

# antioxidants and antiozonants

*Most rubber articles need protection against attack and degradation from their environment beyond what the polymer and cure systems can provide. Protection against exposure and decomposition from environmental conditions such as solvents, oils, detergents, heat, cold, light, ozone, and oxygen are to name a few. This two-part Solutions insert will deal with the Selective Protective Materials known as Antioxidants and Antiozonants.*

## Part I – oxidation / ozonation of rubber

### a brief history

In the late 19th and early 20th centuries, articles made from rubber had very poor weathering characteristics. Natural rubber was the only elastomeric polymer available for commercial use at that time. Articles made from natural rubber would soon become soft and tacky. They would no longer be serviceable. Chemists determined the cause of degradation and pre-mature failure of rubber articles was due to reaction with oxygen in the atmosphere. Knowing this, chemists worked at identifying chemicals that would extend the useful service life of a rubber product by protecting the rubber article from “**oxidation**”. Naturally occurring materials such as waxes, coal tar, creosote and many other products were used early on to “coat” rubber articles; providing the needed protection from oxidation. These protective coatings would be “scuffed” or “worn” off and the unprotected rubber would soon fail; resulting in the need to find a more permanent solution. As a result, it was found that certain phenols, hydroxylamine derivatives and secondary aromatic amine derivatives were useful in retarding the degradative effects of oxygen. Instead of “coating” the surface of the rubber article, these chemicals were incorporated into the rubber compound during mixing. **The benefit of this method would allow the protective chemical(s) to: 1) react with oxygen that was entrained in the rubber compound as a result of mechanical mixing and 2) would bleed toward the surface over time; offering a continuous supply of protection for the rubber article.** These chemicals became known as “**Antioxidants**”.

The discovery of “**Antiozonants**” occurred early in the 20th century, but it wasn’t until mid-way through the century before they became widely used. It was discovered that rubber articles (mainly tires) stored for several years quickly failed when put into use. Chemists were baffled because these tires were failing so quickly. After all, they contained antioxidants to protect them against attack from  $O_2$ . Chemists analyzed this “static storage” type of failure, and determined it was not the result of oxygen, but due to ozone ( $O_3$ ) in the atmosphere that attacked the rubber and resulted in the catastrophic failure of these tires.

## definitions

Often the terms “antioxidant” and “antiozonant” are used synonymously; even though they have different functions in a rubber compound.

**Antioxidants** – are chemicals that are used to protect rubber articles against attack from oxygen ( $O_2$ ).

**Antiozonants** – are chemicals and / or waxes that “bleed” to the surface of a rubber article, to protect it against attack from ozone ( $O_3$ ).

For long-term storage protection, some rubber articles are sealed with an exterior coating of wax or similar substance for additional protection against attack from ozone.

Oxygen comprises approximately 20 percent of the earth’s atmosphere. On the other hand, ozone comprises only a few parts per hundred million (pphm). The attack of ozone on unprotected rubber is much more aggressive than is oxygen. There can be a synergistic effect between antioxidants and antiozonants. Most antiozonants have a dual functionality. They not only protect against ozonation, but most **will** protect against oxidation as well. Antioxidants however, **will not** protect against ozonation.

To the naked eye, a rubber article that has been degraded by either oxygen or ozone looks like there is a “cloudy,” silver-gray film on the surface of the rubber. This is commonly referred to as “frosting”. Often this film is mistaken for “bloom”. The key is, a chemical that is blooming to the surface of a rubber article, resulting in a cloudy film, can be washed or rubbed off. Surface degradation due to attack from either oxygen or ozone can not. Upon close examination under low power microscope you can see the “cracks” on the surface of the rubber article.

***Key: A way to tell the difference between a rubber article that has been degraded by oxygen and one that has been degraded by ozone is by observing the direction of “cracks” that appear on the surface of the article.***

**Cracks that appear due to the attack of ozone run perpendicular to the direction of the “grain” or stress applied to the rubber article.**

**Cracks that appear due to the attack of oxygen upon a rubber article are random in their orientation.**

The picture on the next page shows evidence of degradation of a rubber matt due to prolonged exposure to both ozone and oxygen.



**Effect of  $O_3$  on unprotected rubber**      **Effect of  $O_2$  on unprotected rubber**

**Note: The orientation of the cracks on the surface of the rubber.**

Photo courtesy of Akron Rubber Development Lab

Non-polar polymer systems provide the most protection against attack from either oxygen or ozone due to the saturation of their C-C bonds in the polymer backbone. Due to unsaturation in the polymer backbone, polar (diene) polymer systems lack the ability to withstand prolonged exposure to weathering (exposure to oxygen and/or ozone.) An example would be the C=C double bonds in natural rubber. The greater the degree of unsaturation in the polymer, the more severe the degradative attack from oxygen / ozone will be upon the rubber article. It only takes about **two percent saturation** of the polymer, with oxygen, for a rubber article to fail and become unserviceable. Once oxidation of rubber has started, the reaction becomes auto-catalytic and can only be terminated under certain conditions.

## theory of oxidation

There are two chemical radicals that, when formed, work to oxidize rubber, degrading it and causing a rubber article to fail. They are **peroxide** radicals and **hydroperoxide** radicals. Antioxidants (and antiozonants) react with these radicals to terminate the chain reaction causing oxidation of polar polymer systems; thereby prolonging the serviceability of a rubber article. Antioxidants also react with hydrocarbon radicals when they are formed. In doing so, antioxidants block the reaction sites that are available for the formation of peroxide and/or hydroperoxide radicals; thus retarding the oxidative process.

Chemically, antioxidants work to:

- 1) **eliminate peroxide radicals before they are able to form and do their damage.**
- 2) **destroy hydroperoxide radicals before they can do their damage. and /or**
- 3) **react with hydrocarbon radicals to “short-stop” the formation of oxy radicals.**

In a nut shell. . . . .

- **Peroxide radicals** are formed when oxygen ( $O_2$ ) reacts with a **hydrocarbon radical**. And, hydroperoxide radicals are formed when two peroxide radicals react with each other.
- **Hydrocarbon radicals** are formed when a hydrogen atom (-H) is “knocked off” the **hydrocarbon chain**.
- **A hydrocarbon chain** will lose a hydrogen atom when enough energy is introduced into the system to liberate a hydrogen (-H) atom.
- **Energy** is introduced into a rubber system when the temperature of the rubber is elevated.
- The **temperature** of a rubber article is elevated when **heat, UV light** and/or **motion** (stress or dynamic force) is applied to the system.

**There is a second way hydrocarbon radicals are formed.**

Hydrocarbon radicals are formed by “mechanical” chain scissioning resulting from the mixing process.

During mixing, the polymers’ macromolecules are “scissioned” by the shearing action of the mixer. When this happens, these severed ends constitute **hydrocarbon free radicals**.

Also, during mixing, air ( $O_2$ ) is trapped in the polymer matrix. The trapped oxygen will react with severed ends of the hydrocarbon chains forming destructive peroxides.

Antioxidants that are blended into the compound are available to react with the mechanically formed hydrocarbon radicals. . . . . thus inhibiting oxidation.

Rubber does not have to be mixed or cured for the destructive forces of oxygen to attack. Unsaturated synthetic polymers are susceptible to attack from oxygen and/or ozone. To protect these polymers from oxidation, manufacturers will often add small amounts of a secondary (synergist) antioxidant (i.e. Phosphites) to the emulsion stage of polymer processing. This ensures that the polymer is protected when it is coagulated and stored before use. Nitrile, SBR, polychloroprene and synthetic polyisoprene are examples of polymers that have antioxidants added to their latex phase of processing to protect them from oxidation. Natural rubber polymers normally do not need the addition of “polymer stabilizers” to be protected against oxidation. Natural rubber already contains naturally occurring antioxidants that protect the polymer from oxidation.

## solubility . . . . in rubber

One of the key properties of antidegradants (antioxidants and /or antiozonants) is their solubility in the rubber matrix. The faster the rate of bloom, the **less soluble** the antidegradant is in the polymer system. The rate of bloom of antidegradants is not a fixed constant. It varies according to the polymer system and type of antidegradant used. Antidegradants are intended to bleed slowly to the surface of a rubber article ensuring a continuous supply of the protecting chemical at the surface. The introduction of long-chain aliphatic hydrocarbons into a stabilizer molecule decreases volatility and increases the solubility of the antidegradant in hydrocarbon polymers. Slowing volatility and increasing solubility of antidegradants improves their performance.

Other factors that have an effect on the rate of bloom are other chemical additives such as waxes, process aids, plasticizers and cure systems. The state of cure, temperature and dynamic conditions will also determine the rate an antidegradant bleeds toward the surface.

Generally, waxes and process aids will form a film on the exterior surface of a rubber article; providing a temporary, physical barrier of protection against attack from ozone.

Once on the surface of the rubber, antidegradants will react with free radicals when they are formed. A “re-freshening” of the surface with antidegradants, over time, ensures prolonged serviceability of the rubber article.

## oxidation reaction mechanism

**The Oxidative Reaction Mechanism**  
**Depicting the Attack of Oxygen on**  
**an Unsaturated Hydrocarbon Chain**  
**is outlined below.**

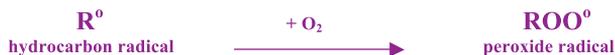
<b>RH</b>	<b>= hydrocarbon chain</b>
<b>Ro</b>	<b>= hydrocarbon radical</b>
<b>ROo</b>	<b>= peroxide radical</b>
<b>ROOo</b>	<b>= peroxide radical</b>
<b>ROOH</b>	<b>= hydroperoxide</b>
<b>ROOR</b>	<b>= stable bond</b>
<b>R-R</b>	<b>= stable bond</b>

### Initial Rxn:



In the **initiation reaction**, energy is used to start the reaction by severing a hydrogen atom from the polymer chain. This forms a hydrocarbon free radical and hydrogen. At this point, antioxidants can react with the hydrocarbon radicals to “short-stop” the formation of peroxide and/or hydroperoxide free radicals resulting in terminating the oxidation process.

If left unchecked, the next step, **propagation reaction** is auto-catalytic. Hydrocarbon free radicals are reacted with oxygen to form peroxide radicals.

**Propagation Rxn:**

Peroxide radicles are very unstable and react very quickly.



If a peroxide radical reacts with a hydrocarbon, a hydroperoxide radical and a hydrocarbon radical is produced. The production of a hydrocarbon radical starts the process all over again.

Hydroperoxide radicals are thermally unstable and decompose to generate two new free radicals.



When two hydroperoxide radicals are formed, they will react to form an alkoxy radical and a peroxide radical. Then the process starts all over again! (As shown in the rxn above)

**Termination Rxns:**

The auto-catalytic oxidation reaction process can be terminated in either of three ways.

1) When two hydrocarbon radicals react, they form a stable cross-link.



2) When a hydrocarbon radical reacts with a peroxide radical, they will form a stable cross-link.



3) When two peroxide radicals react, they form a stable bond.

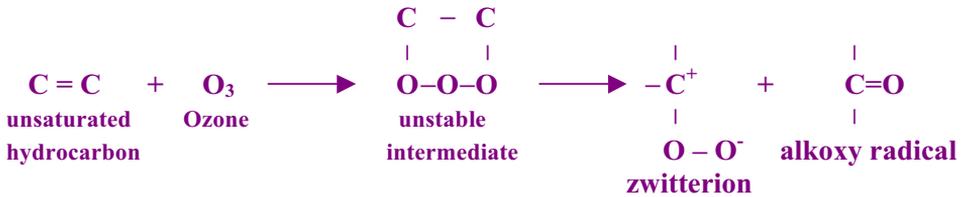


## ozonation reaction mechanism

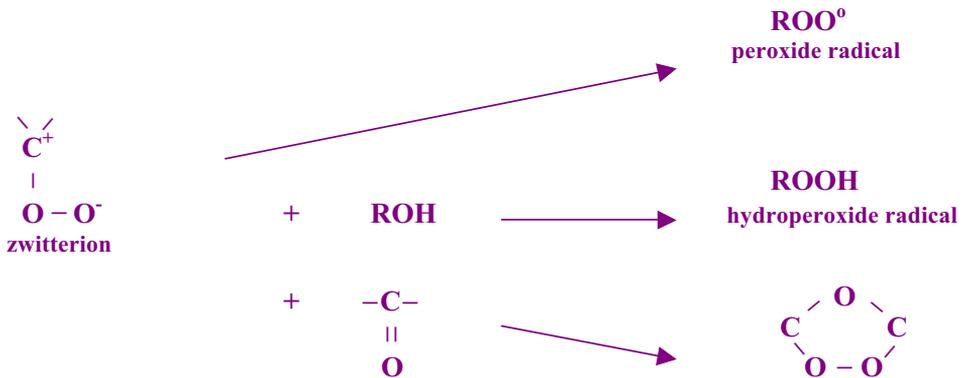
The initial ozonation reaction mechanism is different from the reaction of oxygen.

**Ozone reacts at the C=C double bond sites on the hydrocarbon backbone.**

This C=C reaction with O<sub>3</sub> forms an intermediate ion (**Zwitterion**).



The Zwitterion will react to form oxy radicals (either a peroxide free radical or a hydroperoxide free radical). A more stable ozonide can be formed if the Zwitterion reacts directly with an alkoxy radical



At this point, the **auto-catalytic** and the **termination rxn mechanisms** are similar to those shown above in the oxidative reaction process.

**Note:** *The difference between the reaction mechanism of oxygen and ozone is that the reaction of ozone is a surface phenomenon while the reaction of oxygen can be both surface and an internal phenomenon.*

## effect of heat

Elevated temperatures are another key property that plays a major role in the degradation of rubber products. Heat is detrimental to rubber products and accelerates oxidation. Generally, there are two conditions that will elevate the temperature of rubber articles. 1) curing and 2) dynamic flex.

**curing** – certain antidegradants are designed to protect uncured rubber during mixing and storage. These antidegradants lose their effectiveness at curing temperatures. (i.e. Phosphites) While phosphite antioxidants are very effective as polymer stabilizers, they are burned up during higher vulcanization temperatures.

**dynamic flex** – refers to the stress applied to a rubber product during its intended use. Most antiozonants and certain amines are designed to provide anti-flex cracking properties to rubber products.

The free radical scavenging ability of certain chemical groups of antidegradants are limited by elevated temperatures. As an example, most, if not all, hindered phenols are capable of providing long-term thermal stability with temperatures ranging from 0–575°F. On the other hand, phosphites, hydroxylamines and thiosynergists lose their effectiveness during vulcanization. Thiosynergists are most effective at free-radical scavenging or hydroperoxide decomposition during polymer processing. They are not effective as long-term thermal stabilizers. By sacrificing themselves during the curing process, they lessen the workload on the more thermally stable antidegradants.

## peroxide decomposers:

Most peroxide decomposers are derived from di- and tri-valent phosphorus compounds. They are thermally activated to decompose peroxides and hydroperoxides. In the presence of dialkyl esters, hydroperoxides are reduced to alcohols, and the sulfide group is oxidized to an acid which is capable of further catalyzing the decomposition of hydroperoxides to more stable molecules.

## effect of uv light

The degradation of rubber can also be triggered by UV light. Hindered amines (HALS), commonly thought of as being effective UV light stabilizers, are also useful for long-term thermal stability. Their effectiveness is the result of free-radical scavenging. However, HALS are virtually ineffective at temperatures higher than 300°F. Therefore, hindered amines should be used in combination with benzimidazole or certain hindered phenols in order to provide long-term thermal stability.

## effect of metallic ions

Metal ions will react with oxy radicals and “poison” rubber. In particular, metallic ions of copper, manganese, cobalt and/or iron will catalyze the oxidative process in rubber. They break down peroxide radicals and accelerate the oxidation process. The ability of metal ions to catalyze oxidation can be inhibited by metal deactivators. Certain antidegradants have the ability to chelate metal ions which decreases the ability of the metal ions to produce radicals. They are referred to as “metal deactivators”. They can be either antioxidants or antiozonants. **Antiozonant PD-1** and **Antioxidant 58** are examples of Akrochem products that are excellent metal deactivators.

## effect of oxidation on polymers

Upon oxidation, polymer systems will either become soft and tacky or hard and brittle. This is caused by either polymer chain scissioning (softening) or cross-linking (hardening). Natural and synthetic polyisoprene, Butyl and “G” type Neoprene polymers tend to undergo chain scissioning and become soft and tacky. Nitrile, SBR and PBR are some of the polymer systems that tend to harden or undergo cross-linking.

Non-polar polymer systems such as EPR / EPDM, Silicone / Fluorosilicone and FKM have very little reaction sites available for oxidation or ozonation to occur. Generally, these saturated polymer systems do not need the addition of antidegradants. In fact, non-polar polymers can be used as antidegradants themselves. By blending a non-polar polymer with polar polymer system, the non-polar polymer will provide added protection to the rubber article from oxidation. As an example, blending 25 to 30 phr EPDM with natural or synthetic polyisoprene will significantly retard the oxidative process. The effect of oxidation is highlighted for various polymer systems in **TABLE I** on the next page.

**TABLE I**  
**RELATIVE ORDER OF POLARITY WITH THE EFFECT OF**  
**OXIDATION ON VARIOUS POLYMER SYSTEMS**

High Polarity	Chemical Name	Common Name	ASTM D 1418	Effect of Oxidation	Resistance to Oxygen	Resistance to Ozone
↑ ↓	Nitrile (50% ACN)	Nitrile	NBR	<b>Hardens</b>	Fair	Poor
	Urethane (Polyester/Polyether)	Urethane	AU / EU	<b>Hardens</b>	Excellent	Excellent
	Ethylene Vinyl Acetate	Ethylene Vinyl Acetate	EVA	<b>Hardens</b>	Outstanding	Outstanding
	Nitrile (30% ACN)	Nitrile	NBR	<b>Hardens</b>	Fair	Poor
	Polyacrylate	Acrylic	ACM	<b>Hardens</b>	Excellent	Excellent
	Epichlorohydrin	Epichlorohydrin	ECO	<b>Hardens</b>	Very good	Very good
	Chlorosulfonated Polyethylene	Hypalon®	CSM	<b>Hardens</b>	Excellent	Excellent
	Chloroprene	Neoprene (G types)	CR	<b>Softens</b>	Good	Excellent
	Chloroprene	Neoprene (all others)	CR	<b>Hardens</b>	Good	Excellent
	Nitrile (20% ACN)	Nitrile	NBR	<b>Hardens</b>	Good	Fair
	Chlorinated Polyethylene	Chlorinated Polyethylene	CPE	<b>Hardens</b>	Excellent	Excellent
	Highly Saturated Nitrile	Nitrile	HNBR	<b>Hardens</b>	Good	Good
	Styrene Butadiene	GRS	SBR	<b>Hardens</b>	Good	Poor
	Polybutadiene	Butadiene	BR	<b>Hardens</b>	Excellent	Poor
	Natural Polyisoprene	Natural Rubber	NR	<b>Softens</b>	Good	Poor
	Synthetic Polyisoprene	Synthetic Rubber	IR	<b>Softens</b>	Good	Poor
	Polysulfide	Thiokol®	PTR	<b>Hardens</b>	Excellent	Excellent
	Halogenated Butyl	Butyl	HIIR	<b>Softens</b>	Excellent	Excellent
	Ethylene Propylene (dimer)	EPDM	EPDM	<b>Hardens</b>	Good	Excellent
	Ethylene Propylene (monomer)	EPR	EPR	<b>Hardens</b>	Good	Excellent
Isobutylene-Isoprene	Butyl	IIR	<b>Softens</b>	Excellent	Excellent	
Fluorinated Hydrocarbon	Fluorocarbon	FPM	<b>Hardens</b>	Excellent	Outstanding	
Polysiloxane	Silicone	PSi, VSi, PVSi	<b>N/A</b>	Excellent	Excellent	
Fluorinated Polysiloxane	Fluorosilicone	FVS	<b>N/A</b>	Outstanding	Outstanding	
Low Polarity						

*Akrochem carries a variety of antioxidants and antiozonants that are commonly used in rubber compounding. Part II of this “Solutions” paper is a discussion of the chemistry and use of these antidegradants.*



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