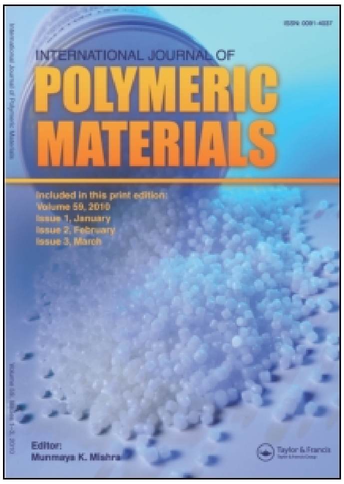

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Synthesis of Antiozonants for the Preparation of Rubber

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Detailed information on the preparation and application of antiozonants to the production of rubber has been collected from the patents published till 1987 inclusive. From among the numerous organic compounds acting as antiozonants and antioxidants, several classes can be distinguished and grouped on the gasis of the type and number of heteroatoms in their molecules: N_1, N_2, N_3, N_4, N_1O_2, O_2S_1, O_1, P_2S_4, P_1 etc. The principal method used for the synthesis of antiozonants depend on the type of the chemical compound and the initial products which are mostly obtained from petroleum.

N-alkyl, *N'*-aryl-paraphenylene diamines and quinolines are the most appropriate antiozonants under dynamic conditions, whereas *N,N'*-dialkyl-paraphenylene diamines and nickel dithiocarbamate suit static conditions. Among nonstaining antiozonants, some phosphorus and sulphur-containing compounds are used.

Antiozonants are usually added to rubber mixtures along with various waxes.

KEYWORDS: Antiozonants, synthesis, rubbers, ozone, degradation, stabilization, mechanism

INTRODUCTION

There is an increasing tendency to prolong the lifetime of rubber products, i.e. to use the rubber mixtures from which they are obtained as long as possible. On the other hand, the environment, in which rubber materials are used, is subjected to increasing pollution. The most harmful effect is that of ozone. That is why many researchers try to develop methods of preparation of new organic substances having a high efficiency with respect mainly to ozone and oxygen.

The purpose of the present paper is to make a survey of patents published in recent years and elucidate new technological methods, raw materials and efficiency of the new compounds and stabilizing systems to be used in rubber industry.

The amount of scientific information on organic substances used as antiozonants is continuously increasing. Patents proposing new technological methods for the preparation and application of antiozonants are prevailing.

A. PREPARATION OF ANTIOZONANTS

I. PARAPHENYLENEDIAMINE ANTIOZONANTS (PPHDA)

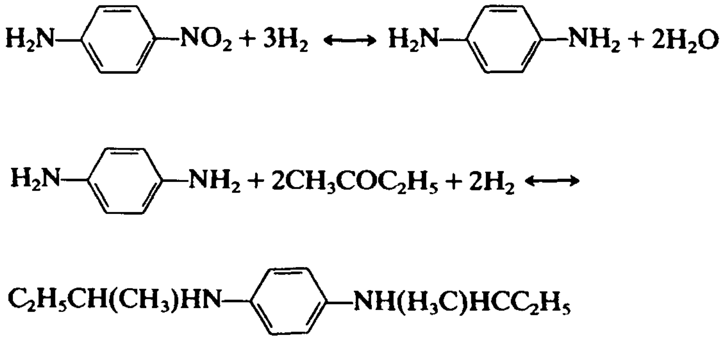
During the praparation of PPHDA it is aimed at achieving a principal technological process (reducing alkylation) where a higher conversion degree is attained under milder conditions, and applying low-cost raw material such as benzene, aniline, and their derivatives as well as mixtures of ketones, aldehydes, alcohols etc.

1. Catalytic alkylation in the presence of hydrogen

Reducing alkylation is widely applied to the synthesis and industrial preparation of substituted *N,N'*-alkyl, aryl and alkyl aryl PPHDA. This is a process of introducing an alkyl group into the molecule by the interaction of amino, nitro or nitroso compounds with ketones, aldehydes or alcohols in the presence of H_2 and appropriate catalysts. In industry, ketones or aldehydes are usually preferred. Alcohols should be preliminary dehydrogenated, which makes the process more expensive.[1] The most used ketones are methyl ethyl ketone, methyl isobutyl ketone, methyl isoamyl ketone, methyl hexyl ketone etc.[2] They are prepared by oxidation of α-olefines, secondary alcohols, aldehydes and paraffins.[3] Catalysts based on Pt, Pd, Ni, Co, Cr, Zr and other metals are most suitable for the reducing alkylation process.

In Ref. 4 some methods are developed for the preparation of *N,N'*-dialkyl PPHDA. The initial products, paranitroaniline or paraphenylenediamine mixed with at least 2 moles of aldehydes or ketones are hydrogenated at a temperature of 100–200°C and a H_2 pressure of 10–200 atm in the presence of Cu, Cr and Ba oxide catalysts. The catalysts used in Ref. [5] are CaO, Cr_2O_3 and BaO, with a ratio between the carbonyl compound and the aniline (or *p*-NO_2-aniline) of 2:1 to 10:1. *N,N'*-dialkyl PPHDA are obtained by heating a mixture of paraphenylene diamine and ketones under hydrogen ($P_{H_2} = 34\text{–}136$ at) with Ba, Cu chromite[6] or Cu on ZnO as a catalyst.[7]

The interaction of paranitroaniline with methyl ethyl ketone (MEK) in the presence of Cu chromite at temperature 110–180°C and $P_{H_2} = 50$ atm leads to *N,N'*-di sec butyl PPHDA.[8] The reaction proceeds according to the scheme:



On the basis of Refs. 9, 10 concerning the conversion of paranitroaniline into *N,N'*-di sec butyl paraphenylene diamine, the most suitable conditions for this reaction are a temperature of 180–220°C, $P_{H_2} = 30\text{–}60$ atm, and a molar H_2O: PPHDA ratio of 0.2 or MEK : PPHDA = 10.

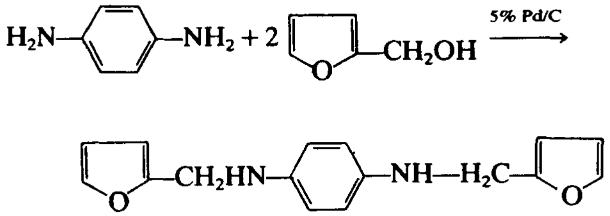
Methods of alkylation of *p*-NO_2 aniline with MEK (8 : 1) are developed in Refs. 11–19.

Copper chromite has been used as a catalyst not only in the above reaction but also in the preparation of $4\text{-}C_6H_5NCH_6H_4NHCH(CH_3)C_5H_{11}$ from 4-aminodiphenyl amine and methyl hexyl ketone in a ratio of 1 : 2.[20]

Substitution of $4\text{-}CH_3O\text{—}4\text{—}CH_3$-pentene-2-one for methyl hexyl ketone leads to the formation of $4(4\text{—}CH_3O\text{—}4\text{—}CH_3$-pentyl)-amino diphenyl amine.[21,22]

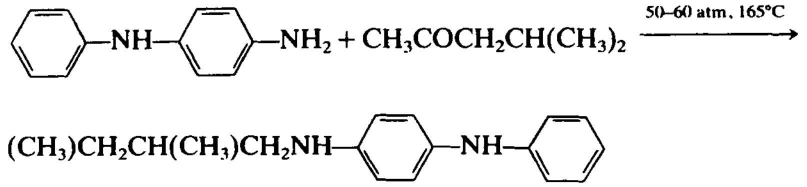
Alkylation with a sec butyl alcohol proceeds in the presence of 15% Ni, 5% Cu and 1% Mn on SiO_2 and $P_{H_2} = 14$ atm.[23] The yield of the final product increases after re-distillation of aniline or *p*-nitroaniline.[24,25]

When PPHDA or *N*-aryl-*N*-(4-amino phenyl)amine is alkylated with furfurol or tetrahydrofurfuryl alcohol, *N,N'*-difurfuryl-PPHDA is obtained on the Pd/C, $LiAlH_4$ or Raney-nickel catalysts.[26,27]



If a mixture of diphenyl amine and furfuryl alcohol is allowed to stand for 80 days at room temperature, 4,5-di(diphenylamino) cyclopentene-2-one with antiozonant properties is obtained.[27]

Diatomite-supporeted Ni (63%) is used for the preparation of *N*(1,3-dimethyl butyl)-*N'*-phenyl-PPHDA from 4-amino diphenyl amine and methyl isobutyl ketone in a ratio of 1 : 2.[28,29]



Modification of Ni catalyst with cobalt leads to an increase of its selectivity.[30] This catalyst is very active and can cause hydrogenation of the phenol ring. That is why it is recommended to add negligible amounts of organic sulphur compounds such as sulphates, mercaptans, thio acids and sulphides to the reaction mixture.[31,32]

Selenium and tellurium as catalysts preserve their activity for a long time. They are not poisoned by sulphur compounds (no purification of hydrogen is needed) and lead practically to no side reactions.[33,34]

Nickel catalysts are also used during the conversion of *N*-alkyl-4-nitrosoaniline into *N*-alkyl-*N*-phenylenediamine, while iron–copper–chromium catalysts are utilized in the reaction of the *N*-alkyl-*N*-phenylenediamine with ketones. The yield (74%) can be enhanced up to 96.3% by the addition of 0.34% triphenyl methane.[35,36]

N-(1,3-dimethyl butyl)-*N'*-phenyl-PPHDA is an effective antiozonant to be obtained from nitro, nitrozo or *p*-aminophenylenediamine and isobutylmethyl ketone in the presence of the catalyst Pd/C.[37–41] The reaction proceeds according to the following general scheme:

$$\left.\begin{array}{l} C_6H_5NHC_6H_4NO_2 \\ C_6H_5NHC_6H_4NO \\ C_6H_5NHC_6H_4NH_2 \end{array}\right\} + CH_3COCH_2CH(CH_3)_2 \xrightarrow{H_2}$$

$$C_6H_5NHC_6H_4NHCH(CH_3)CH_2CH(CH_3)CH_3$$

If alkylation is conducted with acetone at a hydrogen pressure ranging from 5 to 300 atm and a temperature of 100–250°C, the final product will be *N*-isopropyl-*N'*-phenyl-PPHDA.[42–44] The yield can be enhanced by modification of the catalyst with thiocarbamide.[45]

$$C_6H_5NHC_6H_4NO + CH_3COCH_3 \rightarrow C_6H_5NHC_6H_4NHCH(CH_3)_2$$

Another catalyst used is Pt (0.3 to 2%) on an appropriate support.[46] This catalyst is re-reduced at a temperature of 95°C and its activity is enhanced by allowing to stand in $(CH_3)_2S$ or hexyl mercaptan for a certain time.[47]

When platinum catalysts are used, the initial *p*-nitrosodiphenylamine should contain neither sulphur nor chlorine since these elements deactivate the catalyst.[48]

N,*N'*-di(1-ethyl-3-methylpentyl)-PPHDA, *N*,*N'*-di(1-methyl-heptyl)-PPHDA and *N*,*N'*-di(1,3-dimethyl pentyl)-PPHDA obtained on 1% Pt/C belong to the most usual antiozonants.[49,50] *N*,*N'*-di-(1,3,3-trimethyl)-PPHDA with a m.p. of 98°C is more appropriate from a technological viewpoint than are liquid PPHDA. It is obtained from *p*-nitroaniline and methyl neopentyl ketone according to the scheme:

$$O_2NC_6H_4NH_2 + 2CH_3COCH_2C(CH_3)_3 \xrightarrow[P_{H_2}]{CH_3COOH,\ Pt/C}$$

$$(CH_3)_3CCH_2CH(CH_3)NHC_6H_4NHCH(CH_3)CH_2C(CH_3)_3$$

The preparation of lower-toxicity antiozonants such as *N*-(1,3-dimethylbutyl)-*N'*-(1,4-dimethylpentyl)-PPHDA and *N*-isopropyl-*N'*-methylheptyl-PPHDA is described in Refs. 51–53.

When halogens are present in the alkyl chain of substituted PPHDA, their antiozonant activity increases.[54] For instance, *N*-(2-chlorallyl)-*N*-phenyl-PPHDA has a 75% higher activity than *N*-alkyl-*N'*-phenyl-PPHDA.

A mixture of two more differently substituted PPHDA is prepared by reducing alkylation of 4-nitrodiphenyl amine or (*N*-isopropyl-*p*-nitroaniline, *p*-nitroaniline, PPHDA) with two or more ketones at a temperature of 25–120°C, a hydrogen pressure of 28 atm and 1% Pt/C catalyst.[55,56]

Hydrogenation of a mixture of $O_2NC_6H_4NH_2$ and the ketones $CH_3COCH_2CH(CH_3)_2$ and $CH_3COCH_2CH_2CH(CH_3)_2$ in a ratio of 1:2 leads to 4.2% *p*-$(CH_3)_2CHCH_2CHCH_3NH/_2C_6H_4$ and 41.8% $(CH_3)_2CH_2CH_2$-$(CH_3)CHNHC_6H_4NHCH(CH_3)CH_2CH(CH_3)_2$.[57] When the ratio between the ketones is 1:1, about 20% of symmetric di-sec-alkyl-PPHDA are also obtained as final products.[58] The products of a reaction between *p*-nitroaniline and a mixture of methyl-isobutyl ketone and methylisoamyl ketone (1:1) are 18.6% *N,N'*-di(1,3-dimethylbutyl)-PPHDA, 30.6% *N,N'*-di(1,4-dimethylpentyl)-PPHDA and 50.2% *N*-1,3-dimethylbutyl-*N'*-(1,4-dimethylpentyl)-PPHDA.

2. Catalytic alkylation in the absence of hydrogen

Substituted paraphenylenediamine can be obtained without using hydrogen and expensive noble metals as catalyst.[59] When *N*-alkyl-4-nitroaniline is mixed with *n*-hexanole and 50% NaOH, and heated for 1 hr at a temperature of 100°C, it yields monosubstituted PPHDA:

$$RHNC_6H_3(R_1)NO_2 + 2R_2CH_2OH \rightarrow RHNC_6H_3(R_1)NH_2$$

where R is C_1—C_{12} alkyl, naphthyl radicals, and R_1 is C_1—C_6 alkyl radicals.

Monosubstituted PPHDA can also be obtained by interaction of *N*-substituted aminophenols with ammonia in the presence of an acid catalyst (Lewis acid)[60] yields monosubstituted PPHDA:

$$RNHC_6H_4OH + HNH_2 \rightarrow RNHC_6H_4NH_2$$

Other catalysts used in this reaction are $FeCl_3$ or a mixture of free iodine and powdery iron in a ratio of 6:1[61,62]

$$RNH_2 + HOC_6H_4NH_2 \xrightarrow{I_2,\ Fe} RNHC_6H_4NH_2$$

where R is C_6H_5—, —$CH_3C_6H_4$, —C_6H_{11}.

Heating at 215–220°C in a nitrogen atmosphere of a mixture of aniline, cyclohexylamine and *N*-(1,3-dimethyl butyl)-*p*)aminophenol in the presence of I_2, powdery Fe and NH_4Cl leads to the formation of 10% *N,N'*-(1,3-dimethyl butyl)-PPHDA, 5.5% *N*-cyclohexyl-*N'*1,3-dimethyl butyl)-PPHDA, 30% *N*(1,3-dimethyl butyl)-*N'*-phenyl-PPHDA, 8% *N*-cyclohexyl-*N'*-phenyl-PPHDA and 9% *N,N'*-diphenyl-PPHDA in the final product.[63]

Substituted *N,N'*-diphenyl-PPHDA with low melting points appears after a reaction of hydroquinone with a mixture of amines (35% aniline, 25% toluidine and 40% xylidines) during heating in the presence of a catalyst ($FeCl_3$) of condensation.[64]

Reaction of substituted PPHDA with thiols or formaldehyde in an acid medium results in their conversion into active stabilizers having a complex behavior (suppressing the effect of O_2, O_3, light and heat) and exhibiting three active centers.[65–67] Their general formula is:

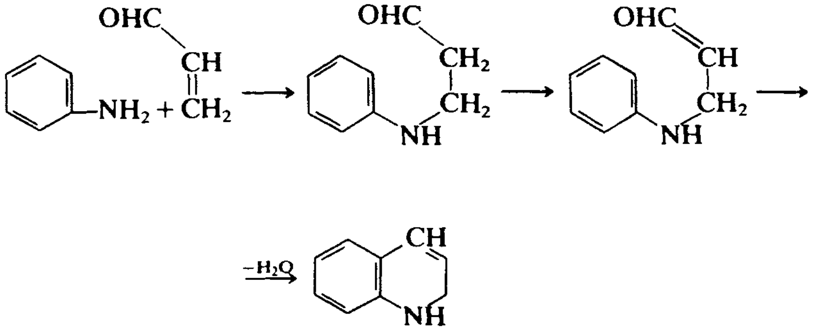
$$R_1—S—CH_2C_6H_2(R_2)(R_3)NHC_6H_4NHR_4$$

where R_1 is alkyl C_1—C_{20}, aryl C_6—C_{14}, alkylaryl; R_2 and R_3 are H, alkyl-C_1—C_7, aryl-C_6—C_{14}, and R_4 is [—C_6H_4—CH_2—S—R_1].

Alkylated toluenediamines are good antiozonants and antioxidants, which interrupt the chain-radical process taking place during the oxidation of polymeric materials.[68] A mixture of 2,4-toluenediamine, dicyclopentadiene and pentene is stirred in the presence of a catalyst (12% L and 87% Si) under elevated pressure in a nitrogen atmosphere. A mixture of 3(cyclo-pent-2-enyl)-2,4-toluenediamine and 5-(cyclopent-2-enyl)-2,4-toluenediamine is obtained. The conversion of 2,4-toluenediamine amounts to 64%.

II. HYDROQUINOLINES

Hydroquinolines are prepared by the classical method of Skraup using a reaction of aromatic amines with aldehydes or ketones in the presence of oxidants and acid catalysts according to the following scheme:



A mixture of aniline and C_8—C_{15}-alkylated anilines (45% C_{12}, 15% C_{11} and 12% C_{13}) in an acid medium is heated up to a temperature of 140°C for 12 hr, after which acetone is added. The final product is an oil containing 58% 6-dodecyl-1,2-dihydro-2,2,4-trimethylquinoline, 6% dodecyl aniline and oligomer 1,2-dihydro 2,2,4-trimethylquinoline.[69,70]

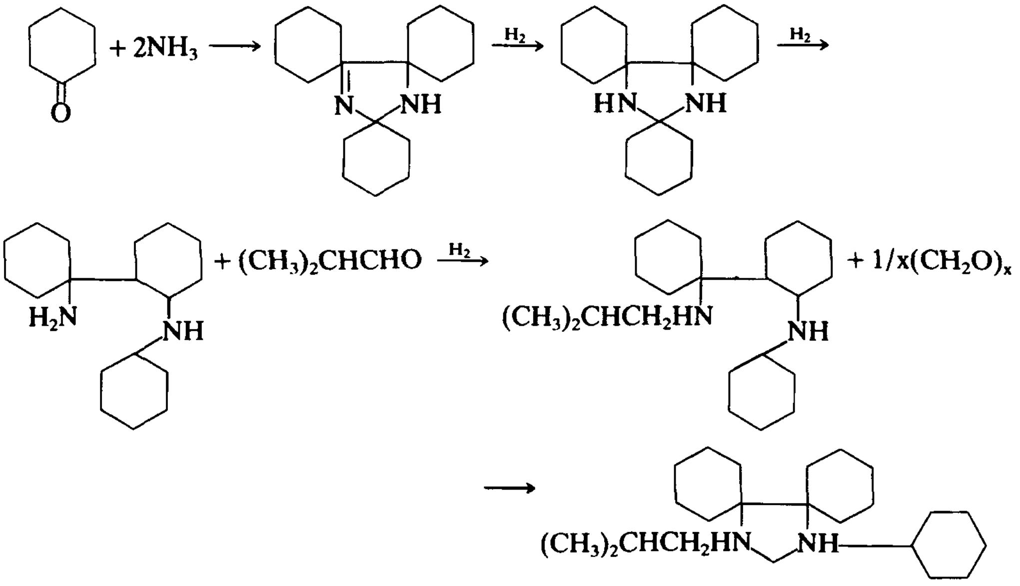
Addition of acetone to 4,4′-(ethylene dioxyl)dianiline for 10 hr in the presence of benzenesulphonic acid at 150–160°C yields 6,6′(ethylene dioxy) di 1,2-dihydro-2,2,4-trimethyl quinoline.[71]

When 2,2,4-trimethyl-1,2-dihydroquinoline is allowed to polymerize in HCL acid, an active polymeric antiozonant is obtained. The monomer is formed during reaction of aniline with acetone at a temperature of 120°C in the presence of *p*-toluenesulphonic acid as a catalyst.[72]

The polymer is isolated by dissolution of the reaction mixture in benzene followed by neutralization and evaporation of the solvent. The reaction mixture can be dispersed in water and then granulated. The obtained antiozonants are usually applied in a combination with *N*-phenyl-*N*′-isopropyl-PPHDA.[73,74]

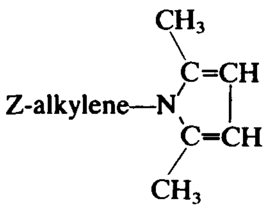
III. *N,N'*-DISUBSTITUTED HEXAHYDROPYRIMIDINES

These are nonstaining antiozonants,[75] which are prepared by condensation of cyclohexanone or its derivatives with ammonia. Tetrahydropyridimine is first formed and then reduced to hexahydropyrimidine whose pyrimidine ring is opened to form diamine. The two amino groups form bonds with aldehydes and yield *N,N'*-substituted hexahydropyrimidine. The reaction proceeds as follows:

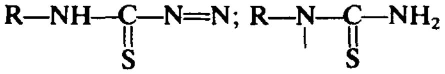


IV. *N*-SUBSTITUTED DIMETHYLPYROLS

These compounds are nonstaining antiozonants.[76] They are obtained from 1,4-dicarbonyl compounds which pass through an enol-form to interact with amines and have the general formula:



where Z is substituted NH_2 group RNH—; R_2N—;



$$R{-}NH{-}\underset{\underset{S}{\|}}{C}{-}N{=}N;\quad R{-}\underset{|}{N}{-}\underset{\underset{S}{\|}}{C}{-}NH_2$$

V ENAMINES

The enamines are nonstaining antiozonants with the general formula:

$$(R_1)(R)N{-}HC{=}C(R_2)(R_3)$$

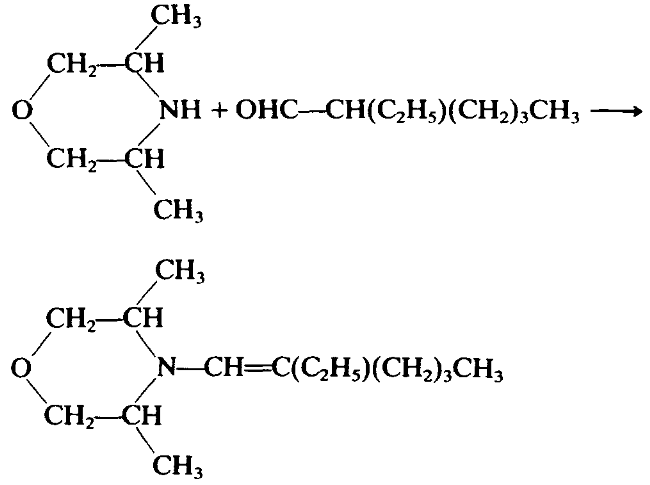
where R, R_1, R_2 and R are alkyl groups with C_1—C_6.

These compounds are prepared by condensation of amines with ketones. The amines used are pyrolidine, pyperidine, substituted morfolines etc.

$$RR_1NH + (R_2)(R_3)CHC(R_4)O \rightarrow (R)(R_1)N{-}(R_4)C{=}C(R_2)(R_3) + H_2O$$

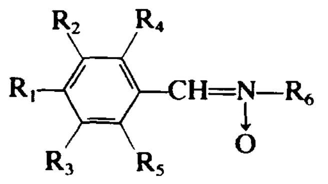
If the ketones are asymmetric, a mixture of products obtained. Condensation of 2,6-dimethyl-morpholine with 2-ethylhexanal yields 1-(2,6-dimethyl-morpholino)-2-ethyl-hexene-1, which is usually applied as natural rubber and butadiene-styrene rubber.[77]

$$RCH_2CHO + HN(R')_2 \rightarrow RCH_2CH(OH)N(R')_2 \xrightleftharpoons[-H_2O]{} RCH{=}CHN(R')_2$$



VI. NITRONE COMPOUNDS

The C-substituted or unsubstituted aryl-*N*-substituted or unsubstituted (branched alkyl or cycloalkyl) nitrone are appropriate not only as antiozonants but also as anti-fatigue.[78] Particularly effective in this respect are the aldonitrones as the formula:



where R_1 is mono or dialkyl-substituted amino group; R_2 and R_3 are alkyl or alkoxy groups; R_4, $R_5 = R_2$, and R_6 is isopropyl, sec butyl or tert butyl group.

The nitrone compounds may be prepared in a variety of ways, for examples:

a) by oxidation of the corresponding aryl-*N*-substituted or unsubstituted (branched alkyl or cycloalkyl) hydroxylamine;

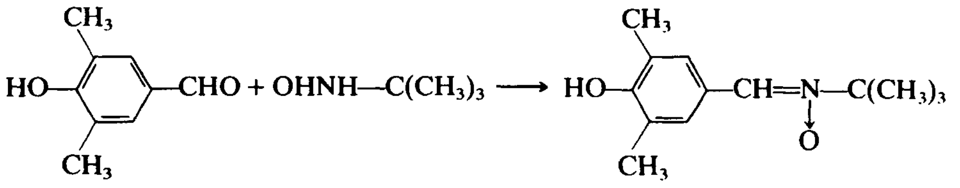
b) by reaction of aryl ketones with primary hydroxylamine;

c) by *N*-alkylation of the corresponding oxime;

d) by reaction of the corresponding ketimine with primary hydroxylamine, and

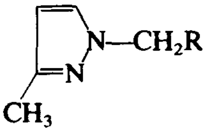
e) by oxidation of the corresponding *N*-substituted imine.

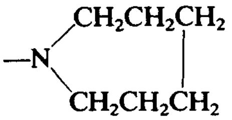
The most used nitrone is 4-hydroxy-3,5-dimethyl-phenyl-*N*-tert butyl nitron obtained when *N*-tert butyl hydroxylamine and 3,5-dimethyl-4-hydroxy benzaldehyde in a ratio of 1:1 are dissolved in absolute alcohol and the mixture is allowed to stand for 5 days at room temperature.[78]



VII. DERIVATIVES OF 3(5)-METHYL PYRAZONE

The general formula of these compounds is:



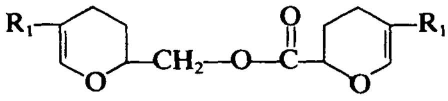
where R is:  or C_5H_5N.

The ozone resistance of rubber mixtures based on natural rubber with ozonin-16(pyperidinomethyl-35-methyl pyrazole) and ozonin-51 (hexamethyleneimino-3,5-methyl pyrazole) exceeds 1.5 to 2 times that of mixtures containing 2246 (2,2′-methylene-bis-4-methyl-6-tert butylphenol) and is close to that reached by tributylcarbamide. A mixture of ozonin-16 or ozonin-51 with 2246 in a ratio of 1:1 displays the highest activity.[79]

VIII. ENOLETHERS

These compounds are used as antiozonants for natural and synthetic rubber. They are slightly staining. The following enolethers are synthesized: 3,4-dihydro-

2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate); 3,4-dihydro-2,5(dimethyl or diisobutyl, didcyl)-2H-pyran-2-methyl-(3,4-dihydro-2,5-dimethyl-2H-pyran-2-carboxylate) with the general formula:[80]

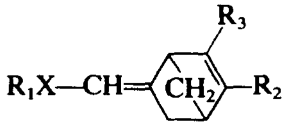


where R_1 is an alkyl, aryl or alkylaryl radical.

By condensation of 3,4-dihydro-2H-pyran-2-carbox-aldehyde and aluminium isopropylate with stirring for 4 hr at a temperature 40°C, 75%, 3,4-dihydro-2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate) is obtained.

Mixing of different enolethers results in a better antiozonant activity. For instance, a mixture of hexanediol-1,6-di-(2-metyl-prop-1-ethyl) ether and 1,1′-bis-(2-methyl-prop-1-epoxy)-diethyl ether is prepared by aldol condensation of isobutyl aldehyde and 1,2-hexanediol in the presence of toluenesulphonic acid, quinoline and cyclohexane as a solvent.[81]

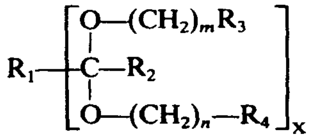
Ethers with the general formula



are odorless antiozonants where R_1 is a hydrocarbon residue which may contain a heteroatome; X is S or O; R_2 and R_3 are H, —CH_3. These ethers are used along with R—CO—NH—NH_2 (R is alkyl group with C_3—C_{10}) and are ozone-resistance.[82]

IX. CYCLIC AND ACYCLIC ACETALS AND KETALS

Cyclic and acyclic acetals and ketals are nonstaining antiozonants with the general formula:[83–86]



$$R_1\left[\begin{array}{l} O-(CH_2)_mR_3 \\ \mid \\ C-R_2 \\ \mid \\ O-(CH_2)_n-R_4 \end{array}\right]_x$$

where n and m range from 0 to 12; R_1, $R_2 = H$, alkyl groups with C_1—C_5, alkylene groups containing halogens, cyclo or bicycloalkenes with C_5—C_7, aryl groups with C_6—C_{10} or alkylaryl groups.

They are prepared by the classical method, i.e. by a reaction of alcohols with aldehydes or ketones in the presence of catalysts.

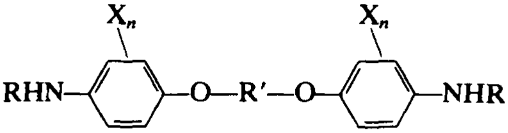
$$RCHO + 2RCH_2OH \rightarrow RCH(OCH_2R)_2$$
$$(R)_2CO + 2RCH_2OH \rightarrow (R)_2C(OCH_2R)_2$$

The catalysts used are H_2SO_4, H_3PO_4, *p*-toluenesulphonic acid, boron trifluoride etc. The cyclic acetals are applied with microcrystalline wax.[87]

Acetals and ketals with unsaturated cyclic groups are less volatile have no odor and are compatible with rubbers.[88]

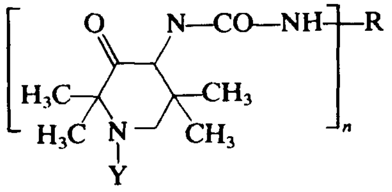
X. OTHER CLASSES OF COMPOUNDS USED AS ANTIOZONANTS

Bis-alkylaminophenoxy alkanes with the general formula



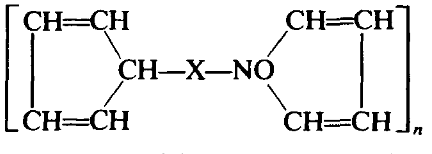
(where X = halogen, R = sec alkyl radical with C_3—C_8, R′ is —CH_2—, —CH_2—CH_2—) are obtained from nitrophenol by reducing alkylation in the presence of Pt/C as a catalyst.[89]

The derivatives of 2,2,7,7-tetramethyl-1,4-diazacycloheptane with the formula



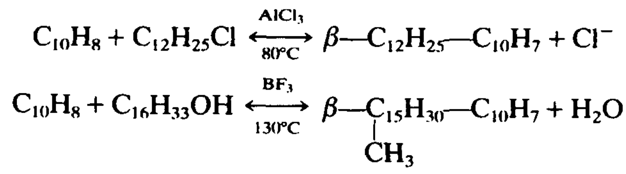
(where *n* is 1, Y is H, CH_3, O and —NH, R denotes alkyl groups with C_1—C_{20}; where *n* is 2, R is alkylene groups with C_1—C_{20}, cycloalkylene groups with C_7—C_{18} or alkylarylene groups with C_5—C_{12}) are also applied as antiozonants for polymers. Their preparation is materialized by a reaction of 1,4-diazocycloheptane-5-one with isocyanate.[90]

Bis-cyclopentadienyl compounds are good antiozonants for polychloroprene.[91] They have the general formula:



where X is (a) α,α'-*p*-xylilene and (b) 4,4′-oxydiphenylene-dimethylene.

Polyolefines are applied as stabilizers of cables and insulating materials.[92] Their preparation scheme is:



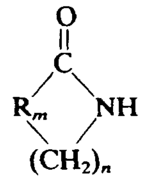
$$C_{10}H_8 + C_{12}H_{25}Cl \underset{80°C}{\overset{AlCl_3}{\longleftrightarrow}} \beta\text{—}C_{12}H_{25}\text{—}C_{10}H_7 + Cl^-$$

$$C_{10}H_8 + C_{16}H_{33}OH \underset{130°C}{\overset{BF_3}{\longleftrightarrow}} \beta\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}}{}_{15}H_{30}\text{—}C_{10}H_7 + H_2O$$

The yield is 60%.

Aminomethylene derivatives of furane are cheaper and nonstaining antiozonants.[93]

Strong antiozonants are the lactams with the general formula



where $n = 3$ to 20; $m = 1$ to 2; R is alkyl or phenyl radical.

Comparison based on antiozonant activities indicates ε-caprolactam and capryllactam to rank first.[94]

XI. S-CONTAINING ANTIOZONANTS

The derivatives of isothiocarbamate used as antioxidants for (natural rubber) NR, (butadiene rubber) BR, (isoprene rubber) IR and (butadiene-styrene rubber) BSR are noncoloring and nonstaining, and have general formula:

$$R_4—N{=}(SR_1)—N—R_2R_3$$

where R_1, R_2, R_3 and R_4 are alkyl C_1—C_{30}, phenylalkyl C_1—C_6 or cycloalkyl radicals.[95]

A high antioxidant activity is exhibited by sulphides R—S—R,[96] where R is $[C_6H_5NHC_6H_4NHCO]_nX$, n is 1 or 2, X denotes methylene, ethylene or 1,2-propylene radicals. When R is H, the sulphides are obtained by a reaction of 4-aminodiphenylamine with acids having the general formula

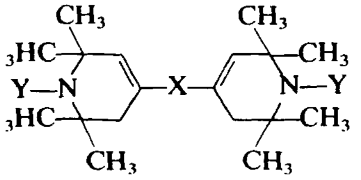
$$H—S—X—(—SO_2H)_n.$$

If $R' =$ —S—R, the acids should have the formula $(HOOC)_n—X—S—S—X—(COOH)_n$ (dithioacetic, β-dithiopropionic).

The sulphides obtained are bis(4-anilino-phenyl aminocarbonyl methyl) disulphide and bis(4-anilinophenyl amino carbonyl ethyl) disulphide. These antioxidants are easily soluble in rubber compositions.

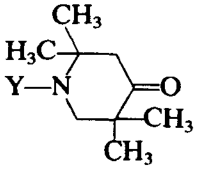
Sulphonate antioxidants with the general formula $R_1R_2SO_3NH_3OH$ (R_1 = alkyl radicals with C_1—C_{13}, R_2 = aryl radicals with C_1—C_6, R_3 = alkylene with C_4—C_6) are nonstaining, nontoxic and, above all, cheap to prepare.[97] The initial substances used are alkylated products, resulting from the preparation of dodecyl benzene (hydrocarbon radicals with C_{24}—C_{30}) which is sulphonated with oleum and then reacted with alkanolamines at pH = 7.5.

The sulphides of 3,4-dehydropyperidine are efficient antiozonants. They have the general formula:



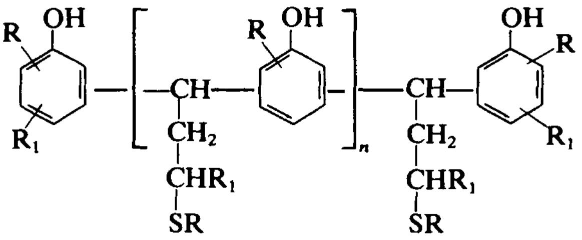
where X = S, SO, SO_2; Y,Y′ = methylene, isopropyl, sec butyl radicals.

Di-4-(3,4-dihydro-2,2,6,6-tetramethyl-pyperydinile)-sulphide or sulphoxide or sulphone are prepared by interaction of



with a gaseous mixture of HCl and H_2S.[98,99]

Ozone resistance is observed with the products of mercaptoaldehyde condensation with phenols.[100–103]

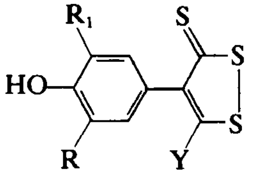


where R, R_1 are H, CH_3, tert-butyl radicals.

The product of *o*-cresol condensation with -*n*-butylmercaptopropionealdehyde demonstrates the best antiozonant effect.

Triazinedisulphide derivatives to be used as antioxidants are relatively easily prepared by a reaction of benzthiazyldisulphide with 2(4-morpholinyl di-thio) benzthiazole and 1,3,5-triazine dithiol in the presence of a neutralizing agent (NaOH).[104,105]

In comparison with Zn-dialkyldithio phosphate, dithiolderivatives exhibit a higher antioxidative activity. They have the general formula:

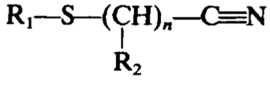


where R_1 and R_2 are alkyl radicals with C_1—C_{12}; Y is H or SR_2; R_2 denotes alkyl radicals with C_1—C_{20}.

Alkylated phenols with S in the presence of a basic catalyst yields 4-(3,5-di-isopropyl-4-hydroxyphenyl)1,2-dithiol-3-thione.[106,107]

2-Vinyl phenothiazine enhances the stability of rubber products towards ozone, temperature and repeated deformation.[108] Butoxyethyl *N,N'*-dimethyldithio carbamate is used as antiozonant of light rubber.[109]

Nitryl antiozonants with the general formula



$$R_1\text{—}S\text{—}(\underset{\displaystyle R_2}{\underset{|}{C}}H)_n\text{—}C{\equiv}N$$

(where R_1 denotes alkyl radicals with $C_1—C_{18}$ or $—(CH_2)_n—C{\equiv}N$ and R_2 stands for H, CH_3 or C_2H_5) are nonstaining and are characterized by a low toxicity ($LD_{50} = 5300$ mg/kg) and a cheap technology of preparation.[110]

XII. Si CONTAINING ANTIOZONANTS

Aminoorganosilanes, $R_nSi(CH_2NXY)_{4-n}$, (where R = monovalent hydrocarbon radical; X = aryl, alkoxyaryl, aminoaryl, phenyl, naphthyl radicals; Y = H, alkylaryl, aminoaryl radicals) demonstrate a good antiozonant and antioxidative activity.

Dimethyl-bis-tert butylhydroxy-benzyloxysilane used for stabilizing butyl rubber, is prepared by interaction of 3,5-di-tert butyl-4-hydroxy-benzyl-alcohol with dimethylchlorsilane.[111,112]

The oligodiphenylsiloxyquinizarilene, which is a good thermostabilizer, is isolated by heterophase condensation of diphenylchlorosilane with aromatic diols in the presence of suitable catalysts.[113]

XIII. PHOSPHORUS-CONTAINING ANTIOZONANTS

Phosphites and phosphates of 5-norbornene-2-methanol are used as antiozonants of polychloroprene rubber $HP(O)(OR)_2$, $(RO)_3P$, $(RO)_3PO$, where R is 5-norbornene-2-yl methyl.

The interaction of PCL_3 with 5-norbornene-2-methanol in a pyridine medium results in a mixture of bis(5-norbornene-2-methyl) phosphite (17%), tris(5-norbornene-2-methyl) phosphate (22%) and tris(5-norbornene-2-methyl) phosphate (15%). The reaction with $POCL_3$ leads to the formation of phosphates only.[114] Aryl phosphites are applied as stabilizers of synthetic rubber.[115,116] Organic polymers are stabilized by amide esters of the phosphoric acid, having the general formula $P(ZR)(Z'R')(NR_2R_3)$, where Z, Z' denote O, NH; R_2, R_3, R, and R', are linear or cyclic, substituted or unsubstituted aliphatic or aromatic residues.[117]

B. USE OF STABILIZING SYSTEMS

In a series of patents attention is paid to the development of effective stabilizing systems based on well-known stabilizers or their mixtures with components obtained by the corresponding author.

The stabilizing systems are presented in Table I.

CONCLUSION

On the basis of the presence survey of patent literature concerning the preparation and use of organic substances as antiozonants and antioxidants, the

TABLE I

No.	Stabilizing system	Rubber	Behavior	Ref.
1.	a) PPHDA b) Imidasole	EPDM	Improve the tensile strength	118
2.	a) 4010 NA b) Neozone D	Diene rubbers	O_3	119
3.	a) React products of acetone and diphenylamine b) Zn-2-mercaptotolylimidasole	EPDM	O_2, O_3, t^0	120
4.	a) 2,6-di-tert buthylcresole b) 4,4′-thiobis(6-tert butlyl) *m*-cresole	BSR	O_3, t^0	121
5.	Cd salts of I. ArNHArNR$_7$—R$_1$—COOH II. ArNHAr—R$_4$—COOH III. OH(R$_5$)(R$_6$)ArR$_2$—COOH R is H, halogen, C$_1$—C$_8$ alkyl, R$_1$ is C$_1$—C$_{20}$ alkylene, —CO—R$_2$ R$_2$ is C$_1$—C$_{20}$ alkylene R$_3$ is C$_1$—C$_8$ alkylene, R$_4$ is —OCO—R$_2$ R$_5$ and R$_6$ are H or C$_1$—C$_8$ alkyl R$_7$ is H or C$_1$—C$_4$ alkyls	Nitrile rubber (NR)	O_3	122
6.	a) *N,N′*-bis(2-hydroxy-4,6-NR dimethylbenzyl)-piperazine b) NG-2246		t^0	123
7.	a) Na aluminomethyl silicate b) carboxylated synthetic rubber latex		Nonstaining, non-toxic	124
8.	a) PPHDA—1–4 phr b) Imidasole-0, 2–4 phr	EPDM Cl-sulfonated polyethylene	t^0, O_2	125
9.	a) PPHDA 0, 1–5 phr b) *p*-dinitrosoarene 0.1 pts	NR	O_2, O_3	126
10.	a) PPHDA b) Bismaleimid a : b = 80–20 : 20–80	S-Vulcanizate		127
11.	a) *N,N′*-Diphenyl-PPHDA, 0.1–5 pts b) petroleum type waxes 0.1–10 pts	IR	O_3 noncoloring	128
12.	a) 2,2,4-trimethyl-1,2-dihydroquinoline b) 4010 NA c) *N*-phenyl-*N′*-(1,3-dimethyl-butyl) PPHDA a : b : c = 50 : 25 : 25	NR	O_3	129
13.	a) *N,N′*-diphenyl-1,4-phenylene-diamine 10–50 wt % b) *N,N′*-ditolyl-1,4-phenylene-diamine 50–90 wt %	NR	nonstaining	130
14.	a) 4010 NA b) montmorilonit	NR	O_3	131
15.	a) Phenothiazin 20–60% b) *N*-alkyl-*N′*-phenyl-1,4-phenylenediamine 40–80%	NR	O_3 nonstaining	132
16.	a) diisopropyldithiophosphate b) dihydrodiphenylpropan c) 4010 NA a : b : c = 1 : 0, 5 : 0, 5	BSR	O_3, light	133
17.	a) Santoflex 13 b) Flectol H c) 6-anilino-2,2,4-trimethylquinoline	DR	O_3, non-coloring	134

TABLE I

No.	Stabilizing system	Rubber	Behavior	Ref.
18.	a) 4010 NA b) Santoflex 13	DR	O_2, O_3, t^0	135
19.	a) Neozone D 0.5–2 phr b) 9-phenyl-10-*p*-vinylphenyl-antracene, 2–7 phr	Vulcanizates	O_3, t^0	136
20.	a) Deca-cis(nonylphenyl) hepta-cis(dipropyleneglykol octaphosphite) b) *N,N'*-di(2-octyl) PPHDA a—0.75–1.75 phr b—1.25–0.25 phr	NR	O_2	137
21.	a) *N*-isopropyl aminodiphenylamine b) 2,6-di-tert butylphenol	DR	t^0	138
22.	a) Phenothiazine 20–80% b) Flectrol H 80–20 wt %	BSR	Heat and flexing resistance	139
23.	a) 2,2-methylenebis-4-methyl-6-tert butylphenol 0.3–0.75% b) mercaptobenzimidazole 0.15–0.5%	NR	O_2, O_3	140
24.	a) 1,1,3-tri(2-methyl-4-hydroxy-5-tert butylphenol) butan a—5–50 wt %; b—95–50 wt %	Synthetic nonvulcanization rubber	O_2	141
25.	a) 1,3 bis piperidino-methylene-imidazoline-2-thione b) 2,2 methylene-bis-(4-methyl-6-tert butylphenol	Vulcanizable unsatd. rubbers	O_3	142
26.	a) *N*-phenyl-*N'*-(1,3-dimethylbutyl)-PPHDA b) poly(2,2,4-trimethyl-1,2-dihydroquinoline	NR	O_3	143
27.	a) *N*-anilinophenylphosphoramidate ester b) Zn dihydrocarbyldithiophosphates	NR, synthetic rubbers non-staining, non-pigmenting		144
28.	a) S-contg. sulphur ester b) amine or phenol	NR, synthetic rubbers	t^0, O_2	145
29.	a) 1,1,3-tris(2-methyl-4-hydroxy-5-*t* butylphenol butan, 5–50 wt % b) trisbutoxyethylphosphate 55–50 wt %	Synthetic unvulcanized rubbers	Improved dispersion, penetration propr.	146
30.	a) diethyl-dithiocarbamate b) Co diethyl-dithiocarbamate c) *N*-phenyl-*N'*-isopropyl PPHDA	Vulcanizable unsaturated	O_3	147
31.	a) Phenylhydrasone b) Amine or S-containing antioxidant	NR	O_2	148
32.	a) 2-mercaptomethylbenzimidazole b) 2,2,4-trimethyl-1,2-dihydroquinoline	EPDM	O_2	149
33.	a) 4010 NA b) 2,2,4-trimethyl-1,2-dihydroquinoline	BSR	O_3	150
34.	a) 4010 NA, 1.7 phr b) Flectol H, 1.3 phr or c) Santowhite Crystals, 1.1 phr	IR, BSR	t^0, O_3	151
35.	a) 4010 Na b) Flectol H a:b = 1–2.5:0.5–2 phr	NR, IR, BSR	t^0, O_3	152
36.	a) 4010 NA b) Santowhite Crystals a:b = 1–2.5:0.5–2 phr	NR, IR, BSR	O_3	153

TABLE I

No.	Stabilizing system	Rubber	Behavior	Ref.
37.	a) Santoflex 77 b) Santowhite Crystals a:b = 1–2.5:0.5–1 phr	NR, IR, BSR	O_3	154
38.	a) Santoflex 77 b) Flectol H a:b = 1:0.5 phr	NR, IR	O_3	155
39.	a) Santoflex 77 b) 2-methylmercaptoimidazole a:b = 1–2.5:0.5:2 phr	IR, BSR	O_3	156
40.	a) 4010 NA b) Flectol H a:b = 1.7:1.3 phr	BSR	O_3	157
41.	a) 2-mercaptomethyl benzoimidazol b) *N*-phenyl-*N'*-octyl PPHDA	NR	Flex resistance, O_3, t^0	158
42.	a) 4010 NA b) Neozone D	Vulcanizate	t^0	159
43.	a) Unsatd. cycloaliphatic carboxilate ester, 1 phr b) wax—0.25 wt prts	All rubbers	O_3, odorless	160
44.	a) mercaptobenzoimidazole b) perilla oil or castor	Chloroprene rubber	O_3	161
45.	a) 2,2'-methylene-bis(4-ethyl-6-*t* butylphenol) 0.5 phr b) tetrakis(2,4-di-*t* butyl-phenyl)-4,4'-diphenylene phosphite 0.25 phr	NR, BSR	O_3, t^0	162
46.	a) PPHDA 1–3 phr b) wax 1–5 phr	Vulcanizate	O_3, t^0	163
47.	a) *N*(1,4-dimethylbutyl-*N'*-phenyl PPHDA, 1 phr b) Petroleum type waxes 0.5–10 phr	Alkylmethacrylate type polymer	discoloring	164
48.	a) Hindered di-*t* butyl phenol b) Zn salt of mercapto imidazol, 2–8 phr	EPDM 31	t^0, O_3	165
49.	a) Amines b) Imidazoles	EPDM	t^0, O_3	166

following conclusions may be drawn:

1. The greatest part of compounds characterized by a very high antiozonant effectives are based on paraphenylenediamines.

2. The principal reaction used for the preparation of paraphenylenediamines is reducing alkylation which proceeds in the presence of hydrogen or, sometimes, in a reducing medium containing no hydrogen

3. Among the catalysts utilized during reducing alkylation of hydrogen, those based on Pt, Pd and Ni are prevailing, whereas Lewis acids are appropriate as reducing media without hydrogen.

4. About 13 classes of organic and Si-containing compounds are applied as antiozonants.

5. A trend to obtaining polyfunctional high-efficiency stabilizers, such as those based on para-phenylenediamines and sulphur-containing compounds, is noticed.

6. *N,N'*-disubstituted hexahydropyrimidines, substituted dimethylpyrols, enamines, pyrazole derivatives and cyclic and acycle acetals and ketals are applied as nonstaining antiozonants.

7. Of the stabilizing systems for rubber and rubber products, those based on PPHDA stabilizers and containing hydroquinolines, phenols and imidazoles are most effective and have the widest application. Stored rubber is mostly stabilized by compounds containing hindered phenols.

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