Base Catalyzed Oxidation of Antioxidants

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Base catalyzed oxidation of primary antioxidants in polyolefins is as common today than in previous generations. The cause is complex but understood. However, as changes in our industry rotate technical expertise and eliminate sources of past knowledge through retirements or downsizing the problem is constantly rediscovered or reinvented by less experienced in the field.

One common cause is the interaction of low levels of weak primary antioxidants that are inherently prone to base catalyzed oxidation in the presence of a basic environment.
Concentrations have constantly changed in the industry from a common of use of 0.10-0.20% of a primary antioxidant to levels today in the range of 0.02-0.05% making the issue more problematic!

The in-situ environment required in the polymer is typically a pH of 8 to 12 to cause the reaction. Common phenolic antioxidants prone to this are Octadecyl-3-(3,5-di-tertiary butyl-4-hydroxyphenyl)-propionate, Pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), 2,6 di-tertiary butyl phenol, and 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione. These are notable phenolics due to their current popularity today and known historical issues with discoloration. However, there are exceptions to this rule and will not be discussed in this article.

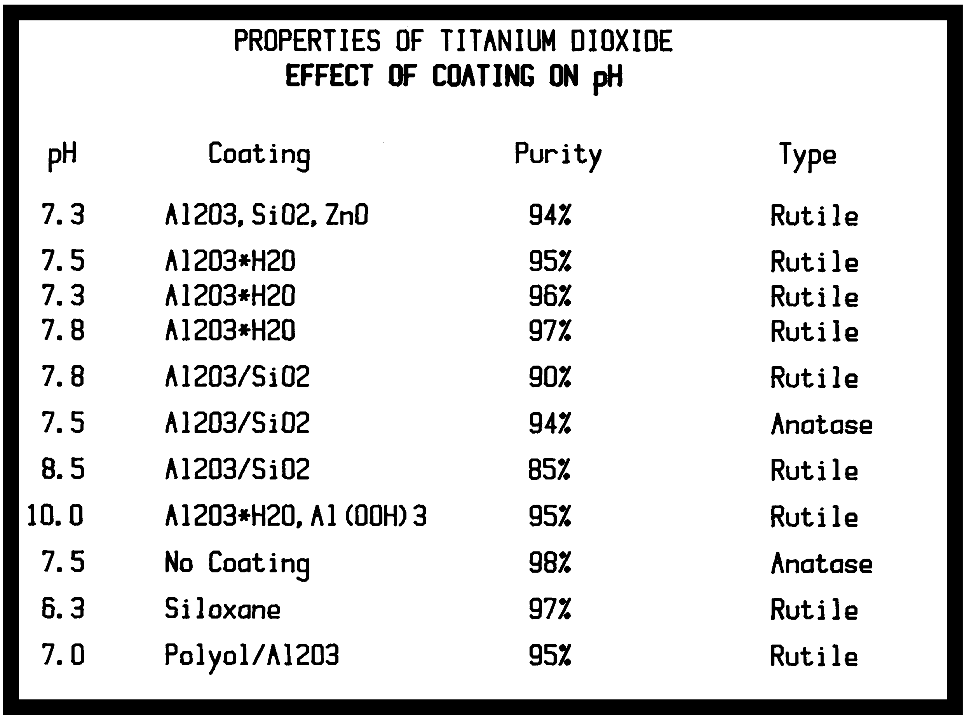
These is the one primary antioxidant Octadecyl-3-(3,5-di-tertiary butyl-4-hydroxyphenyl)-propionate that is used in over 85% of the PE and PP resins today at levels from 100-1000 ppm. This primary antioxidant is inexpensive and typically combined with a secondary antioxidant for enhanced synergisms to improved melt rheology during compounding and fabrication.

This antioxidant is produced and sold by multiple sources since the product came off patent. Therefore, the purity and quality of the product has changed and more prone to discoloration than when initially introduced.

In addition, the performance as a processing stabilizer to control melt flow at temperatures higher than recommended by the resin manufacturer is far less effective than other primary antioxidants alone or in combination with a secondary antioxidant. Furthermore, when thermo-oxidative stability is required this antioxidant does not perform as effectively as other primary antioxidants in its chemical class.

Sources of basic substances in polyolefin resins include internal and external lubricants, acid acceptors, antistatic agents, pigments, fillers, and light stabilizers.

Titanium dioxide is very basic and depending on the coating used will alter the pH from 7.5 to 10. White backgrounds accentuate the yellowing reaction at parts per million of the chromophores.

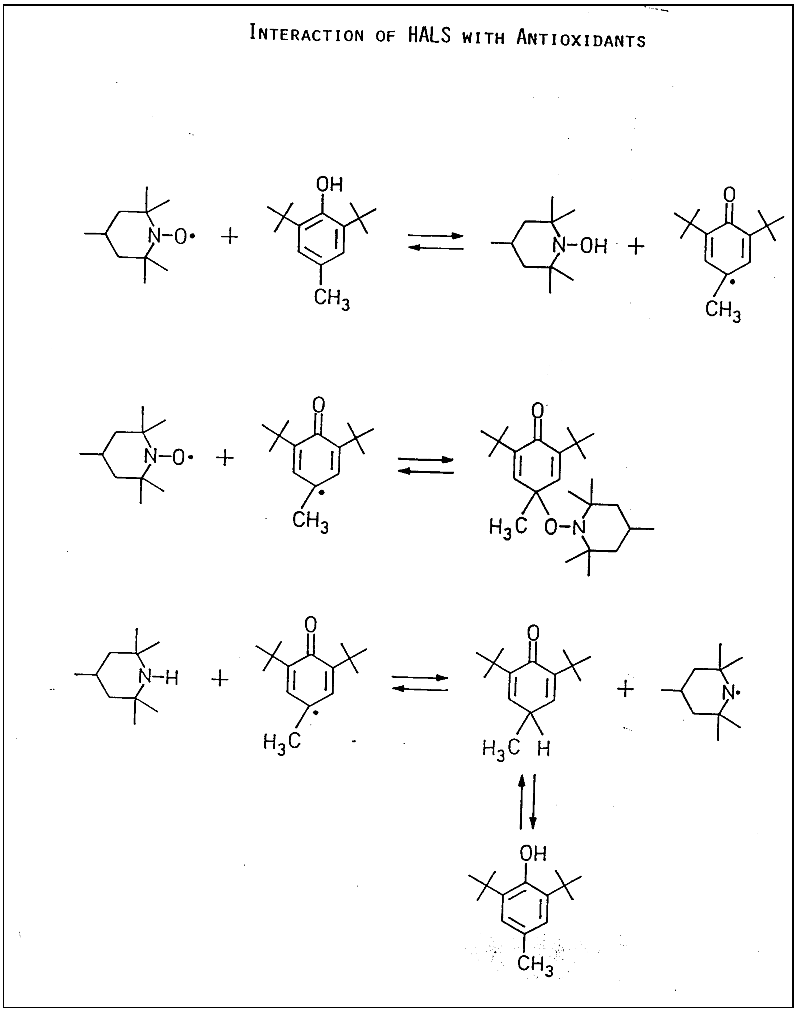


PROPERTIES OF TITANIUM DIOXIDE

EFFECT OF COATING ON pH

pH	Coating	Purity	Type
7.3	A1203, Si02, Zn0	94%	Rutile
7.5	A1203*H20	95%	Rutile
7.3	A1203*H20	96%	Rutile
7.8	A1203*H20	97%	Rutile
7.8	A1203/Si02	90%	Rutile
7.5	A1203/Si02	94%	Anatase
8.5	A1203/Si02	85%	Rutile
10.0	A1203*H20, A1 (OOH) 3	95%	Rutile
7.5	No Coating	98%	Anatase
6.3	Siloxane	97%	Rutile
7.0	Polyol/A1203	95%	Rutile

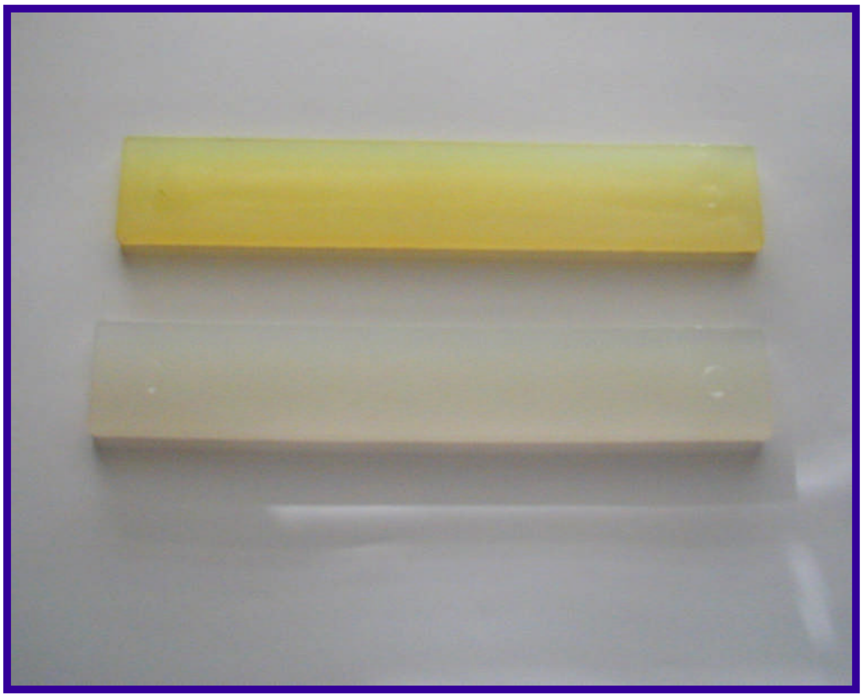
Reactions of Hindered Amine light stabilizer with antioxidants are known. See the graphic below.



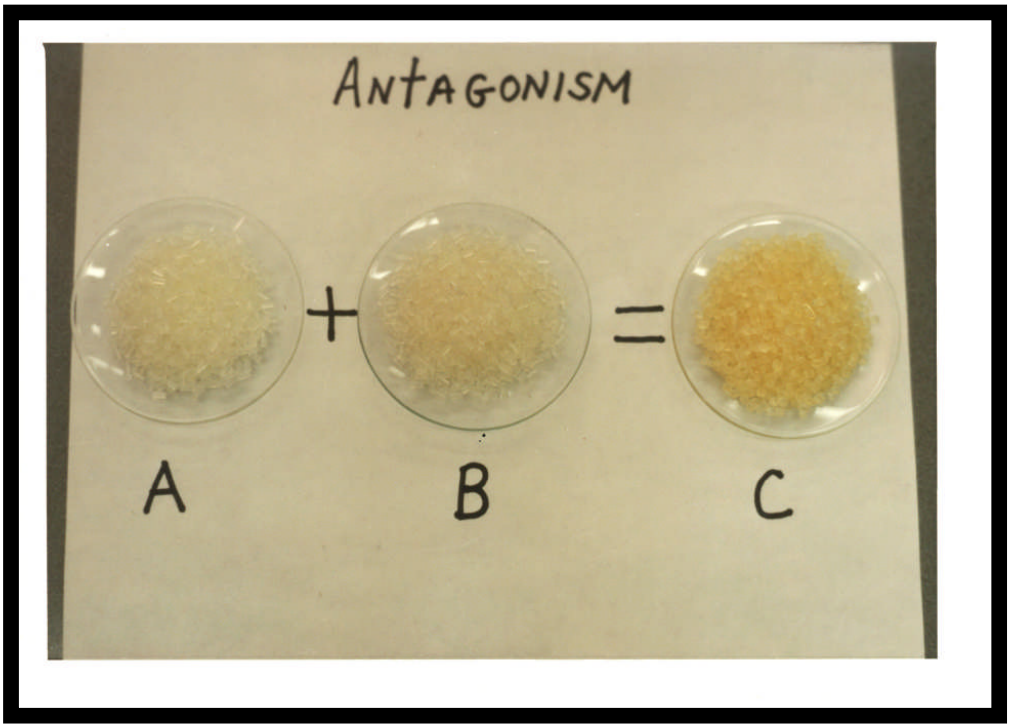
INTERACTION OF HALS WITH ANTIOXIDANTS

Secondary hindered amines being more basic than tertiary, acetylated or amino ethers amines are more prone to reactions with phenolic antioxidants to cause discoloration.

Transformation of antioxidants by base catalysed oxidation reactions in solution: PP bars with antioxidant yellowing

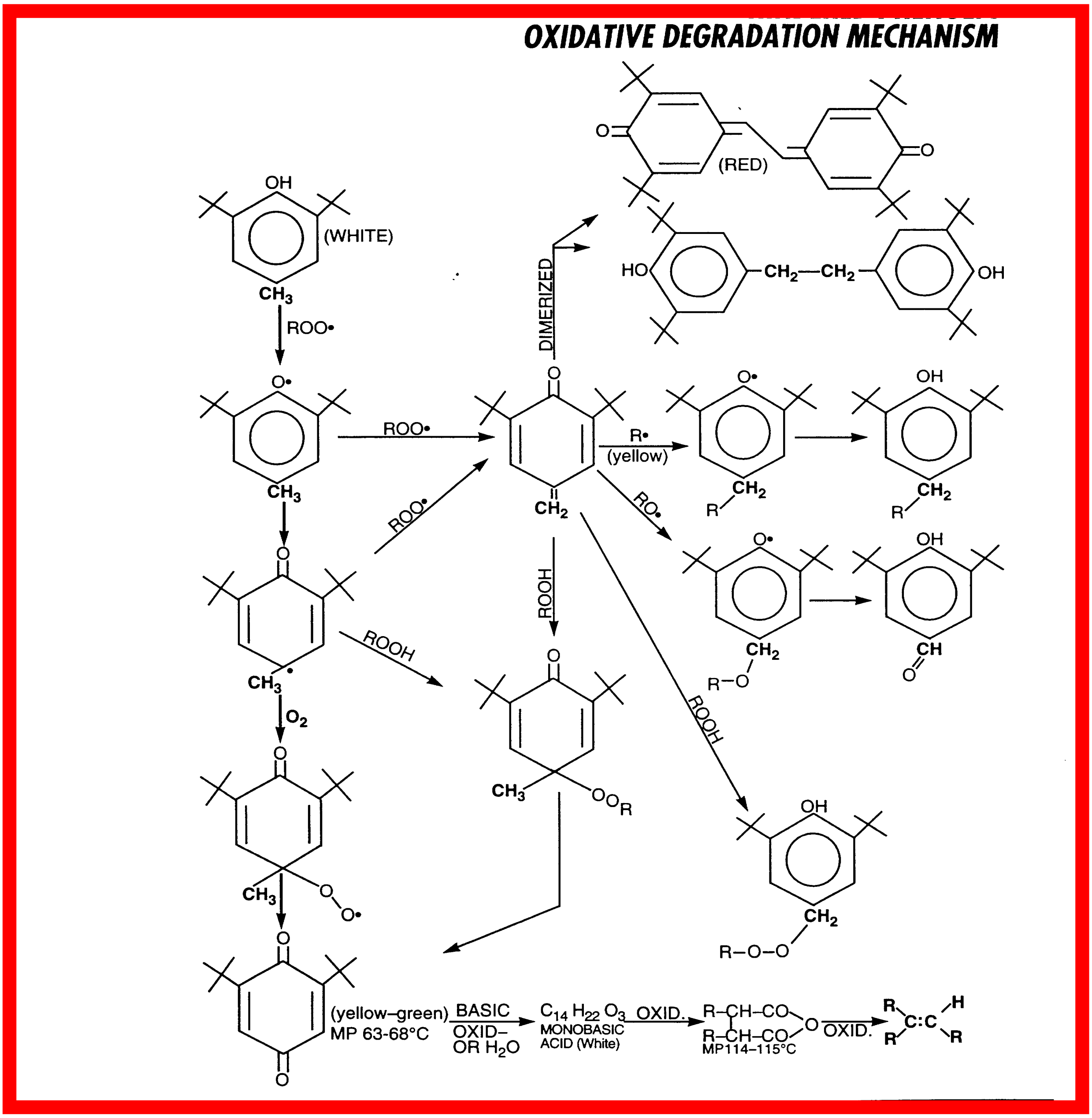


Antagonisms between two resins containing two distinctly different antioxidants mixed together to give a greater yellowing than the sum of each individual yellowing.



**Based Catalyzed oxidation of Octadecyl-3-(3,5-di-tertiary butyl-4-hydroxyphenyl)-propionate.
The three phases of discoloration are common based on the degree of base catalyzed oxidation.**

Mechanism of Antioxidant Transformation:



OXIDATIVE DEGRADATION MECHANISM

Although this is a standard chemical route to free radical chemistry of a phenolic antioxidant it is not the complete picture regarding the many sources for discoloration.

Besides based catalyzed transformation and free radical chemistry we have gas staining otherwise referred to over the many years as gas fading and gas yellowing. The terms are used randomly to refer to the affects of prompt oxides of nitrogen on discoloration of phenolic antioxidants. In most cases yellowing occurs but a host of other colors can manifest themselves from green and red shade yellows, oranges, red and blue. These chemistries will be discussed in future bulletins.

The main purpose of this bulletin was to illustrate basic substances will alter the nature of the stabilization system in polyolefins.

Discoloration may occur during melt compounding or in post storage in the dark. Dark storage yellowing is different in that either gas staining can occur or interactions with cardboard contaminants in boxes that diffuse into the pellets stored in the box causing yellowing or Cardboard yellowing. Pinking and Canary yellowing are also alternative forms of discoloration common today.

Furthermore, current changes in global availability of off patent primary and secondary antioxidants present a new problem related to purity of the substance.

Purity down to 83% is very common for Octadecyl-3-(3,5-di-tertiary butyl-4-hydroxyphenyl)-propionate.

The reason so few are aware of this information is simple. Few ever receive or request a Certificate of Purity and in many cases those who do receive the certificate find later the information was false.

The cost affiliated with routine testing of incoming additives is avoided and the risk downstream becomes exponential when the problem manifest itself in storage or at the customer.

Competition in the market globally forces many to ignore checks and balances in their production and take the risk daily of creating problems that could be avoided by routine checks analytically.

This trend continues globally when better alternatives exist to control discoloration! Considering the limited research and product development efforts today we must rely on past experience and a knowledge base that is becoming scarce. Global supply of additives must be routinely checked to insure quality and purity to avoid problems with inconsistent performance.