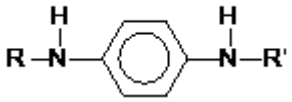
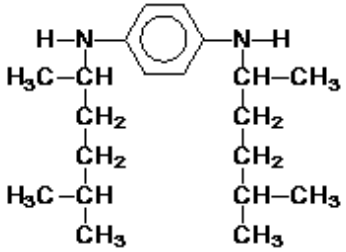
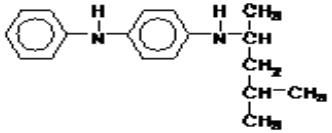
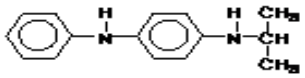
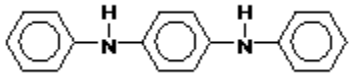
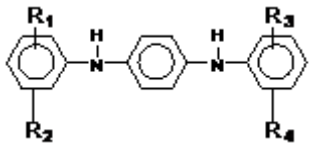
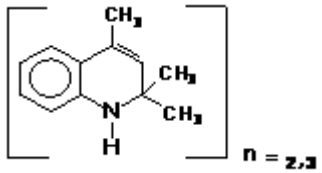
Summary Table:

Antidegradants & Antioxidants						
Chemicals	**Structure**	**Staining or Non Staining**	**Protection against**			**Notes**
			Heat & Oxidation	**Ozone**	**Flex Fatigue**	
ASTM D 4676 Class 1 PPD Anti - degradants	 Para phenylenediamines (PPDs) (General Structure)	ST	Excellent	Excellent	Excellent	Primary Antioxidants. Donate reactive Hydrogen (**N-H)** to the polymer peroxy free radicals (RCOO**.**) during the propagation stage of polymer degradation. All PPDs migrate to the surface of the rubber product and react directly and competitively with ozone. Migratory losses can occur to adjacent compounds. Effectiveness of PPDs can be improved by incorporation of waxes and synergistic antioxidants. PPDs decrease the rate of cut - growth of rubber vulcanizates. Use of antioxidants along with PPDs protects the PPDs from direct oxidation. Di alkyl & Alkyl-Aryl PPDs increase polymer's critical stress necessary for ozone crack initiation. The Dialkyl-PPDs are initially the most active antiozonants followed by Alkyl-Aryl-PPDs & then the Di-Aryl-PPDs. Order of activity reverses as the ageing progresses due to oxidation and exposure of PPDs. The solubility of PPDs antiozonants depends on the solubility parameter of the rubber itself. (Example, Diaryl PPDs have low solubility in NR and bloom above 1.0 phr dosage.) All PPDs exhibit high solubility in NBR based compounds and hence do not migrate easily to the surface to offer ozone protection. Diaryl-PPDs are more effective and persistent compared to other PPDs in polychloroprene (CR) compounds. However, PPD antiozonants can cross link CR or other halogenated polymers causing 'bin cure'. PPD antiozonants are easily oxidized by oxidizing agents (e.g. Lead Oxide) or even during storage. PPD antiozonants are not added in the Rubber-Carbon black master batch as oxidation of this blend destroys the activity of PPDs.
Type 1 Dialkyl PPD Antidegradant **77PD**	 N,N'-Bis (1,4-dimethylpentyl)-p-phenylenediamine	ST	Excellent	Excellent	Fair	A liquid at room temperature. Excellent static ozone resistance. Offers long term static ozone protection. Not very effective under dynamic conditions. Highly basic nature& hence scorchy. Does not leach out in water. High volatility at elevated temperatures. More sensitive to oxygen and heat hence poor persistency & shelf-life. A metal ion (Cu, Mn, Fe) deactivator. Causes severe contact & migration staining. Used with alkyl-aryl PPDs to obtain static and dynamic ozone protection for NR based tire compounds. Dosage:1.0 to 2.0 phr.

Chemicals	Structure	Staining or Non Staining	Protection against			Notes
			Heat & Oxidation	Ozone	Flex Fatigue	
Type 2 Alkyl-Aryl PPD Antidegradant **6PPD**	 N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	ST	Excellent	Excellent	Excellent	Offer excellent antioxidant, static & dynamic ozone resistance and anti-flex cracking properties. Exhibit optimum migration rate. Are less volatile than di-alkyl PPDs. Lower losses during storage, processing & cure. Offer long term protection to rubber vulcanizates. IPPD is highly basic in nature and influence scorch & cure. IPPD is easily leached out in water but 6PPD does not. 6PPD is much less volatile & basic than IPPD. If the losses of IPPD due to volatility & water leaching are taken into account, then at equal dosages 6PPD shows better performance than IPPD. 6PPD exhibits high solubility in rubber hence no blooming. IPPD is a skin irritant hence is substituted by 6PPD in most parts of the world. IPPD & 6PPD are stable & have good shelf-life. Dosages: 1.0 phr to 4.0 phr. Effectiveness of these PPDs increases as the dosages are increased.
Type 2 Alkyl-Aryl PPD Antidegradant **IPPD**	 N-phenyl-N' isopropyl-p-phenylenediamine	ST	Excellent	Excellent	Excellent	
Type 3 Diaryl PPD Antidegradant **DPPD**	 N,N'-diphenyl- ppd	ST	Very Good	Very Good	Excellent	Slower migration rate hence persistent, non-extractable by fuels & solvents and retained in the compound to offer long term protection. Limited solubility in rubber hence bloom over 0.7 phr in NR & 1.0 phr in SRs. Good antioxidant, static & dynamic ozone resistance and anti-flex cracking properties. **Do**es not influence scorch or cure rate. Used in combination with alkyl-aryl PPDs. Resume activity when other PPDs get depleted. Dosage: 0.3 to1.0 phr.
Type 3 Diaryl PPD Antidegradant **DTPD+DPPD**		ST	Very Good	Very Good	Very Good	
ASTM D 4676 Class 2 Polymerized Trimethyl Quinoline Antioxidant **TMQ**	 Polymerized 2,2,4-Trimethyl-1,2-dihydroquinoline	Mild Discoloration No Contact staining	Excellent	Modest (Static)	Modest	TMQ is widely used in the Rubber Industry as general purpose, high activity amine class antioxidant. TMQ is highly persistent, non-blooming antioxidant and has minimal effects on processing and curing characteristics of rubber compounds. TMQ offers excellent resistance to thermo-oxidative ageing of elastomers. Its low volatility (due to polymeric nature) ensures maximum retention, low mobility, and minimized losses through diffusion and extraction by solvents / fuels / oils. Due to Very high activity TMQ is effective even at lower dosages. TMQ antioxidant along with 6PPD offers improved oxidative heat ageing resistance proportional to the dosages of 6PPD and TMQ. TMQ is only mildly discoloring and does not cause contact staining. TMQ also exhibits a weak antiozonant activity. The composition and performance of TMQ varies from supplier to supplier. Dosage: 0.7 – 2.0 phr.

Chemicals	Structure	Staining or Non Staining	Protection against			Notes
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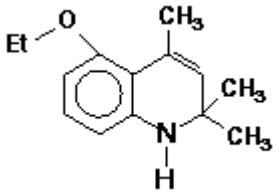
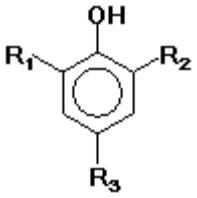
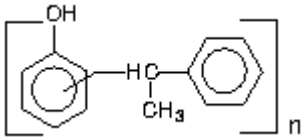
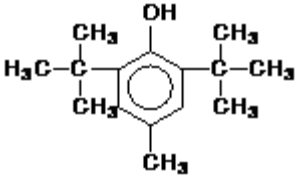
ASTM D 4676 Class 2 Antidegradant **ETMQ**	 6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	ST Discolor	Excellent	Excellent	Very good	A liquid at room temperature. ETMQ is used in the Rubber Industry as Antiozonant & Antioxidant for general purpose rubber based compounds (e.g. Tire side walls, cushion gums etc. & Beltings). Particularly effective in SBR compounds. Non blooming. Causes severe contact staining. Also used as an antioxidant for animal feeds. Dosage: 2.0-3.0 or higher (alone) , Or 2:1 ratio with 6PPD/IPPD.
ASTM D 4676 Class 3 Phenolic Type 1 Monofunctional	 General Structure	Non Staining Pale Yellow Or pink Discoloration	Good	Modest (Static)	Fair	Phenolic antioxidants are primary antioxidants. Classified by the number of phenolic groups in the molecule. More Sterically hindered antioxidants are less discoloring but have lower antioxidant activity in rubber application. The Phenolic Antioxidants are Non-Staining type and are used for the manufacture of white/colored rubber products and as stabilizers of raw Synthetic Rubbers. The Phenol radical can cause polymer degradation but this is prevented by the hindered physical structure (e.g. substitution by styrene) at **2, 6 position.** Sterically Hindered phenols act by scavenging $RO^{\cdot}$ And $ROO^{\cdot}$ Radicals via Hydrogen atom transfer from the OH group to form hydro peroxides and phenoxyl radicals.
Type 1 Monofunctional Antioxidant **SPH**	 n=1-3 Styrenated Phenol	Non Staining Pale Yellow Discoloration	Good	Modest (Static)	Fair	Low cost, comparatively weaker, less persistent antioxidant. Slight discoloration tendency on long term ageing of the rubber vulcanizates. Styrenated Phenol is much less volatile & provides long term protection and is widely used in white / coloured latex based goods, general mechanical goods and footwear products. Dosage:1.0 - 2.0 phr.
Type 1 Monofunctional Antioxidant **BHT**	 Butylated hydroxytoluene	Non Staining Pale Yellow Discoloration	Good	-	-	BHT is more volatile and provides only short term protection. It is mostly used as 'in process stabiliser' for synthetic polymers to impart raw polymer storage stability. BHT also finds non-rubber applications (e.g. Food) and is used as polymer stabilizer at 0.5 to 1.5 phr dosage. Dosage: 1.0 to 2.0 phr for rubber products manufacture.

Chemicals	Structure	Staining or Non Staining	Protection against			Notes
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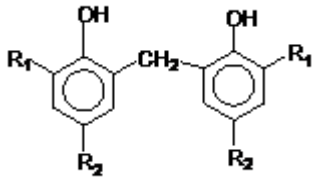
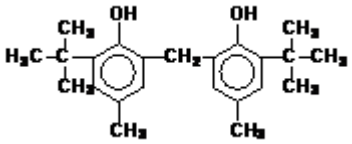
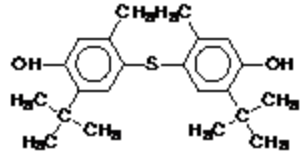
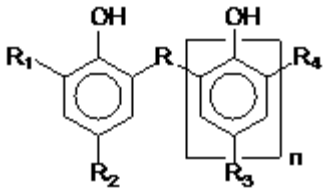
ASTM D 4676 Class 3 Phenolic Type 2 Bifunctional	 General Structure	Non Staining Pale Pink Discolor ation	V. Good	-	-	These antioxidants have low volatility, good antioxidant activity and exhibit minimal discoloration to rubber vulcanizates. Depending upon the position of linkages, bisphenols are subdivided into 'ortho' or 'para' bridged bisphenolic antioxidants.
Type 2 Bifunctional Antioxidant **22M46**	 2.2'-methylenebis (6-t-butyl-4methyl phenol)	Non Staining Pale Pink Discolor ation	V. Good	-	-	22M46 is a highly potent and is most effective antioxidant for sulfur cured rubber products. 22M46 is also an effective antioxidant for polychloroprene based products. 22M46 has a very low volatility and is most suitable for high temperature processing or product performance. 22M46 does not bloom on uncured stocks and gives protection against Copper and Manganese ion catalyzed oxidative ageing. These properties of 22M46 make it an interesting antioxidant even for critical carbon black reinforced rubber compounds! 22M46 is used in colored compounds; however; white colored products may show slight pink coloration on prolonged exposure to light. 22M46 is an excellent polymer stabilizer and is also used as an antioxidant for Hot Melt Adhesives based on EAM, EVA etc. Dosage: 0.5-2.0 phr
Type 2 Bifunctional Thiobis phenols Antioxidant **TBMC**	 4,4'-thiobis-6-(t-butyl metacresol	Non Staining Pale Pink Discolor ation	V. Good	-	-	Thiobisphenols exhibit high antioxidant activity compared to similar bisphenols. Thiobisphenols generate sulphur compounds which react with polymers during antioxidant protection reaction and compliment antioxidant activities of thiobisphenols. Thiobisphenols cause comparatively higher discoloration of rubber vulcanizates than bisphenols. Dosage: 0.5-2.0 phr
ASTM D 4676 Class 3 Phenolic Type 3 Multifunctional **Ortho bridged**	 General Structure	Non Staining Pale Pink Discolor ation	V. Good	-	-	Multifunctional phenolic antioxidants are very high performance antioxidants, exhibit extremely low volatility and do not cause contact / migratory staining or discolorations of the rubber products. Higher molecular weight of multifunctional phenolic antioxidants also contributes to practically no leaching and extraction from rubber products by water or solvents and ensuring long term protection against oxidation. The 'ortho' bridged bisphenolic antioxidants exhibit excellent antioxidant performance but show discoloration (pinking) tendency to rubber vulcanizates.

Chemicals	Structure	Staining or Non Staining	Protection against			Notes
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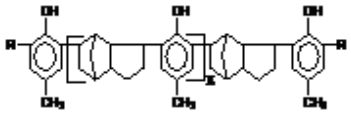
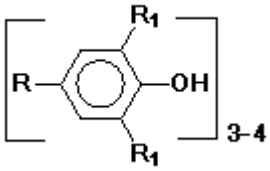
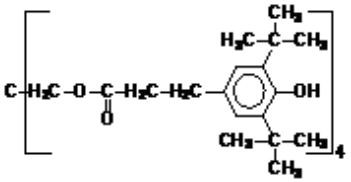
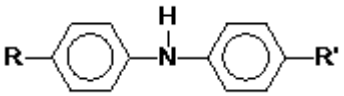
Type 3 Multifunctional Polyphenol Antioxidant **Wingstay L (Goodyear)**	 Reaction product of Butylated p-cresol & dicyclopentadiene.	Non Staining No Discoloration	V. Good	-	-	Butylated reaction product of para cresol and dicyclopentadiene (Wingstay L) Is the most popular multifunctional phenolic antioxidant used both in dry rubber and latex based products where color stability, low volatility and long term protection against heat and oxidative degradation is desired. The resistance to oxidative degradation is due to a particularly favorable pattern of substitution on the phenolic group. Color stability is due to the stearic impossibility to form highly conjugated and colored by-products like quinones. Dosage: 1-2 phr.
ASTM D 4676 Class 3 Phenolic Type 3 Multifunctional **Para bridged**	 General Structure	Non Staining No Discoloration	V. Good	-	-	The 'para' bridged bis phenolic antioxidants show slightly lower antioxidant performance but do not exhibit discoloration effect on rubber vulcanizates.
Type 3 Multifunctional **Para bridged** Antioxidant **Irganox 1010 (Ciba)**	 Tetrakis [Methylene 3-(3,5 di-t-butyl - 4 hydroxyphenyl) propionate] methane		V. Good	-	-	Irganox anti-oxidants are phenolic based anti-oxidants that hinder thermally induced oxidation of polymers where high temperature applications are used. Unlike hindered amines, anti-oxidants are consumed - and not regenerated - in the stabilization process. Irganox 1010 offers excellent protection against over bake yellowing by terminating free radicals in conventional solvent-based and powder coating systems. The major usage of Iraganox 1010 is in Thermoplastics rather than rubbers. Dosage: 0.5-1.0 phr
ASTM D 4676 Class 4 Alkylated DPAs (Antioxidant)	 Diphenyl amines (General Structure)	ST Discolor	Good	-	-	This class of antioxidants represents 'Substituted Amine Antioxidants' which are complex reaction products of diphenylamine and various alkylating agents. The substituents are selected to achieve a desired balance of cost and performance characteristics. Alkylated Diphenyl Amines are moderately staining and discoloring. These antioxidants are generally used as stabilizers of raw synthetic polymers and as general purpose antioxidants for rubber vulcanizates.

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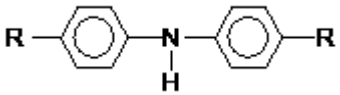
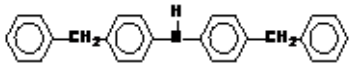
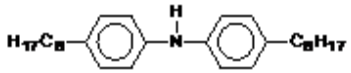
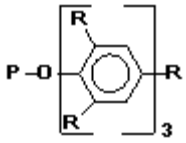
Diphenyl Amines (DPAs) (Antioxidant)	 Alkylated diphenylamines (Styrenated, Octylated, Heptylated, Nonylated)	NST Discolor	Good	-	-	Styrenated Diphenyl amine a straw colored-amber liquid. Is highly active, low volatility antioxidant and protects rubbers against degradation due to heat, light and oxygen. It is non blooming, non hydrolysable, non staining but discoloring type antioxidant and does not influence the cure rate of the rubber compound. Styrenated Diphenyl amine is widely used as a polymer stabilizer for the manufacture of staining type synthetic rubbers. It is used in some non critical tire compounds, automotive & mechanical molded goods. Dosage: 1.0 – 3.0 phr.
Antioxidant SDPA Wingstay 29 (Goodyear)	 p-oriented Styrenated Diphenyl amine	NST Discolor	Good	-	-	Dark tan liquid. Mostly di substituted with some mono & tri substitution. Some ortho substitution. Highly active non-staining & mildly discoloring antioxidant for NR & Synthetic Rubbers. Low volatility. Offers very good heat resistance to rubber vulcanizates. Non-blooming. Suitable for CR based compounds. Dosage:1.0-2.0 phr
Antioxidant DCDPA Naudard 445 (Chemtura)	 4,4, bis (α,α-domethylbenzyl) diphenylamine	ST Discolor	Good	-	-	4,4'-Bis (α,α-dimethylbenzyl) diphenylamine (DCDPA) is a grayish white powder with melting point of 90 deg C. DCDPA is a slightly staining type antioxidant which offers good heat and flex-cracking resistance to rubber vulcanizates and is used in the rubber products based on NR, IR, BR, SBR, NBR, CR & ACM. DCDPA is less discoloring than ODPA and is especially effective against heat for ACM based compounds. Dosage: 1.0 – 4.0 phr.
ODPA (Antioxidant)	 Octylated Diphenyl amine	ST	Good	-	Good	Octylated diphenylamine (ODP) is a brownish to purple colored antioxidant (Flakes) with melting point of 75 deg C. Octylated diphenylamine (ODP) is used as a stabilizer in the manufacture of synthetic rubbers. Octylated diphenylamine (ODP) is a staining and blooming type antioxidant which offers good heat and flex-cracking resistance to rubber vulcanizates and is used in the rubber products based on NR, IR, BR, SBR, NBR, & CR. It is most widely used antioxidant in CR based rubber compounds since it does not influence the bin storage properties. Dosages: 1.0 – 2.0 phr.
ASTM D 4676 Class 5 Aromatic Phosphites	 General Structure	NST	Good	-	-	Phosphite antioxidants are hydro peroxide (ROOH) decomposers and are always used in combination with H-donors e.g. hindered phenols. The phosphites are oxidized to phosphates and RO· & ROO· Radicals are reduced by the reaction with the formation of trivalent phosphorus compounds. The phosphites are hydrolyzed easily in presence of acidic materials. They are also destroyed during sulphur vulcanization and hence are not effective with sulphur cured products.

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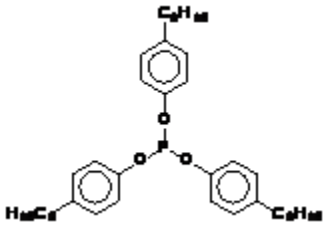
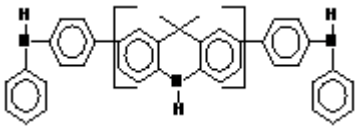
Antioxidant TNPP	 Trinonyl phosphate	NST	Good	-	-	Phosphite antioxidants are used as in-process stabilizers and as stabilizers during Synthetic Rubber e.g. SBR manufacture. Phosphites can be used with non-sulphur cured products. Phosphites give excellent color retention properties because they act as reducing agents. Phosphite antioxidants are also widely used in the manufacture of adhesives for tack retention. The recommended dosages are 1.0 – 2.0 phr.
ASTM D 4676 Class 6 **Diphenylamine - Ketone Condensates** (Antioxidant)	 Acetone Diphenyl amine condensates (ADPA)	ST	Modest	Modest	Modest	These antioxidants are complex reaction products of diphenylamine and alkyl ketones (primarily acetone), some of which are further condensed with formaldehyde to produce products of high molecular weight. These antioxidants are low melting point resins or liquids. There are two different types of ADPA condensates viz. low temperature reaction products and high temperature reaction products. The high temperature reaction products are reactive towards oxygen and provide some flex – cracking resistance but are severely staining and discoloring. They are also volatile and do not provide long term protection against the degradative forces that constantly act on rubber products. These products are mostly used in mechanical rubber products, some non critical tyre applications and as a stabilizer for emulsion SBR. These antioxidants reduce the building tack of uncured rubber compounds making product (e.g. tyres, conveyor beltings etc) building process more difficult. The low temperature condensation products are not very reactive towards oxygen but are less staining and discoloring. These are comparatively less volatile and can provide medium term protection to the rubber vulcanizates. These types of ADPAs have low solubility in oil and hence suitable for oil resistant compounds based on NBR. Dosages: 1.0 – 2.0 phr.

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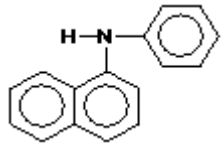
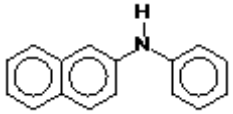
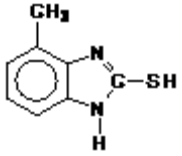
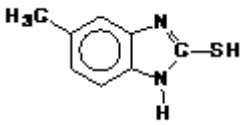
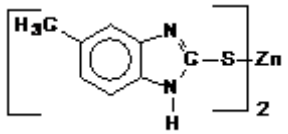
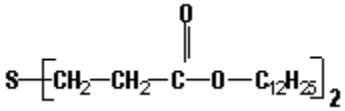
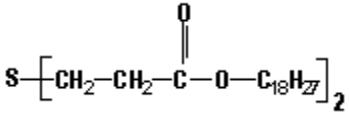
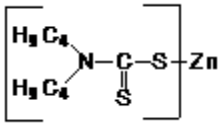
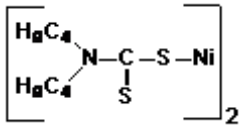
Other Antioxidants **Napthyl Amines** PAN (Antioxidant)	 Phenyl –α-napthyl amine	ST	Good	-	-	Highly effective antioxidants, but toxicological risk! (Carcinogenic). Usage discontinued in the Rubber Industry.
PBN (Antioxidant)	 Phenyl –ß-napthyl amine	ST	Very Good	-	-	
MMBI & ZMMBI Antioxidants	 and  1,2-Mercapto-4(5)-methylbenzimidazole  Zinc salt of 1,2-Mercapto-4(5)-methylbenzimidazole	NST	Very Good	-	-	These are heterocyclic SH-compounds and are different from the usual phenol/amine antioxidants. These are used with other antioxidants for synergistic effect on heat resistance properties & metal as metal deactivators. This effect depends on the vulcanization system. x MMBI is more effective in vulcanizates produced with Thiuram and Dithiocarbamate accelerators than in sulfenamide or thiazole accelerators. The combinations are particularly suitable for compounds which contain low levels of sulfur and high levels of accelerators. These products offer no protection from cracking, whether caused by flexing, ozone or the action of light and oxygen. MMBI and ZMMBI give little protection from heavy metal poisoning when used individually. However, the protection is enhanced by using combinations with other antioxidants like 22M46. TMQ & MMBI and ZMMBI combinations ore suitable antioxidants for rubber products based on peroxide-cured rubber products. Dosage: 1:1 in combination with phenolic antioxidants/amine antioxidants.

Chemicals	Structure	Staining or Non Staining	Protection against			Notes
			Heat & Oxidation	Ozone	Flex Fatigue	
Other Antioxidants Thioesters TDPE type	 DIdodecyl 3.3' thiodipropionate	NST	Good	-	-	The Thioesters are esters of thiodipropionic acid. These are secondary antioxidants and are used with phenolic or amine antioxidants. Thioesters are highly effective peroxide decomposers for long term heat resistance when used in combination with phenolic antioxidants. Thioesters are destroyed during sulphur vulcanization. Hence, not used for Sulphur vulcanized rubber products. Thioester antioxidants find applications in Plastics and TPE s. Exhibit blooming tendency at higher dosages.
	 DIoctadecyl 3.3' thiodipropionate	NST	Good	-	-	
Other Antioxidants Dithio Carbamates ZDBC	 Zinc dibutyl dithiocarbamate	NST	Good	-	-	Dithiocarbamates are moderate antioxidants but their use is limited due to the activating effect on sulphur based cure systems. One of the widely used dithiocarbamate is Nickel Dibutyl dithiocarbamate (NBC). It is used as an antiozonant for SBR, BR, NBR, ECO and CR based compounds. It is also used as an antioxidant and heat age resistor for CSM and EPDM. Nickel Dibutyl dithiocarbamate should not be used with NR since it is a pro-oxidant with NR. Another dithiocarbamate is Zinc dibutyl dithiocarbamate. This product is used as a stabiliser for Butyl rubber production and as an antioxidant for rubber based adhesives.
NiDBC (NBC)	 Nickel dibutyl dithiocarbamate	NST	Good	-	-	

For selecting a proper antioxidants / antidegradants for specific end-use requirements following factors are considered to be important for the choice.

a) Discoloration & Staining
b) Volatility
c) Solubility
d) Chemical Stability
e) Physical form
f) Antioxidant/Antidegradant concentration
g) Cost
h) Health & Toxicity concerns