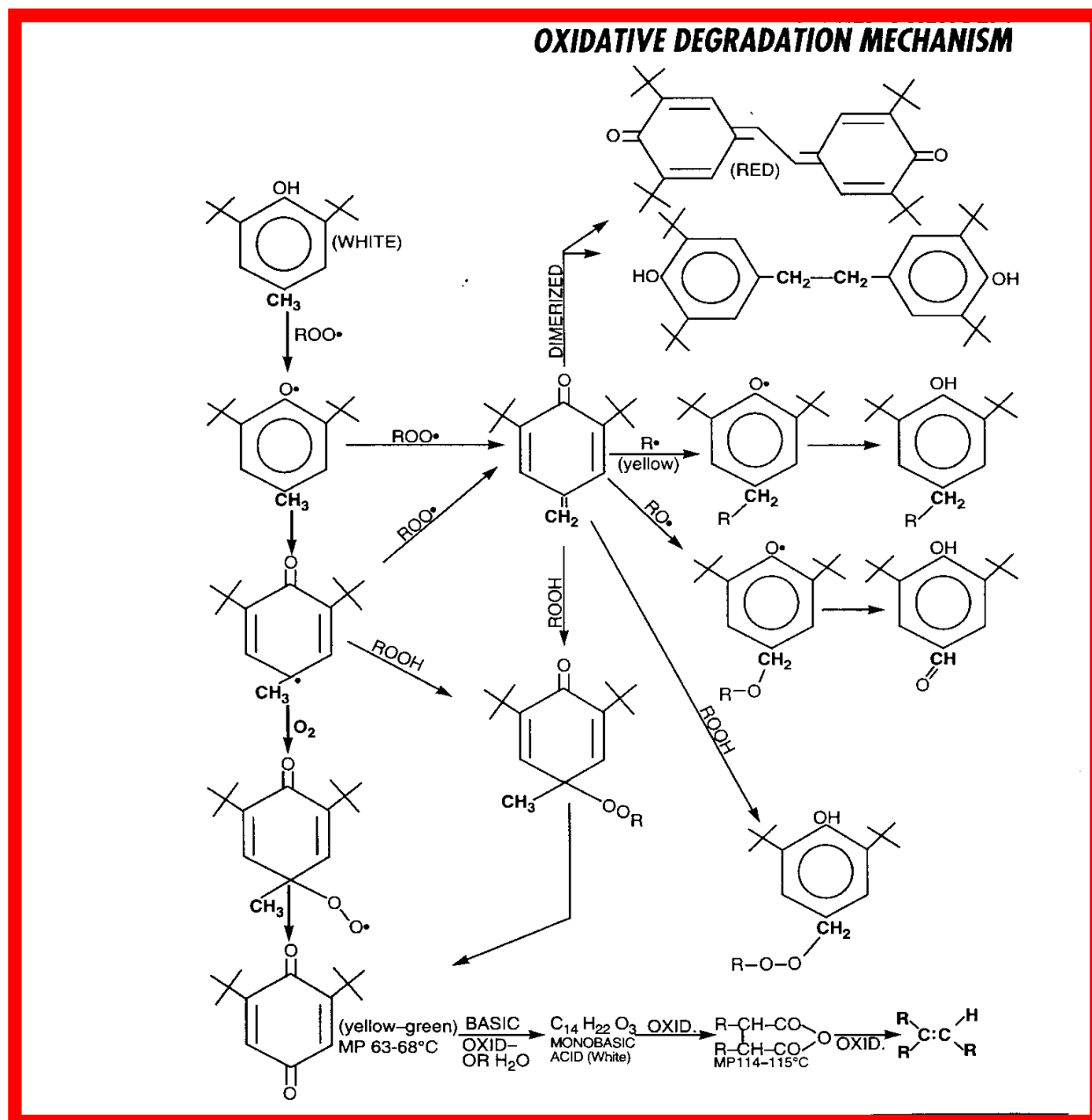


Figure 4:



The more appropriate mechanism of a simple hindered phenolic antioxidants depends on the many routes the chemistry can take during free radical attack or matrix environment including Hammett Function.

Figure 5:



The type of discoloration of the two most prevalent hindered phenolic antioxidants is consistent with the chemistry of both the simple molecule shown above and the higher molecular weight versions. However, Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate appears to be highly prone to more discoloration than its older brother Pentaerythritol Tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate).

Much of this has to do with the purity of the two additives and typically manifests itself more in post storage of the pellets or fabricated parts.

Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate can be induced into its chemical transformation forms of discoloration by solution chemistry and in other modes known in the art e.g. gas staining (gas yellowing). Solution methods are ideal to show the nature of the additive during transformation and what could happen in the plastic.

The utility of this method provides the chemist a rapid means to determine whether a specific chemical structure will cause discoloration problems in the polymer and what potential colors could be manifested. It is used solely as a guide. However, its been our experience a very reliable test to show what could be a potential problem.

Figure 6: Transformation of Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate



Yellow to Orange to Red (Pink) transformations.

Figure 7: Isolation of transformation products from plate out of resin containing Transformation of Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate and stored in the dark.

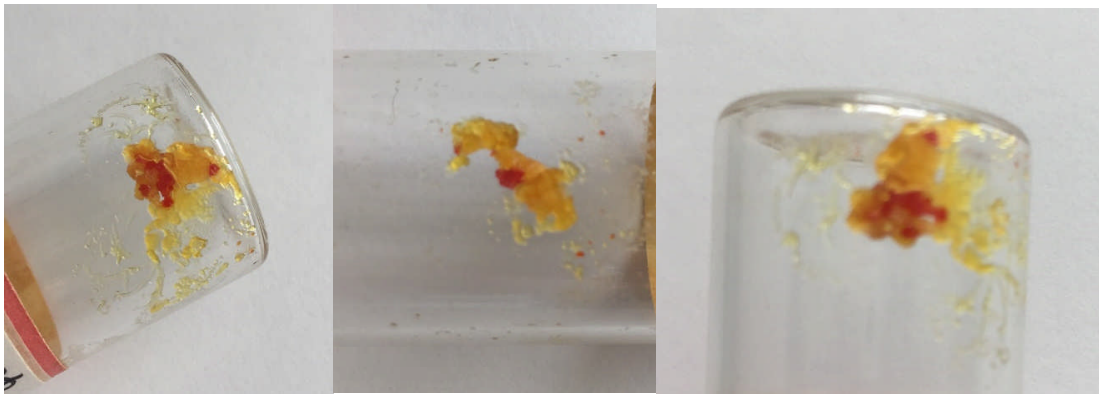
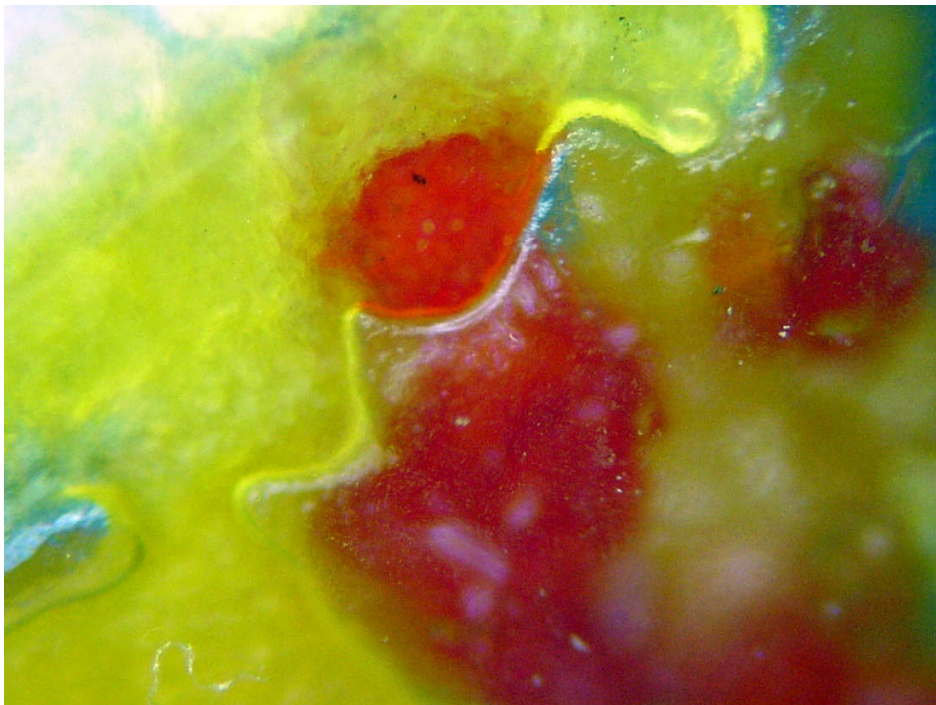
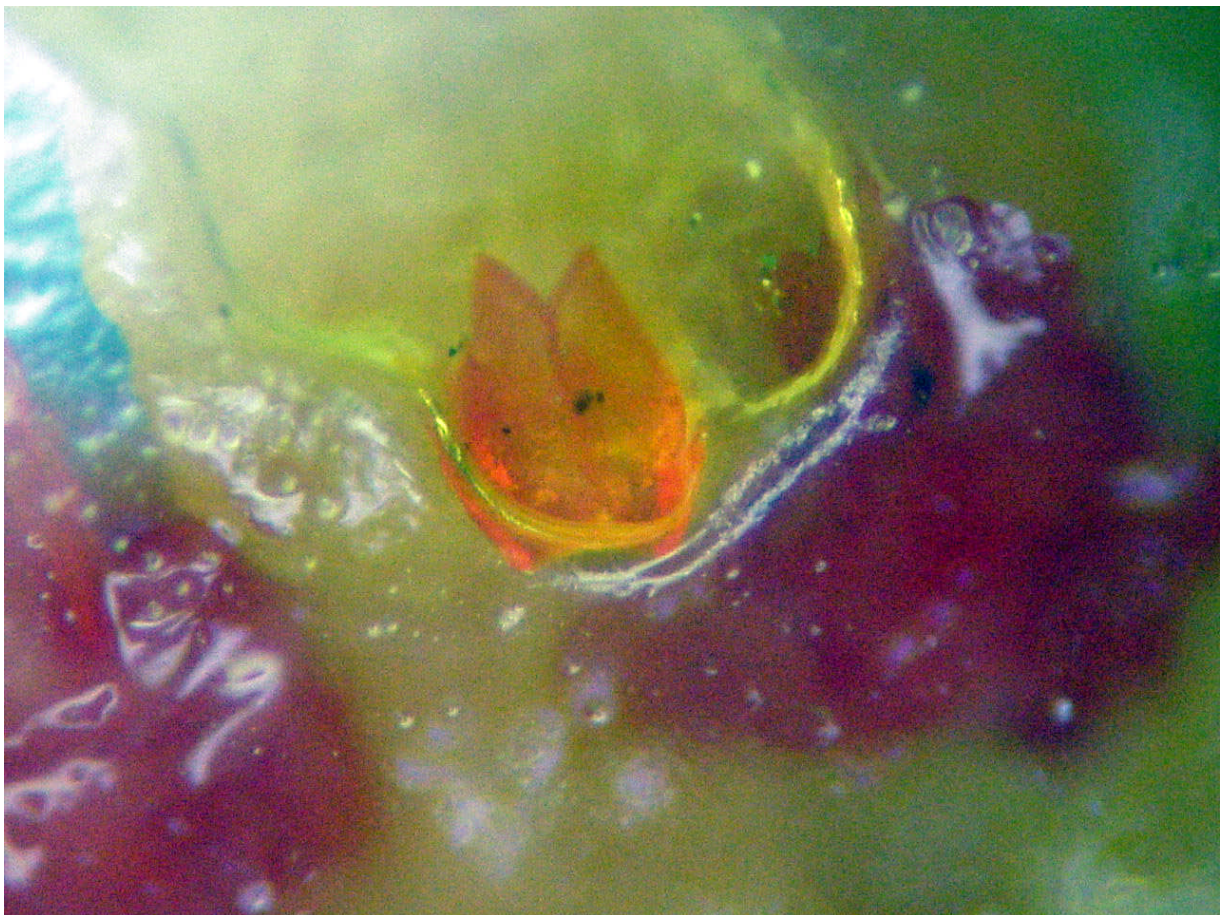


Figure 8: Digital Photo Microscopy (40X) Stereo



The quinone methide is yellow while the stilbene quinone is red.

Figure 9: Intermediate transformation product before complete dimerization into stilbene quinone red color or pink in plastics



Therefore, what we see in solution is duplicated in long term dark period storage of the plastic and plate out or die drip!

Dark period storage accelerates free radical chemistry over time and the concentration of hydroperoxides increase in the dark period. Exposure to light dissociates the hydroperoxides into new free radical species to continue the process.

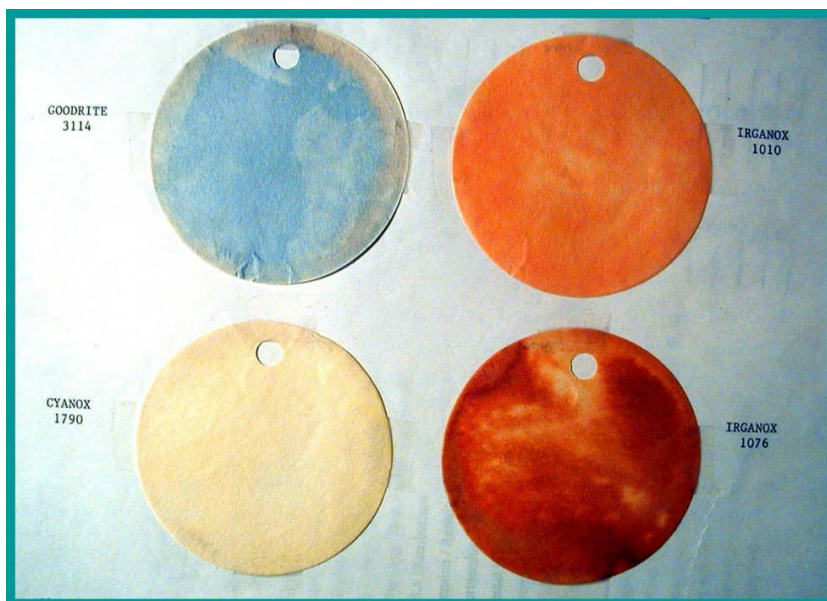
Figure 10: Pinking of Polyolefins



The relationship between other phenolic antioxidants and prompt oxides of nitrogen and in rare cases curing gases used in textile carpet manufacturing for urethane backing is more involved but the consequences are the same.

This too can be seen in artificial accelerated test using solutions and filter paper suspended in an ASTM AATCC Gas Chamber used to test textiles.

Figure 11: Exposure of hindered phenolics from solution on filter paper exposed to prompt oxides of nitrogen using AATCC Protocols and temperatures.



Again, we observe the type of discoloration that can be expected from various hindered phenolic antioxidants. This is consistent with real world experience in textiles from the same phenolics.

Figure 12: Textile Gas Chamber for Gas Staining



Figure 13: Exposure of Filter papers in Accelerated testing protocols.

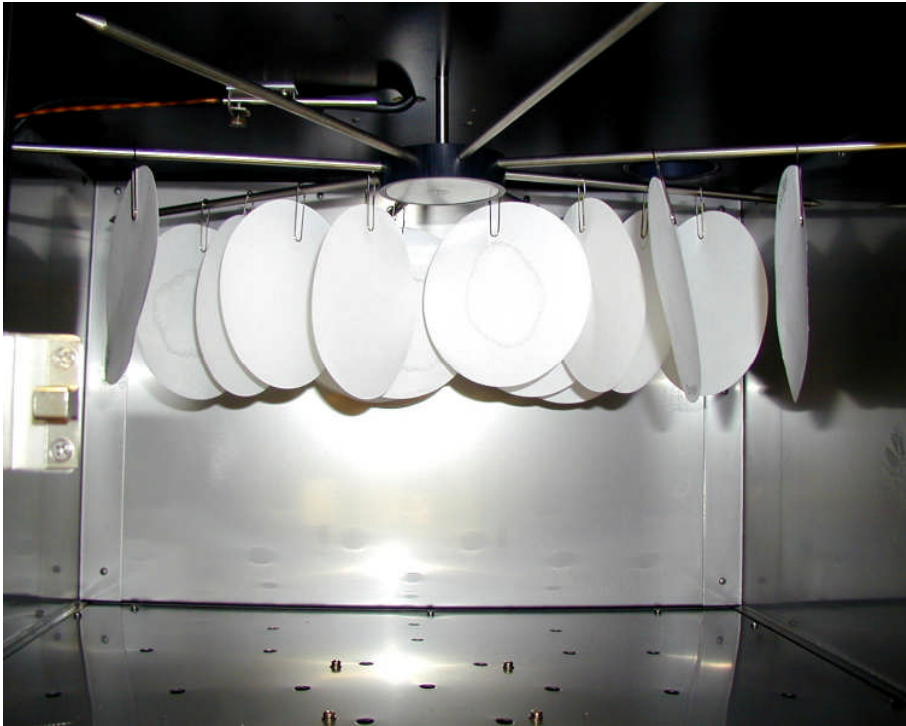
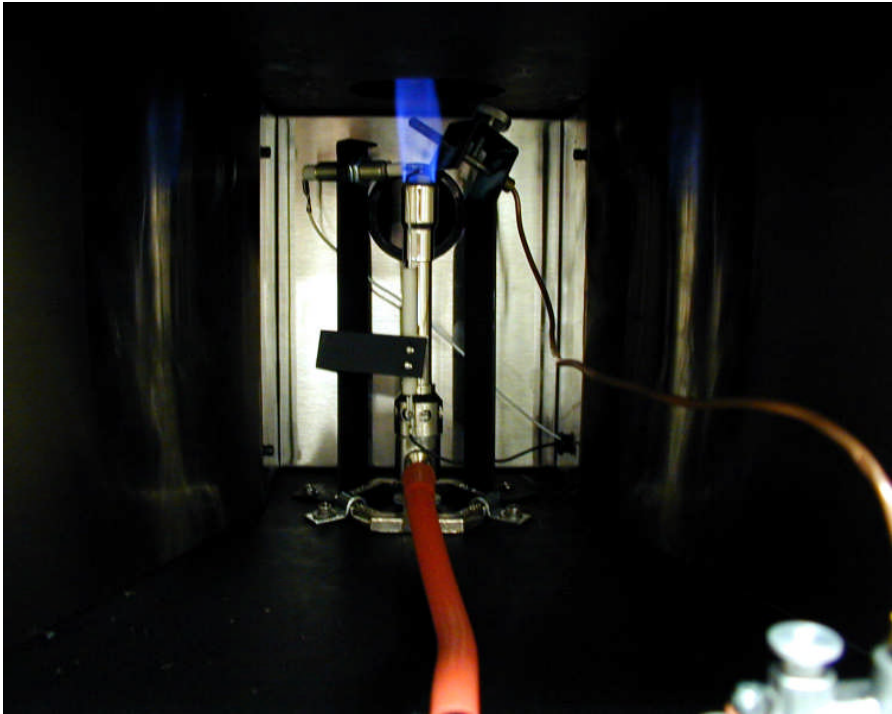
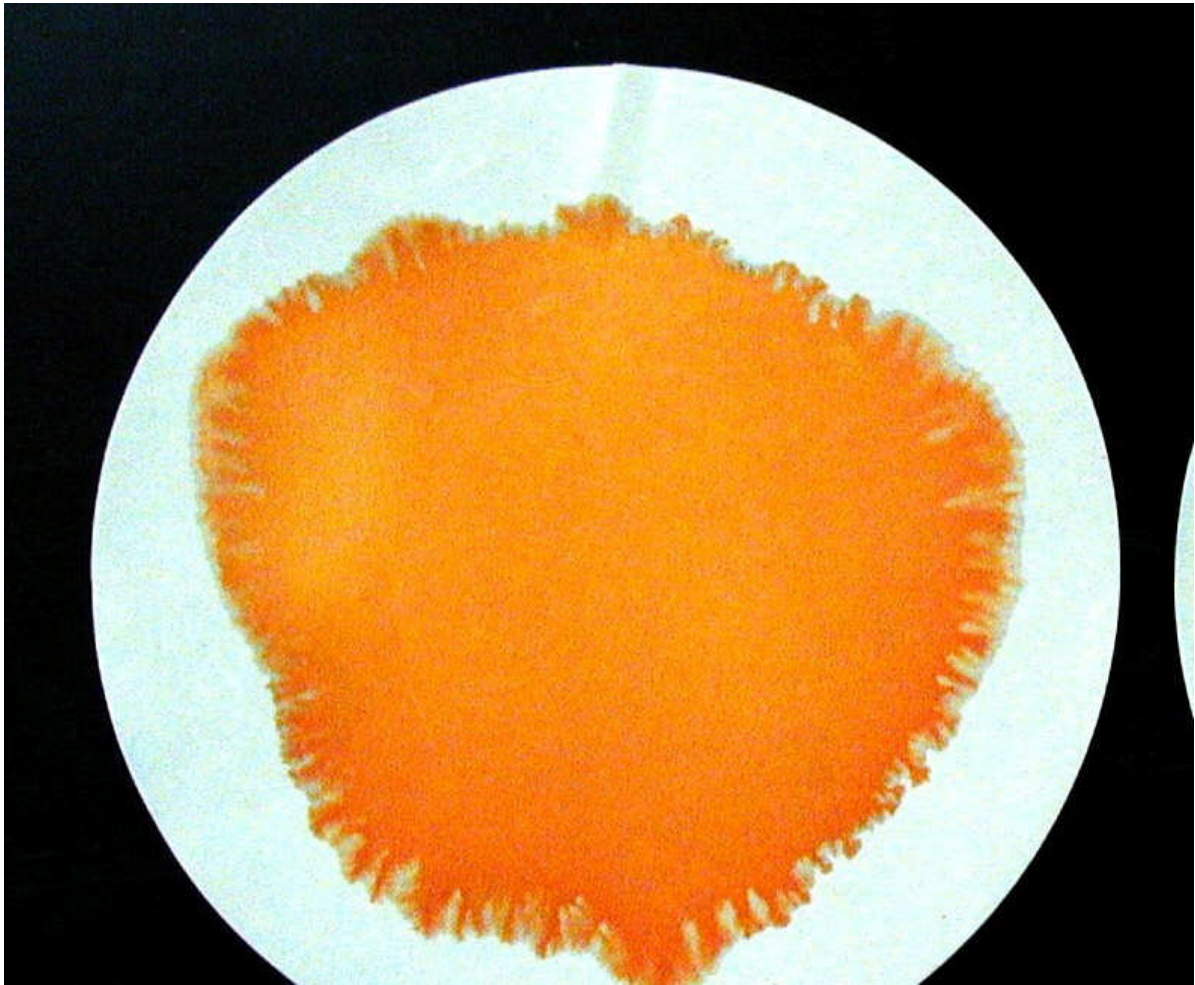
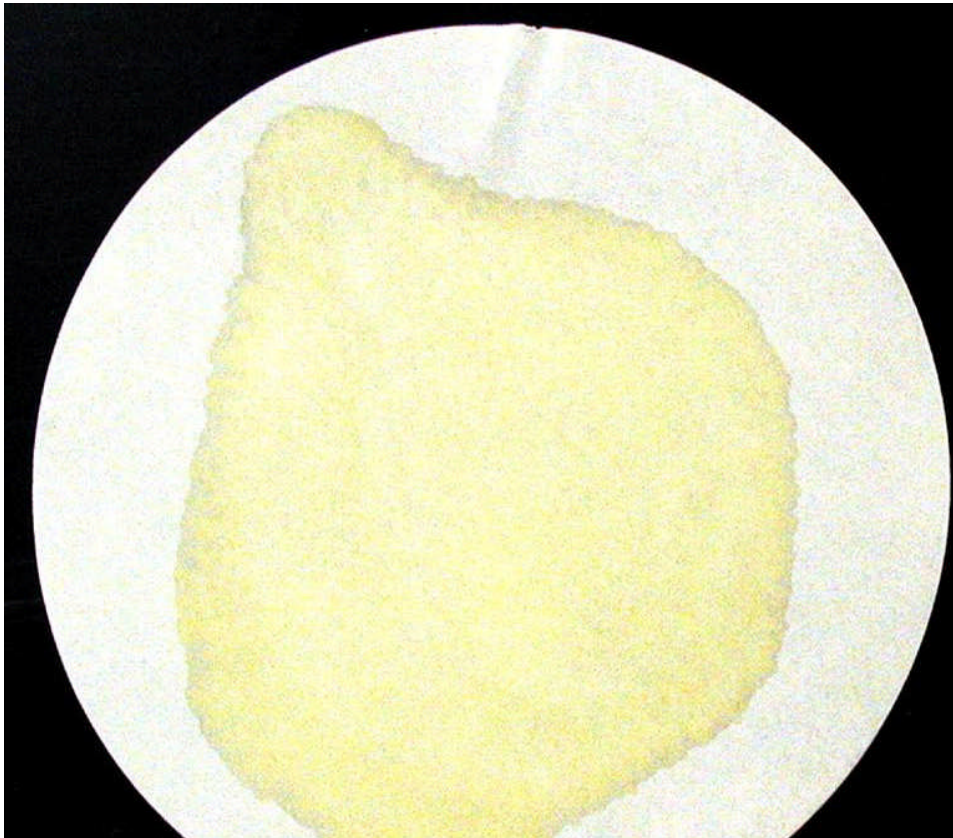


Figure 14: Gas Staining of Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate in the presence of a oligomeric hindered amine.



We see that the chemistry of this phenolic antioxidant in the presence of a more basic environment goes from yellow to orange on exposure.

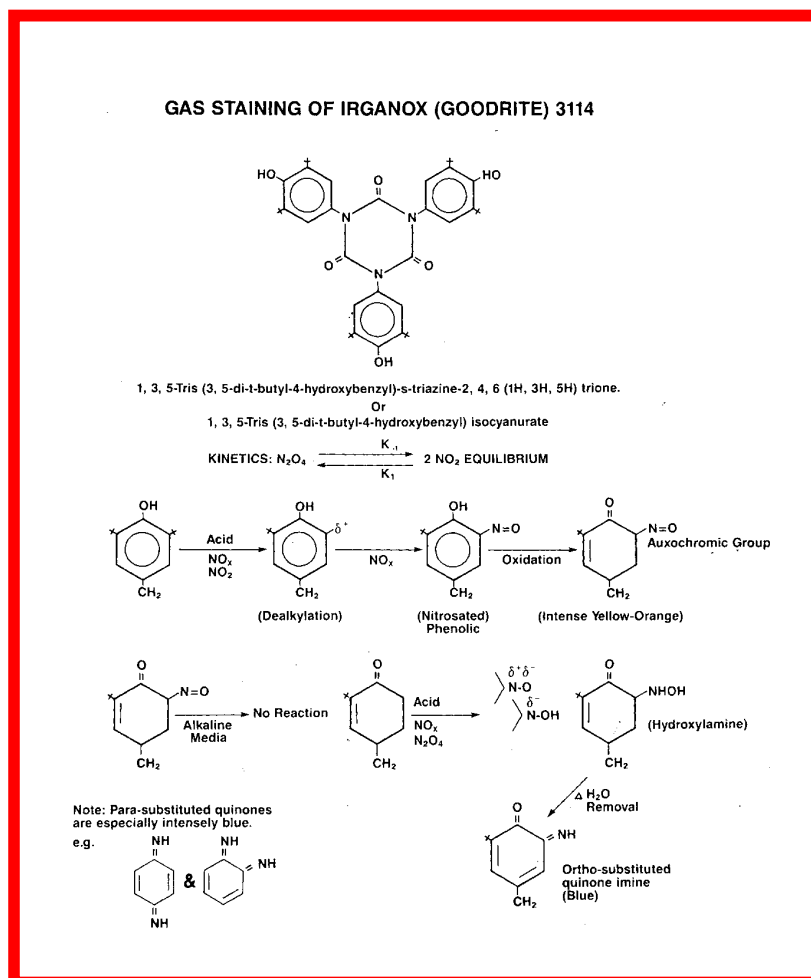
Figure 15: 2,6 di-tertiary butyl phenol and basic hindered amine light stabilizer same concentration accelerated gas staining reaction.



In Figure 15 we compare a less commonly used but simple molecule used prior to the introduction of Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate and perceived to be a problem for years.

In both cases the accelerated gas yellowing or sometime referred to as gas staining or gas fading reactions lead to various but consistent discoloration in the fabricated polymer.

Figure 16: Proposed Gas Staining Chemistry of 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione



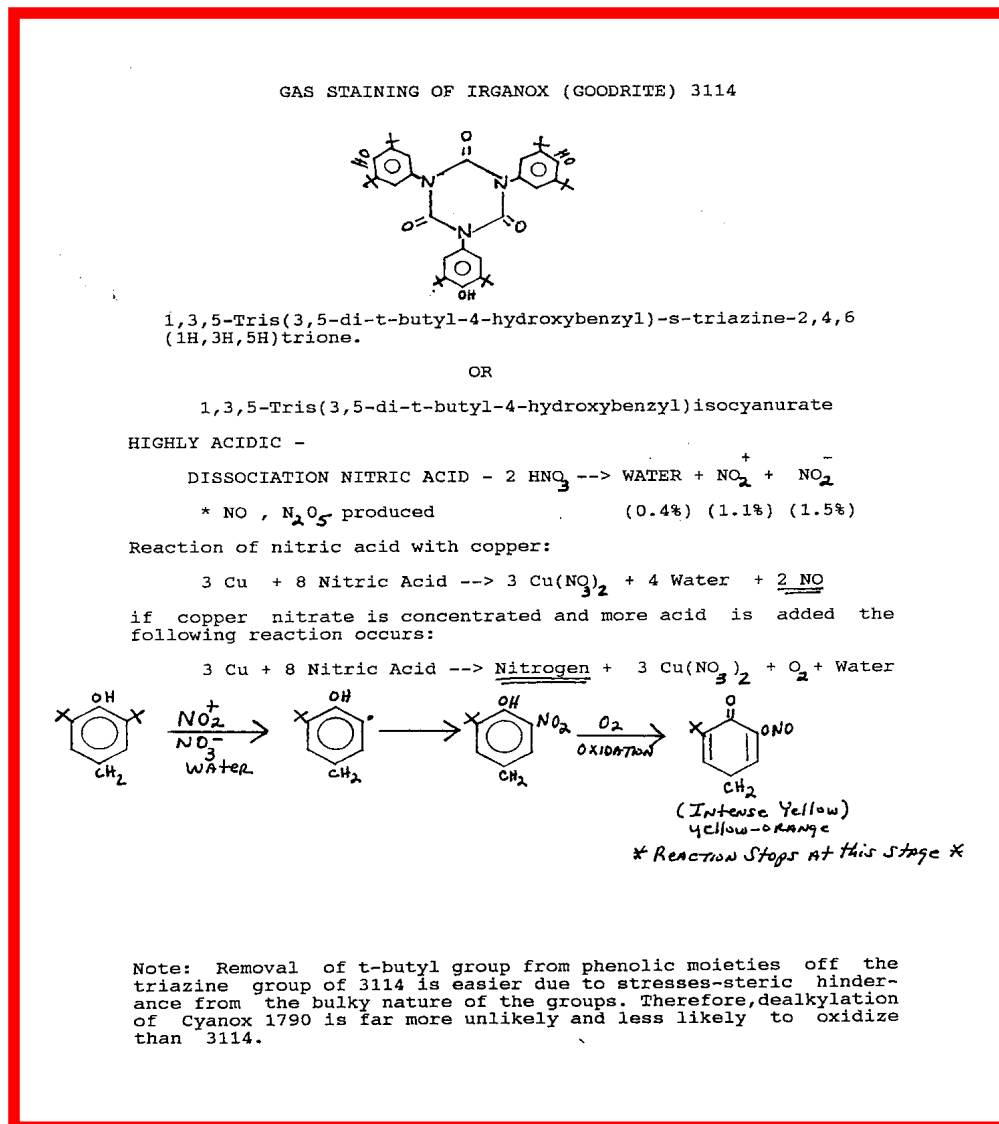
Auxochromic transformation is temperature dependent and at 60C test temperatures consistently forms the ortho-substituted quinone imine which is the blue color.

The formation of prompt oxides of nitrogen is an equilibrium reaction shown above. At temperatures below 60C the dimeric form of the prompt oxides of nitrogen is the reactive species and at 60C another species of the prompt oxide of nitrogen. Therefore, where the gas chamber is located will determine results. If the metal drum that makes up the chamber is near an air conditioning vent blowing on one side is enough to change the internal test temperature and change results of the test. This is more common than you would expect globally.

Another problem is the source of the gas used for the chamber. Purity of the gas determines the prompt oxides of nitrogen and other gas that is formed during combustion. In some countries no

gas combustion is used and is more reliant on acid decomposition reactions to expose the textile.

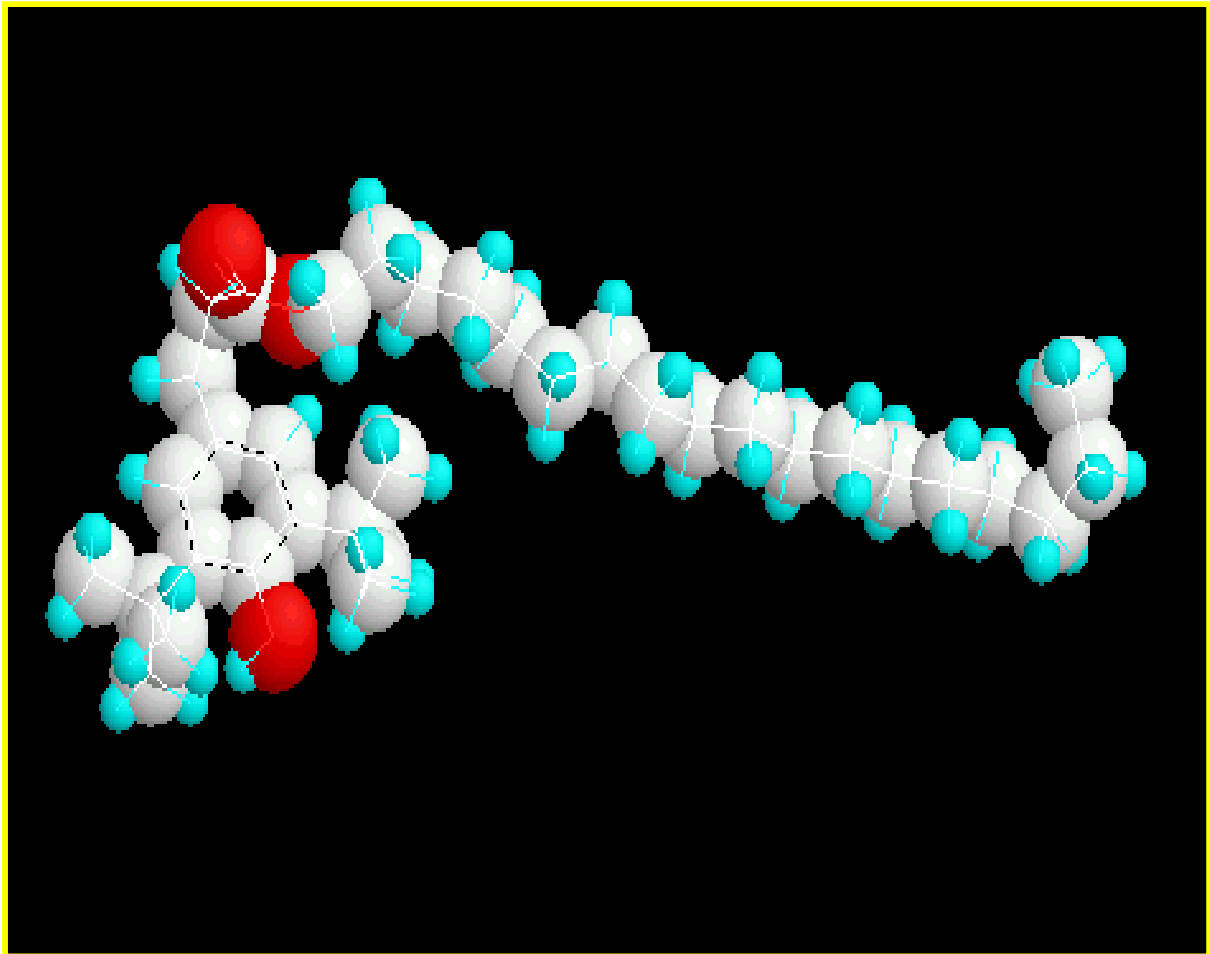
Figure 17: Chemistry proposed using Acid decomposition products



No blue chromophore is possible.

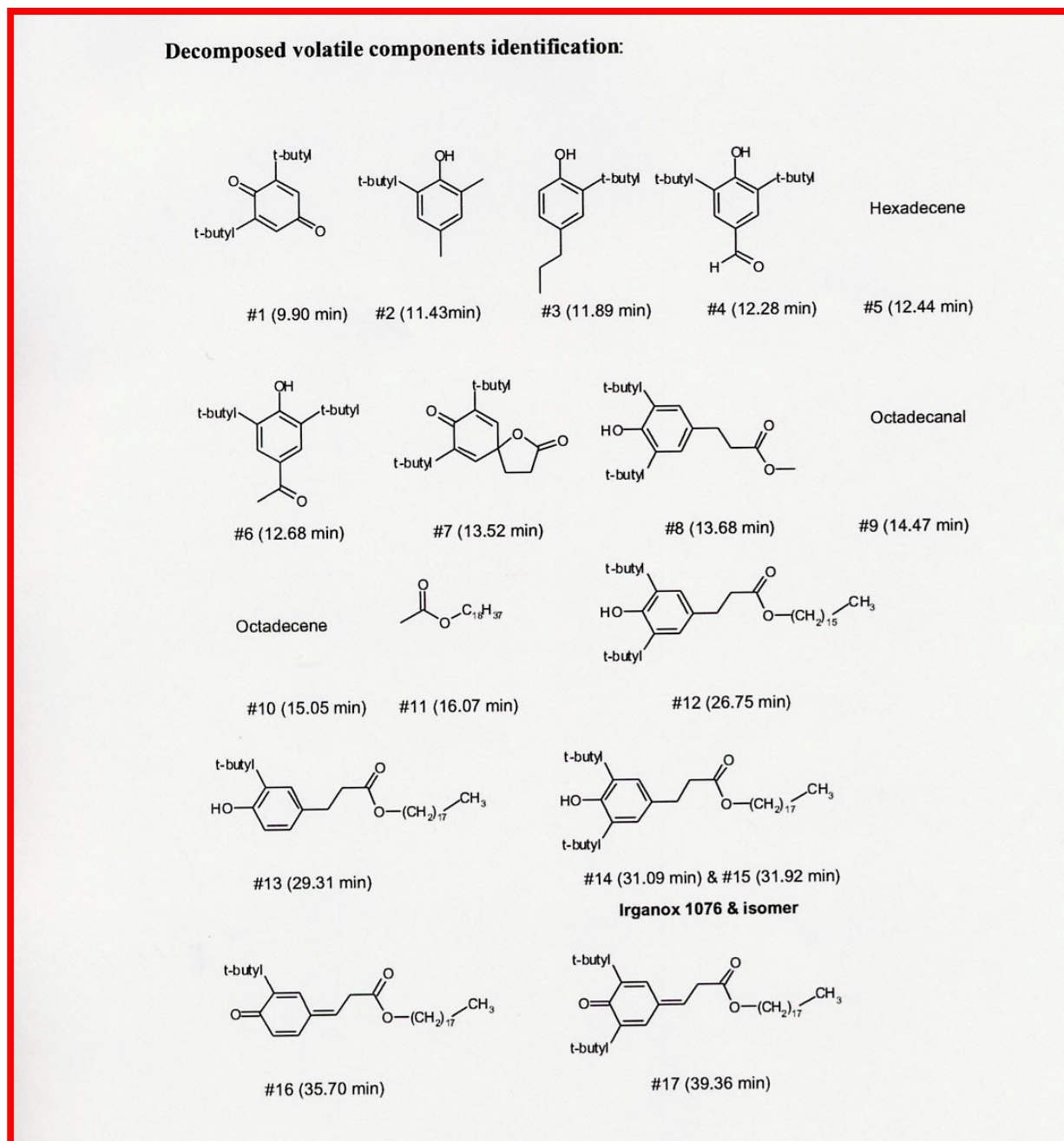
Last and most important in the overall discoloration by hindered phenolics is the purity.

Figure: 18 Purity of Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate



This simple structure is manufactured by many companies globally and differs in purity from lot to lot.

Figure 19: Purity Testing by GCMS and HPLC of Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate neat additive.



Therefore, buyer beware of purity and cross over contamination from low priced stabilizers. Storage and shipping conditions also have a negative effect on the additives shelf life.

Ideally analytical testing of the neat additive as received and retains of materials being used is key to long term consistent product formulations. This is the best insurance policy for maintaining product quality.
