# antioxidants and antiozonants...cont'd

Part I of this Solutions, was a discussion of the destructive nature that oxygen and ozone have on rubber and articles made from rubber. In part II we will discuss the chemistry and use of antidegradants for extending the serviceability of rubber articles.

Akrochem carries a variety of antioxidants / antiozonants that are commonly used in the compounding of rubber and plastics.

# Part II - antidegradants

Key: "The usefulness of an antidegradant depends largely on three factors: 1) its solubility in the substrate, 2) its radical-scavenging capability, and 3) its volatility under dynamic conditions."

# classifying antidegradants

Besides the chemical group associated with an antioxidant or antiozonant, they are classified by other characteristics. They can be classified as either: staining / non-staining, discoloring / non-discoloring or whether they are primary or secondary.

# primary / secondary

**Primary** antidegradants are mixed into a rubber compound. They are generally heat stable and are not fugitive. (Examples are: Amines and Phenolics)

**Secondary** antidegradants are generally used to stabilize polymer systems during their solution phase of manufacture. They are deactivated by cure systems and are not heat stable. (examples are: Phosphites and Thioesters)

# staining / non-staining:

Staining occurs in two forms. . . . . . contact and migratory.

**Contact staining** is the discoloring of an object that comes in contact with a rubber article containing a staining antidegradant. An example of contact staining is located on page 2, in the picture on the left. This is shown by the trailing tread design.

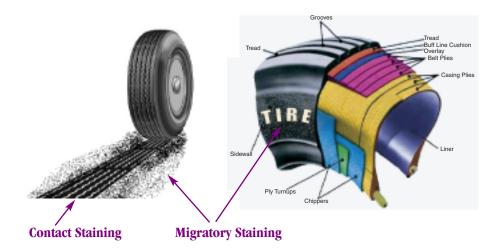
**Migratory staining** is the discoloring of an object that is in close proximity, *but does not touch*, the rubber article containing a staining antidegradant.

Migratory staining can occur two ways.

- 1. By not touching the object being stained. This is presented by the picture below in the left. Migratory staining is represented by the trailing stains on either side of the tread.
- 2. By penetrating through a solid. . . . . staining a solid on the other side. An example of this type of migratory staining would be a tire inner liner or ply compound that contains a staining antidegradant, bleeding through to the outer sidewall affecting the "jet-blackness" of the tire.



If the tire has a colored sidewall or colored raised lettering, when stained, they will turn a dirty yellow. Examples of migratory staining are shown in the pictures below



Another example of migratory staining is if the rubber door seal on an automobile contains a staining anti-degradant, the stain will migrate onto the car paint. . . . causing a discoloration of the paint.

# discoloring / non-discoloring

An antidegradant is considered to be discoloring if it is compounded into rubber compound and it causes a significant change in the color of the cured rubber article. Some antidegradants are discoloring as well as staining.

A good way to keep staining and discoloring separate is to remember that discoloring / non-discoloring relates to a change within the rubber compound; while staining /non-staining is a result of what the compound does to its environment.

# types: amines & amine derivatives, phenols, phosphites, quinolines & thioester derivatives

The oxidation/ozonation of rubber can be slowed down considerably by the addition of anti-degradants. These are chemicals that scavenge and neutralize "oxy" radicals before they have a chance to auto-catalyze the polymer. Antidegradants are divided into several different chemical categories with 1) Amines and Quinolines (staining), 2) Phenolics (non-staining) and 3) Phosphites (non-staining) and Thioesters (non-staining) being the most common. **TABLE II** on page 7 lists some common antidegradants and their characteristics.

#### **Amines & Amine Derivatives**

Examples of amine antioxidants are **AKROCHEM® A.O. S and PANA**. Certain amines and amine derivatives were the first chemical antidegradants to be used in rubber and are still some of the most common types of antidegradants used by the rubber industry. Amines offer heat resistance, anti-flex cracking properties and neutralize heavy metal poisoning. However, their

use is limited to black or non color sensitive applications due to their highly staining and discoloring characteristics.

#### **Phenylenediamines**

Examples of phenylenediamine antiozonants are:

**AKROCHEM® PD-1, PD-2** and **MPD-100.** Phenylene-diamines are divided into three (3) major groups. They are differentiated by the attached functional group(s). These functional groups are: 1) diaryl, 2) dialkyl or 3) alkyl-aryl.

**Basic Chemical Structure** 

1) <u>Diaryl</u>-p-phenylenediamines have limited solubility, are the least volatile and are slow to migrate. They should be used with waxes. 2) <u>Dialkyl</u>-p- phenylenediamines are very active, more volatile and they rapidly deactivate oxy radicals. They are highly staining, fast migrating and can activate scorch. 3) <u>Alkyl-aryl</u>-p-phenylenediamines are very active with carbon groups ranging from 3 to 8. Above eight (8) carbon groups, their activity rapidly decreases. Low molecular weight products are easily leached by water. Higher molecular weight products are less volatile. As a group these antidegradants are considered to be antiozonants. Most offer protection against oxygen as well. They are highly effective peroxide radical scavengers and provide outstanding flex-cracking resistance. They are more effective than phenolics. Typical loading is 0.5 to 4.0 phr. They are more effective in Polychloroprene at lower concentrations  $(0.4-1.5\,\mathrm{phr})$ . They are effective with most cure systems and have no significant effect on physical properties. However, they are highly staining. Phenylenediamines can be used synergistically with certain benzimidazole antioxidants to improve thermal stability and inhibit metal poisoning.

### **Hydroxylamines:**

Hydroxylamines are very powerful when compared to conventional phenolic antioxidants and phosphite stabilizers. Hydroxylamines are effective during the mixing phase, but they do not exhibit long-term thermal stability. They are considered to be staining, primary antioxidants. Typical loadings are from 0.5 to 2.0 phr.

Basic Chemical Structure

They are most effective in NR, IR, SBR, Nitrile and CR polymer systems and are most effective with sulfur cure systems. They do not have any significant effect on physical properties. They can be used synergistically with other amine antidegradants.

#### **Benzofuranones:**

Benzofuranones are similar to hydroxylamines in that they are more powerful than conventional phenolic antioxidants or phosphite stabilizers. Benzofuranones are <a href="hydrogen atom donors">hydrogen atom donors</a>. They are scavengers of <a href="hydrocarbon">hydrocarbon</a>, peroxide and hydroperoxide free radicals. By scavenging hydrocarbon free radicals, benzofuranones act more like "preventive maintenance," as compared with more traditional antioxidants; which operate by reacting with peroxide and hydroperoxide radicals. By neutralizing hydrocarbon free

Basic Chemical Structure

radicals, benzofuranones inhibit the auto-oxidation cycle by shutting it down as soon as it starts. As a group, Benzofuranones are non-staining non-discoloring, primary antioxidants. Typical loadings are 0.5 to 3.0 phr. They are effective in most polymer systems and with sulfur cure systems.

#### **Hindered Amines:**

Most hindered-amines are classified as "light stabilizers" (HALS). They are derivatives of 2,2,6,6-tetramethylpiperidine and are extremely effective in protecting polymeric materials against UV light degradation. As a group, hindered amines are primary antioxidants and are effective in low concentrations at neutralizing free radicals. Typical loadings are 0.5

**Basic Chemical Structure** 

-2.0 phr. For anti-flex cracking protection, higher loadings are needed (2.0-3.5 phr). Unlike other amines, hindered amines are considered to be non-staining and non-discoloring. They are effective in most polymer and cure systems. Their effect on cure systems is minimal and they do not have any significant affect on physical properties.

#### Phenolics:

Examples of phenolic antioxidants are: **AKROCHEM® BHT, 12, 235, 250-SVA, 358-SWC and 383-SWP**. With the increasing popularity of latex products and the coloring of rubber, there was a need to develop antidegradants that were non-discoloring and non-staining. This led to the discovery and use of phenolic, phosphites and hindered amines (as mentioned above). The effectiveness of phenolics is greatly reduced in the presence of carbon black. Their main use is in color sensitive applications. They are effective over a wide temperature range.

#### **Hindered Phenols:**

Examples of hindered phenolic antioxidants are:

**AKROCHEM® 32, 33, 43, 1010, 1024** and **1076**.

Even the simplest phenolic antioxidants have a very complex chemistry compared to other types of antidegradants. Upon reacting with free radicals, phenolic antioxidants impart much less color change than aromatic amine antioxidants and are considered to be non-discoloring and non-staining.

**Basic Chemical Structure** 

As a group, they are considered to be primary antioxidants. Typical loadings are 0.25 to 2.0 phr and they are effective in most polymer and sulfur cure systems. They do not have any significant affect on scorch or physical properties. They can be used synergistically with certain phenylenediamine antiozonants.

# **Phosphites:**

An example of a phosphite antioxidant is: **AKROCHEM® TNPP**. Phosphite antioxidants are characterized by having a trivalent phosphorous atom bridging three phenol groups. Phosphites will hydrolyze readily and loose their effectiveness with prolonged contact with water or during vulcanization. For this reason, they are used almost exclusively as "emulsion stabilizers" during the latex phase of synthetic polymer pro-



**Basic Chemical Structure** 

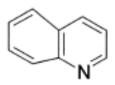
duction. As a group, they are considered to be non-staining / non-discoloring, secondary antioxidants. Trivalent phosphorus compounds reduce hydroperoxide radicals to their corresponding alcohols. Phosphite polymer stabilizers are used most frequently in combination with hindered phenols.

Esters of phosphorous acid are derived from aliphatic alcohols and unhindered phenols. They hydrolyze readily and special care must be taken to minimize exposure to water or high humidity. The hydrolysis of phosphites is retarded by the addition of a small amount of a base. The phosphorous acid formed by exposure to moisture (hydrolysis) can be very corrosive to processing equipment; especially at elevated temperatures. Aromatic amines and phenolic antioxidants work to eliminate **peroxide radicals** before they are formed. Phosphites and thioesters work to destroy **hydroperoxide radicals** before they can react with the hydrocarbon chain. Phosphites are especially active in unsaturated polymer latex systems such as IR, CR, SBR and Nitrile. Typical loadings are: 1 to 2 percent. They can be used synergistically with most hindered phenols. By introducing longer, aliphatic chains into these stabilizer molecules, their volatility can be decreased and solubility increased. This improves the stability and performance of the primary antioxidant.

# Quinolines:

An example of a quinoline antioxidant is: **AKROCHEM® DQ**. Quinoline antioxidants have been a workhorse for the rubber industry for decades.

They are particularly useful in rubber goods requiring resistance to high temperatures. They are also used as a copper and manganese inhibitors. Quinolines are extremely effective in protecting rubber products based



**Basic Chemical Structure** 

on natural rubber, polyisoprene, SBR, EPR/EPDM, NBR and polybutadiene against oxygen and heat simultaneously. Quinolines are less suitable for polychloroprene systems. They provide some anti-flex cracking properties in NR. Quinoline antioxidants are not transient, but are discoloring and cause some staining. Increasing amounts improves scorch resistance but increase cure time. Excellent antioxidant for peroxide cures due to minimal interference.

#### Thioesters:

Thioesters are divalent sulfur derivatives of phosphites where the adjoining aliphatic hydrocarbon chains are joined together with a divalent sulfur instead of

R-S-R

Basic Chemical Structure

the trivalent phosphite atom. They are similar to phosphites in that they hydrolyze readily and loose their effectiveness during vulcanization. They are dialkyl esters of thiodipropionic acid. 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. Thioesters tend to decompose at high processing temperatures. Their odor tends to limit their use. As a group, they are considered to be secondary antioxidants. Typical loadings are 1 to 2 percent in synthetic <u>latex systems</u>. They can be used synergistically with hindered phenolic antioxidants.

# synergy: mixtures of antidegradants

The effective use of antidegradants is not linear. Generally, about three (3) phr is the maximum usage level for a <u>single</u> antioxidant or antiozonant in a rubber compound. Beyond this, the rubber compound will become "saturated" with the antidegradant and the excess chemical will "bloom" to the surface. This is when synergy between antidegradants can help. If using three (3) phr of antioxidant "A" does not provide the needed protection, a second antioxidant "B" can be added to the rubber compound. As an example, if using 3.0 phr of **antioxidant 60** did not provide the necessary long-term

protection required, then reformulating and using a combination of two different (but chemically compatible) antidegradants can be used to provide the level of protection needed. By using 2.0 phr of **antioxidant 60** plus 2.0 phr **antioxidant S**, the risk of "bloom" is minimal while the combination of the two antidegradants provides <u>outstanding</u> heat resistance. These antioxidants have different chemistries and work synergistically to provide a higher level of protection that would not be able to attainable with a <u>single</u> antidegradant.

Another example would be a blend of a phenolic antioxidant with a phosphite process stabilizer. This combination can supply the processing stability needed (phosphite – **A.O. TNPP**) while providing the <u>long-term</u> protection against rubber poisoning (phenolic – **A.O. 33**). Thermal stability of the above example can be improved by adding a third antidegradant (**A.O. 353-SWP**). (Effective loading of antidegradants are given in **TABLE IV** on page 9.)

For an application that calls for thermal stability and ozone protection, a blend of **A.O. DQ** and **A.Oz. PD-2** could provide the properties needed.

When outstanding dynamic flex properties are desired, a combination of **A.O. 58** and **A.Oz**. **PD-2** would be an excellent choice. If FDA acceptance is needed, substitute **A.Oz. PD-1** in place of **A.Oz. PD-2**.

If the application is color sensitive, and ozone protection is needed along with heat stability, **Nibud PM 70** in combination with a phenolic antioxidant (i.e. **A.O. 58**) would be a very good combination. Especially if used in Neoprene or Epichlorohydrin compounds. (Anti-degradant synergy with polymer systems is shown in **TABLE IV** on page 9.) Resistance to metal poisoning can be achieved in the above example by adding a third antidegradant (i.e. **A.O. 1024**).

For "color sensitive" applications requiring "phenol-free" stabilization, synergistic mixtures of hindered amine (for long-term thermal stability) with hydroxylamine (for processing stability) can be used to avoid discoloration of the final product.

A rubber compounder can use an amine antioxidant (i.e. **A.O. S**) to eliminate peroxide radicals and a phosphite antioxidant (i.e. **A.O. TNPP**) to eliminate hydroperoxide radicals in the same compound. In this example, **A.O. TNPP** will also provide protection against metal poisoning.

Other examples of Akrochem products that work synergistically together are listed in **TABLE II** on the next page.

# antagonistic mixtures of antidegradants

Mixtures of antidegradants can also work against each other. Chemistries that interfere with each other may not necessarily be obvious until the evidence is presented. For example, to ensure long-term thermal stability and good light stability, a combination of a phenolic antioxidant and a divalent sulfur compound can be used for thermal stability and a hindered amine for light stability. However, the oxidation products of the divalent sulfur compound (Thioester) can be quite acidic and can complex with the hindered amine, preventing the hindered amine from entering into its free-radical scavenging cycle. Other types of antagonistic chemistries can involve relatively strong acids or bases that can interact with the antidegradant(s) rendering them ineffective. Examples would be: 1)

1) airfloat clays which are very strong, naturally occurring, Lewis Acids (4-4.5 pH) or certain acidic retarders. 2) Acid scavengers such as magnesium hydroxide or certain silicates with their high pH will also complex with certain antidegradants, preventing them from scavenging free radicals.

TABLE II - Commonly Used Antioxidants / Antiozonants: Types & Property Matrix

					Staining Secondary				E)	Volatility	Anti-flex cross	cking	FDA St.
		Antioxid	Antiozo	mant.	3//Sec	Non-stor.	Dis-coloring	Solubility	, ( <b>L</b> ,	al Sta	Anti-flex cross	A. C.	FDA St.
		ntioxi	ntioz	rima	Stainin	31-10 011-84	is-cole	lubin	herm	olatin	nti-fi	eave	DAG
Chemical Type & Name	AKROCHEM Product	V	V	4	ş	2	Q	Š	=	4	¥	Ħ	E
AMINES													
Phenyl-A-Naphthylamine	Antioxidant PANA	1	-	P	1	-	Y	Н	Y	L	Y	N	Y
Octylated Diphenylamine	Antioxidant S	1	-	P	1	-	Y	Н	Y	L	N	N	Y
PHENYLENE DIAMINES													
N-Isopropyl-N'-Phenyl'-P-Phenylene Diamine	Antiozonant PD-1	-	1	P	1	-	Y	Н	Y	L	Y	Y	Y
N-(1,3-DimethylButyl)-N'-Phenyl-P-Phenylene Diamine	Antiozonant PD-2	_	1	P	1	-	Y	н	Y	L	Y	Y	N
Mixed Diaryl-P-Phenylene Diamine	Antiozonant MPD-100	-	1	P	1	-	Y	Н	Y	L	Y	N	Y
ACETALES													
Bis(1,2,3,6-Tetrahydro-benzaldehyde)- Pentaerythrityl Acetale	Antiozonant 70TBPA		1	P		1	N	н	Y	L	N	N	N
BENZIMIDAZOLES	Antiozonane /orbin		-	•		-	-11		•		-11	-11	- 1
Zn salt 2-mercapto 4 (5)-methylbenzimidazole	Antioxidant 58	1		P	L	1	N	н	Y	L	N**	Y	N
4,5 methyl mercapto Benzimidazole	Antioxidant 60	1	-	r P		1	N	Н	Y	L	N	Y	N
4,4'-bis(a,a'-dimethylbenzyl) diphenylamine	Antioxidant 405	1	-	r P	1	_	Y	Н	Y	L	N	N	Y
PHENOLICS	Antioxidant 403	•	-	1	Ľ	-	1	11	1	L	14	14	1
2,6-Di-t-butyl-p-cresol	Antioxidant BHT	1	_	P	L	1	N	н	Y	L	N	N	Y
	Altioxidalit BH1	Ť	_	Г	-	Ť	IN	п	1	L	IN	19	1
Butylated rxn product of p-cresol and dicyclopentadiene	Antioxidant 12	✓	-	P	-	1	N	н	Y	L	N	N	Y
Hindered Phenol	Antioxidant 32	1	-	P	-	1	N	Н	Y	L	N	N	Y
Hindered Phenolic	Antioxidant 33	1	-	P	-	1	N	Н	Y	L	N	N	Y
Hindered Phenolic	Antioxidant 43	1	-	P	-	1	N	Н	Y	L	N	N	Y
2,2'-Methylenebis (4-methyl-6-t-butylphenol)	Antioxidant 235	1	-	P	-	1	N*	Н	Y	L	N	Y	Y
2,5-di-t-amyl hydroquinone	Antioxidant 250-SVA	1	-	P	-	1	N	Н	Y	Н	N	N	Y
4-4'-thiobis (6-t-butyl-m-cresol)	Antioxidant 358-SWC	1	-	P	-	1	N	Н	Y	L	N	Y	Y
4-4'-butylidenebis (6-t-butyl-m-cresol)	Antioxidant 383-SWP	1	-	P	-	1	N	Н	Y	L	N	N	Y
Hindered Phenol	Antioxidant 1010	1	-	P	-	1	N	Н	Y	L	N	N	Y
Hindered Phenol	Antioxidant 1024	1	-	P	-	1	N	Н	Y	L	N	Y	N
Hindered Phenol	Antioxidant 1076	1	-	P	-	1	N	Н	Y	L	N	N	N
<u>OUINOLINES</u>													
2,2,4-trimethyl-1,2-hydroquinoline	Antioxidant DQ	1	-	P	1	-	Y	Н	Y	L	Y	Y	N
OZONE INHIBITOR													
Nickel Dibutyl Dithiocarbamate	Antiox. NiBud PM-70	-	1	P	-	1	Y	Н	Y	L	Y	N	N
PHOSPHITES													
tris (4-n-nonylphenyl) phosphite	Antioxidant TNPP	1	-	S	-	1	N	Н	N	Н	N	Y	Y

#### RED INDICATES SIGNIFICANCE

<sup>\*</sup> Antioxidant 235 will turn white compounds "pink" upon prolonged exposure to sunlight.

\*\* Except in polychloroprene where it markedly improves flex-cracking.

TABLE III - Synergistic Blends of Antidegradants with Attributes

AKROCHEM Product	Synergists	Affect of Synergy
AMINES		
Antioxidant PANA	PD-1, PD-2, MPD-100	Improves anti-flex cracking and ozone resistance
Antioxidant S	58, 60	Outstanding heat resistance.
PHENYLENE DIAMINES		
Antiozonant PD-1	PANA 58, 60 DQ	Improves anti-flex cracking Metal deactivation Protects against rubber poisons & imp. dynamic flex
Antiozonant PD-2	PANA, 58 DQ	Use in severe dynamic applications Protects against rubber poisons & imp. dynamic flex
Antiozonant MPD-100	PANA PD-1 & PD-2	Improves anti-flex cracking and ozone resistance Slows migration
ACETALES		
Antiozonant 70TBPA	Most phenolics	Outstanding ozone protection in Nitrile/PVC blends
BENZIMIDAZOLES		
Antioxidant 58	DQ, S, & 250-SVA PD-1, 1024 PD-2	Outstanding heat resistance Metal deactivation Use in severe dynamic applications
Antioxidant 60	S, 383-SWP 33, 235, PD-1, PD-2, DQ	Outstanding heat resistance Protection against rubber poisons
Antioxidant 405	58, 60	Outstanding heat resistance in HNBR
PHENOLICS		
Antioxidant BHT	Other phenolics TNPP	General purpose, resists hydrolysis & extends scorch Polymer stability
Antioxidant 12	Other phenolics	Extremely active, does not hydrolyze
Antioxidant 32*	60, PD-1	General purpose antioxidants, providing excellent heat
Antioxidant 33*	60, PD-1	resistance & protection against rubber poisons. In
Antioxidant 43*	60, PD-1	most cases, they can be used interchangeably.
Antioxidant 235	Other phenolics	General purpose, resists migration, low toxicity
Antioxidant 250-SVA	358-SWC	Insures long lasting antioxidant protection
Antioxidant 358-SWC	250-SVA 58	Insures long lasting antioxidant protection Outstanding heat resistance
Antioxidant 383-SWP	60	Outstanding heat resistance
Antioxidant 1010	58, 60	Excellent heat stability & color retention
Antioxidant 1024	58, 60	Improve heat resistance and metal deactivation & improves diesel fuel resistance
Antioxidant 1076	Other phenolics	Excellent heat stability & color retention
<u>OUINOLINES</u>		
Antioxidant DQ	60	Protection against rubber poisons and high temperature stability
OZONE INHIBITORS		
Antioxidant NiBud PM-70	Most phenolics	High temperature stability with specific polymers
PHOSPHITES		
Antioxidant TNPP	Most phenolics	Metal deactivation, polymer stabilizer

<sup>\*</sup>Antioxidants 32, 33 & 43 are very similar and generally can be used interchangeably.

TABLE IV - Polymer Type with Recommended Antidegradant & Loading

KEY: P = Preferred R = Recommended N = Not Recommended	Acretic	Butylor	tyl (IIR)	CPE (HIIR)	CRICE	(Stype)	CSM other typ	DAG	Epichk	EVA	Fluoro	Fluorogin	Latex	NR/III	IR IR	HNBD	Polyhus	Polysmic.	R	Siligon	erm	Therm	Uretha	Recommended Loading (phr)
AKROCHEM Product	Ac	Bu	Bu	Ĉ	Č	ð	S	E	Ep	EVA	Flu	FR	La	Ž	NBR	Ħ	Po	Po	SBR	Sil	Ę	Ę	S	Log
<u>AMINES</u>																								
Antioxidant PANA	N	N	N		R	R					N	N	N	R	R	R	R		R	N			N	1.0 - 3.5
Antioxidant S	N				P	P					N	N	N	R	R		R		R	N			N	1.0 - 4.0
PHENYLENE DIAMINES																								
Antiozonant PD-1	N -				- R	- R					N -	N -	N -	P	P	P -	P -		P -	N -			N -	1.0 - 3.5 0.4 - 1.5
Antiozonant PD-2	N										N	N	N	R	R	R	R		R	N			N	1.0 - 4.0
Antiozonant MPD-100*	N	N	N	R	P	P	N	R	N	N	N	N	N	-			R	N	R	N				1.0 - 4.0
	-	-	-	-	-	-	-	-	-	-	-	-	-	R			-	-	-	-				<1.0
ACETALES																								
Antiozonant 70TBPA	N				P	P					N			R	P	P			R	N				1.0 - 3.0
BENZIMIDAZOLES																								
Antioxidant 58	N				P	P					N	N								N				1.5 - 4.0
Antioxidant 60	N	R	R		N	N					N	N		R	R		R		R	N				0.5 - 3.0
Antioxidant 405	N										N	N		R	R	P	R		R	N				1.0 - 4.0
PHENOLICS																								
Antioxidant BHT	N	R	R								N		R	R	R		R		R		P	P	R	0.25 - 2.0
Antioxidant 12	N	R	R	N	P	P	N	R	N	R	N	N	R	P	P	P	R	N	P	N			N	0.25 - 1.5
Antioxidant 32	N	P	P	N	P	P	N	R			N	N	R	P	P	P	P	N	P	N		P	N	0.25 - 1.5
Antioxidant 33	N	P	P	N	P	P	N	R			N	N	R	P	P	P	P	N	P	N		P	N	0.25 - 1.5
Antioxidant 43	N	P	P	N	P	P	N	R			N	N	R	P	P	P	P	N	P	N		P	N	0.25 - 1.5
Antioxidant 235	N			N	P	P	N	R			N	N	P	P			P		P	N		P	N	0.25 - 1.5
Antioxidant 250-SVA	N	R			R	R					N	N		R	R		R		R	N				0.5 - 4.0
Antioxidant 358-SWC	N	R			R	R					N	N	P	R	R		R		R	N		P		0.5 - 2.0
Antioxidant 383-SWP	N	R			R	R					N	N	P	R	R		R		R	N		P		0.5 - 2.0
Antioxidant 1010	R	R	R	P	P	P	R	P			N	N	P		P	P	P		P	N	P	P		0.25 - 2.0
Antioxidant 1024	N							P	P		N	N		P	P	P				N	P	R		0.5 - 2.0
Antioxidant 1076	R	R	R	P	P	R		P			N	N		P	P	P	P		P	N	P	P	R	0.5 - 2.0
QUINOLINES																								
Antioxidant DQ	N			R	N	N		P			N	N		P	P	P	P		P	N				0.5 - 2.0
OZONE INHIBITOR A. Oz. NiBud PM-70	N	R	R		P	P	P		P		N	N		N	R	R			R	N				0.5 – 1.5
PHOSPHITES																								
Antioxidant TNPP	N	R		N			N	N	N		N	N	P	R	R		R		R	N		P		0.5 - 2.0

<sup>\*</sup>MPD-100 is the best known chemical antiozonant for use in Polychloroprene polymers.

RED INDICATES SIGNIFICANCE

TABLE V - Antioxidant / Antiozonant with Cure System Dynamics

AKROCHEM Product	Effective w/Cure Systems	Cure Interference	Effect on Physicals
AMINES			
Antioxidant PANA	Most cure systems	No effect	No effect
Antioxidant S	Most cure systems	Slight retarding	Minimal
PHENYLENE DIAMINES			
Antiozonant PD-1	Most cure systems	Activates Thiazole & Sulfenamides	No effect
Antiozonant PD-2	Most cure systems	Activates sulfur cure systems	No effect
Antiozonant MPD-100	Most cure systems	Activates CR formulations	No effect
ACETALES			
Antiozonant 70TBPA	Most cure systems	No effect	No effect
BENZIMIDAZOLES			
Antioxidant 58	Thiuram & peroxide cure systems	Retards sulfur cured compounds	Minimal
Antioxidant 60	Thiuram & Dithiocarbamate w/o sulfur	Retards sulfur cured compounds	Retarding
Antioxidant 405	Most cure systems	Minimal peroxide interference	No effect
PHENOLICS			
Antioxidant BHT	Most cure systems	Retards peroxide cured cpds.	No effect
Antioxidant 12***	Most cure systems	No effect	No effect
Antioxidant 32	Most cure systems	No effect	No effect
Antioxidant 33	Most cure systems	No effect	No effect
Antioxidant 43	Most cure systems	No effect	No effect
Antioxidant 235**	Most cure systems.	No effect	No effect
Antioxidant 250-SVA	Most cure systems / especially adhesives	Slows drying and "skinning"	No effect
Antioxidant 358-SWC	Most cure systems	No effect	No effect
Antioxidant 383-SWP	Most cure systems	No effect	No effect
Antioxidant 1010	Outstanding w / peroxide	Minimal	Minimal
Antioxidant 1024	Most cure systems	No effect	No effect
Antioxidant 1076	Most cure systems	No effect	No effect
<u>OUINOLINES</u>			
Antioxidant DQ	Most cure sys. / excellent with peroxides	Retarding / Minimal	No effect
OZONE INHIBITOR			
Antiozonant NiBud PM-70*	Most cure systems.	Will accelerate CSM cures	Minimal
PHOSPHITES			
Antioxidant TNPP	Most cure systems	No effect	No effect

#### Tidbits:

- 1) \*NiBud PM-70 should not be used in natural rubber.
- | \*\*A.O. 235 will turn white compounds "pink" upon exposure to UV light.
  | \*\*A.O. 12 is non-pinking.
  | A.O. 58 markedly improves flex-cracking in polychloroprene.

- 4) A.O. 58 is only moderately effective when used alone in sulfur cured compounds.
   5) MPD-100 will bloom in NR & polyisoprene if > 1.0 phr is used.

- 6) A.Oz. 70-TBPA will not provide protection against oxidation, crazing or rubber poisoning.
  7) Most antioxidants and antiozonants will bloom at higher loadings (> 3 phr). For that reason, combinations of synergistic products can be used to achieve higher levels of protection without producing bloom on the rubber surface.



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