

Chemicals used in the rubber industry

An overview

by Lawrence Fishbein, PhD¹

FISHBEIN L. Chemicals used in the rubber industry: An overview. *Scand j work environ health* 9 (1983): suppl 2, 7-14. Hundreds of chemicals illustrative of many structural and use categories are employed in the rubber industry. The present overview has centered on the structural features of a number of compounds representative of several select use categories, eg, vulcanizing agents, accelerators, antioxidants, antiozonants, and blowing agents, with focus on the nature of their impurities, their chemical degradation, and by-products, as well as on those chemicals that can be converted to N-nitrosamines.

Key terms: accelerators, antioxidants, antiozonants, blowing agents, nitroso compounds, vulcanizing agents.

A broad spectrum of chemicals numbering into the hundreds and representative of many structural and use categories are employed in the rubber industry for the purposes of rubber processing, facilitating the fabrication of the product, regulating the rate of vulcanization, effecting vulcanization, affecting vulcanizate properties, and improving the quality and the stability of the product in service (12, 14, 30). It has been reported that some 500 chemically, more or less, well-defined substances are used in quantities ranging from 10 to 10⁶ kg annually in the Swedish rubber industry alone (11, 12).

Several epidemiologic studies have reported that workers in the rubber industry have an increased risk of cancer (4, 7, 9, 14, 19, 20). The number and diversity of chemicals used or formed as by-products during the manufacturing processes and the multiplicity of exposure experienced within the rubber industry make it extremely difficult to attribute a particular toxic effect to a given exposure unambiguously. The exposure pattern is

further complicated by the interaction of chemicals and thermodegradation products (6, 10, 14).

Identification of mutagen exposures in the rubber industry by the sister chromatid exchange method (25, 27) and by monitoring of the urine by bioassay systems (6, 25, 26, 31, 32) has been reported. The International Agency for Research on Cancer (14) has recently devoted a monograph to the evaluation of the carcinogenic risks of exposures in the rubber industry, with emphasis on the tire manufacturing and repair sector, the cable-making sector, and the manufacture of other rubber goods. In addition biological properties of a number of selected compounds used in the rubber industry were described. The chemistry of rubber compounding has also been reviewed by Stern (29) and by Blow (1).

The basic materials used in rubber compounding consist of the following 11 major categories (14): (i) elastomers (natural or synthetic rubber), (ii) fillers (eg, China clay), (iii) antidegradants (antiozonants, antioxidants), (iv) vulcanizing agents (eg, sulfur or sulfur donors, organic peroxides, phenol resins, metal oxides), (v) accelerators (dithiocarbamates, thiurams, benzothiazoles, guanidines), (vi) retarders (eg, organic acids, N-nitrosodiphenylamine), (vii) reinforcing agents (eg, carbon black), (viii) pigments (inorganic pigments,

¹ Department of Health and Human Services, Food and Drug Administration, National Center for Toxicological Research, Jefferson, Arkansas 72079, United States.

Reprint requests to: Dr L Fishbein, National Center for Toxicological Research, Jefferson, AR 72079, USA.

organic dyes and lacquers, (ix) processing aids (eg, mineral oils, solvents, talc), (x) activators (eg, zinc oxide), and (xi) blowing agents (eg, azobisformamide, benzenesulfonylhydrazide). Miscellaneous additives include promoters, mold-releasing agents, bonding agents, and flame-proofing agents. Materials unique to latex processing include dispersing agents, stabilizers, emulsifiers, wetting agents, thickeners, preservatives, coagulants, foaming agents, and antifoaming agents (14).

The principal objective of this overview is to highlight the structural features of a number of compounds representative of several select use categories, eg, vulcanizing agents, accelerators, antioxidants, antiozonants, and blowing agents, with focus on the nature of their impurities, as well as those chemicals that can be converted to N-nitrosamines and their chemical by-products.

Accelerators

Rubber accelerators are highly reactive chemicals used to accelerate the rubber-curing process and ensure better final properties of the product. They function at

normal curing temperatures (140–200°C) and (except in latex) not at lower temperatures. Often a primary accelerator is used, together with a smaller amount of a secondary accelerator, to produce a synergistic effect (14). Accelerators can, to some extent, be classified by the rate of vulcanization achievable. For example, there are slow (amines, thiourea derivatives), moderately fast (sulfenamides, 1,3-diphenylguanidine mercaptobenzothiazole), and very fast (thiurams, dithiocarbamates, xanthates and thiophosphates) accelerators. It should be noted that accelerators can often behave differently in different polymer systems (14). Fig 1 illustrates the accelerator types classified by chemical structure; they include aldehyde-amine condensates, dithiocarbamates, benzothiazoles, amines, thiophosphates, guanidines, thioureas, xanthates, sulfenamides, and thiuram sulfides (14).

Typical accelerators from the mentioned categories include (i) aldehyde-amine reaction products (eg, acetaldehyde/ammonia, acetaldehyde/aniline, formaldehyde p-toluidine), (ii) arylguanidines (eg, diphenylguanidine, triphenylgani-

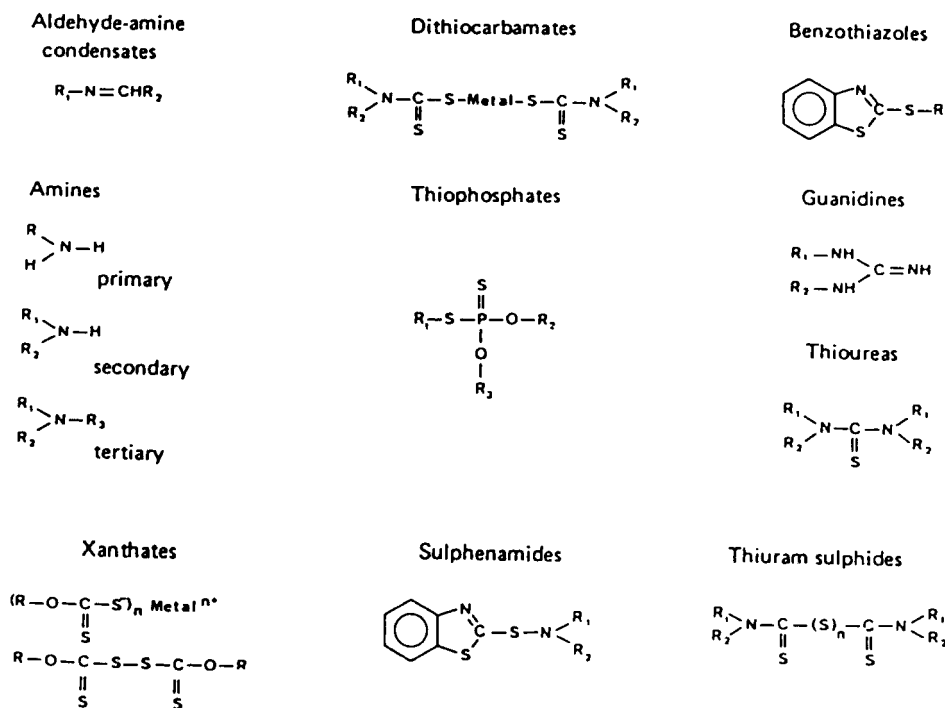


Fig 1. Accelerator types classified by chemical structure.

dine, di-o-tolylguanidine), (iii) dithiocarbamates (eg, copper, lead, bismuth, zinc and selenium, tellerium, and cadmium diethyldithiocarbamates), (iv) thiuram sulfides (eg, tetramethyl- and tetra-butylthiuram monosulfide, tetramethyl- and tetraethylthiuram disulfide), (v) thiazoles [eg, 2-mercaptobenzothiazole, zinc benzothiazolyl mercaptide, 2,2'-dithiobis(benzothiazole)], (vi) sulfenamides (eg, N-cyclohexyl-2-benzothiazole- and N-oxydiethylene-2-benzothiazole sulfenamides), and (vii) miscellaneous [eg, trimethylthiourea, 1,3-diethyl thiourea, 1,3-bis(2-benzothiazolylmercaptomethyl)-urea] (30).

Vulcanizing agents

The most common vulcanizing agent employed in most general purpose natural and styrene-butadiene rubber systems is elemental sulfur, which can produce both cross-links and cyclic structures. Organic sulfur compounds which liberate sulfur at vulcanizing temperatures are also used as vulcanizing agents instead of or in addition to sulfur. These include tetraalkyl thiuram disulfides, morpholine disulfide, dithiocarbamates, alkylphenol disulfides, aliphatic polysulfide polymer, and dithiophosphates. In addition selenium and tellurium and their compounds have also been used as vulcanizing agents (14, 30).

Antioxidants

The deterioration of rubber may be due to a number of factors, including chain breakdown, cross-link breakdown, cross-link formation, development of polar groups, or development of chromosphoric groups in the polymer (3). In addition the sulfide links may undergo oxidative attack, usually resulting in decreased cross-link density (14). Many of these processes are caused by oxidation. For example, in an autocatalytic reaction, the unsaturated polymer itself may be oxidized via free-radical mechanisms in a chain reaction mediated by a hydroperoxide produced during the process. The antioxidants that are employed act either by interrupting chain reactions or by preventing free-radical formation. The most widely used antioxidants that act by the former mechanism are amines and

phenol. Those agents that interfere by the latter mechanism include peroxide-decomposing agents, chelating agents, ultraviolet screens, absorbers, and quenchers (14). While natural rubber requires antioxidants only, the synthetic polymers require both antioxidants and stabilizers (materials which protect polymers during isolation and storage). (Antioxidants are materials which protect the polymers during processing and protect the finished product.) The commercial antioxidants can be divided into the following ten structural classes: (i) aldehyde-amines (eg, aldol-1-naphthylamine and acetaldehyde-aniline product), (ii) ketone-amines (eg, 1,2-dihydro-2,2,4-trimethylquinoline resin), (iii) diaryldiamines (eg, N,N'-diphenyl-p-phenylenediamine), (iv) diaryl-amines (eg, alkylated diphenylamine), (v) ketone-diarylamines (eg, diphenylamine-acetone product), (vi) substituted phenols (eg, 2,6-di-tert.butyl-4-methylphenol butylated hydroxyanisole), (vii) bisphenols [eg, 4,4'-bis(2,6-tert.butylphenol) and 2,2'-methylene-bis(4-methyl-6-tert.butyl phenol)], (viii) hydroquinones (monobenzyl ether of hydroquinone), (ix) aminophenols (eg, N-butyl-p-aminophenol), and (x) phosphites [eg, tri(nonylphenyl)-phosphite] (30).

Antiozonants

The described antioxidants do not, in general, afford protection against rubber deterioration caused by ozone. The most important commercial antiozonants are symmetrical and unsymmetrical derivatives of *para*-phenylenediamine (particularly the branched alkyl aryl derivatives). Additional antiozonants that are employed include the dihydroquinolines and the metal salts of dithiocarbamic acid (eg, nickel dibutyl dithiocarbamate).

Blowing agents

Blowing agents are used to produce foam rubbers by decomposing at curing temperatures to produce gases. The major blowing agents and routes of decomposition are shown in fig 2 (14). They include dinitrosopentamethylenetetramine, azobisbutyronitrile, azobisformamide, benzenesulfonyl hydrazide, and *para*, *para*'-oxybis(benzenesulfonyl hydrazide).

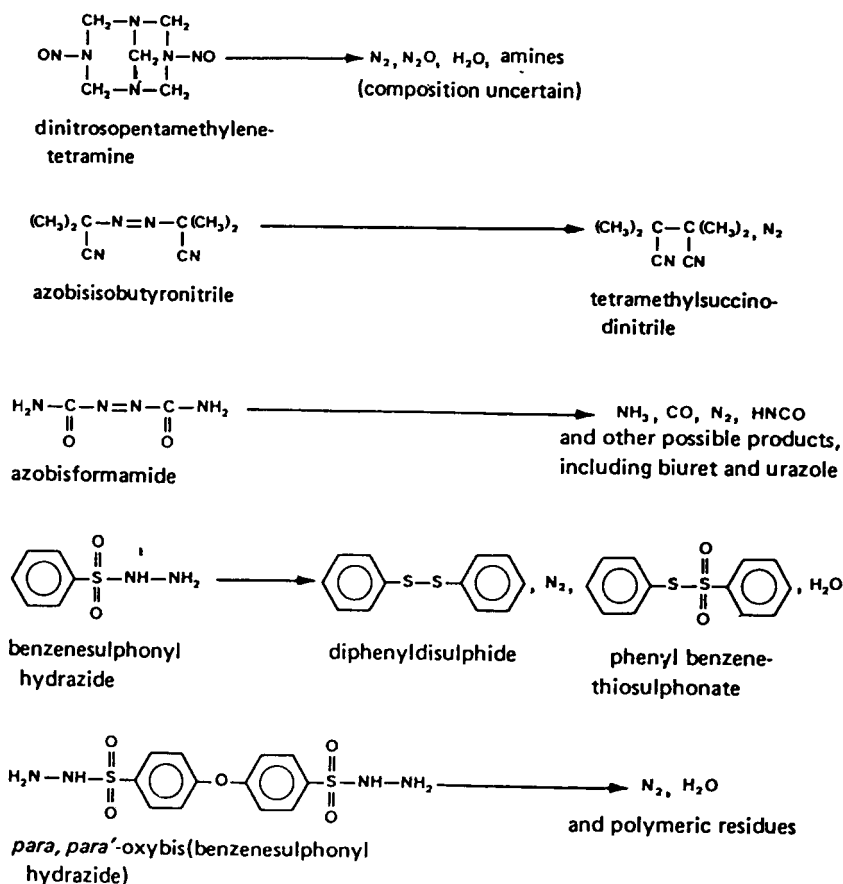


Fig 2. Some blowing agents and their routes of decomposition.

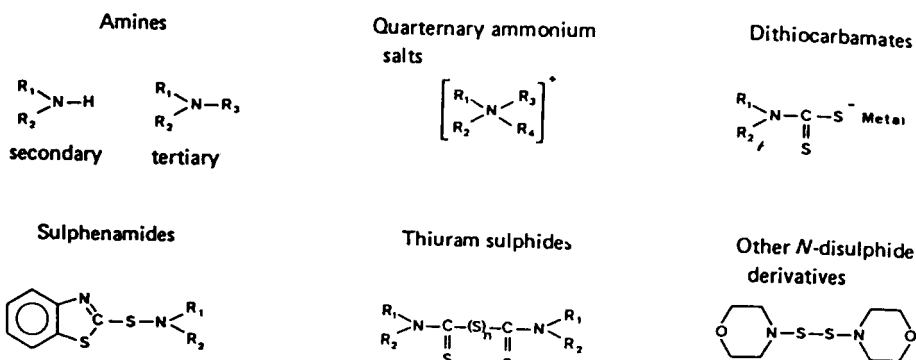


Fig. 3. Groups of chemicals that can be converted to N-nitrosamines.

Nitroso compounds

It is important to note the occurrence of nitrosation, resulting in the formation of volatile N-nitrosoamines during the manufacture and processing of rubber

(5, 14, 15, 18, 22, 28, 34). The following N-nitrosamines have been detected which are among the most potent carcinogens known (13): N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosodibutylamine, N-nitrosopiperidine, N-nitrosopyr-

rolidine, and N-nitrosomorpholine. It should be stressed that the corresponding nitrosatable precursor of each of these compounds (with the exception of N-nitrosopyrrolidine) is used in rubber compounding (14).

In addition to the familiar nitrosation of secondary amines, reactions involving tertiary amines or amine derivatives (eg, dialkyl dithiocarbamates, dialkyl thiuram sulfides, and sulfenamides) are possible since these types of agents are used as vulcanization accelerators and stabilizers. Fig 3 illustrates the groups of chemicals that can be converted to nitrosamines. These include secondary and tertiary amines, quarternary ammonium salts, dithiocarbamates, sulfenamides, thiuram sulfides, and N-disulfide derivatives (14).

Accelerators and stabilizers derived from dialkylamines are ubiquitous in elastomer compounding. Polymers compounded with dialkylamino accelerators or

stabilizers have been found to contain the corresponding extractable N-nitrosamines. For example dipentamethylene thiuram disulfide yielded N-nitrosopiperidine, and zinc dibutyldithiocarbamate yielded N-nitroso-di-n-butylamine. When two different compounds were present, such as in chlorosulfonated polyethylene and ethylene-propylenediene terpolymer, then both the corresponding N-nitrosamines were detected (15). The elastomer need not be cured for N-nitrosamines to be present. If the raw polymer contains a dialkyl amino compound, then the corresponding N-nitrosamine can be extracted.

Previous studies (34) have shown that N-nitrosamines are evolved from heated elastomers. More recent studies of Ireland et al (15) showed that N-nitrosamines can be extracted in water from elastomers. The levels of nitrosamines extracted ranged from 0 to 1,400 ppb from com-

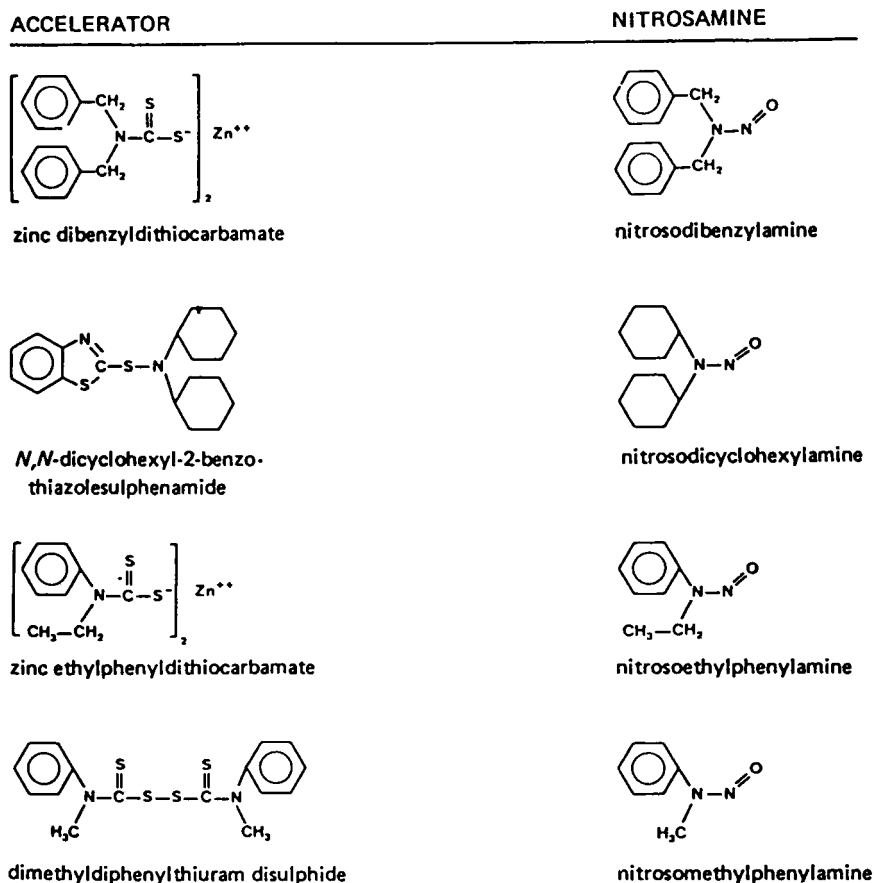
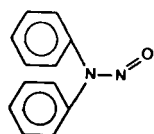
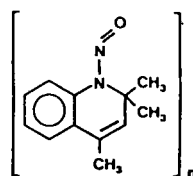


Fig 4. Accelerators and corresponding nonvolatile nitrosamines.

RETARDERS

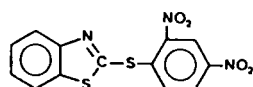


N-nitrosodiphenylamine

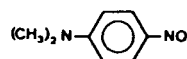


poly-*N*-nitroso-2,2,4-trimethyl-1,2-dihydroquinoline

ACCELERATORS

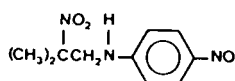


2-(2,4-dinitrophenylthio)-benzothiazole



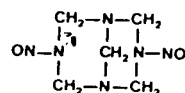
N,N-dimethyl-*para*-nitrosoaniline

PROMOTOR



N-(2-methyl-2-nitropropyl)-4-nitrosoaniline

BLOWING AGENT



dinitrosopenta-methylenetetramine

Fig 5. Nitro and nitroso compounds that are used in the rubber industry and can act as precursors of nitrogen oxides.

Table 1. Examples of nitrosamine contamination in commercial samples of rubber chemicals.

Accelerator	Nitrosamine present	Concentration (µg/kg)
<i>N</i> -pentamethylene dithiocarbamate, piperidine salt	<i>N</i> -nitrosopiperidine	200
Tetramethylthiuram disulfide	<i>N</i> -nitrosodimethylamine	4–800
Tetraethylthiuram disulfide	<i>N</i> -nitrosodiethylamine	25–80
Zinc pentamethylene dithiocarbamate	<i>N</i> -nitrosopiperidine	60–450
Zinc dibutyldithiocarbamate	<i>N</i> -nitrosodibutylamine	65–2,500
Zinc diethyldithiocarbamate	<i>N</i> -nitrosodiethylamine	10–100
Morpholine derivatives	<i>N</i> -nitrosomorpholine	60–3,500

pounded and cured polychloroprene, ethylene-propylene-diene terpolymer, chlorosulfonated polyethylene, and natural rubber, as well as from several commercial rubber articles. It was not possible in this study to identify a nitrosating agent that could act upon the dialkylamino compounds during processing (15).

Some nitrosatable accelerators (eg, zinc dibenzylthiocarbamate, *N,N*-dicyclohexyl-2-benzothiazolesulfenamide, zinc

ethylphenyldithiocarbamate, and dimethyldiphenylthiuram disulfide) which yield nonvolatile nitrosamines after nitrosation are shown in fig 4.

A number of additional chemicals used in the rubber industry as additives contain nitro or nitroso groups that are potential nitrosating agents. Since some of these agents may decompose thermally during processing to yield nitrogen oxides, direct nitrosation of nitrosatable com-

pounds contained in solid rubber must be considered possible (14, 24). Fig 5 illustrates some potential nitrogen oxide-releasing chemicals used in the rubber industry. These include the retarders N-nitrosodiphenylamine and poly-N-nitroso-2,2,4-trimethyl-1,2-dihydroquinoline, the accelerators 2-(2,4-dinitrophenylthio)-benzothiazole and N,N-dimethyl-*para*-nitrosoaniline, the promoter N-(2-methyl-2-nitropropyl)-4-nitrosoaniline, and the blowing agent dinitrosopentamethylene-tetramine (14).

It is also important to restate that nitrosamines can also be present in rubber chemicals as contaminants. It is believed that the origin of these nitrosamines most likely results from nitrosation by ambient nitrogen oxides during production or storage (28). Table 1 lists examples of nitrosamine contamination in seven commercial samples of accelerators (28).

Chemical by-products

With the exception of N-nitrosamines there is a paucity of data relating to the nature of the chemical species generated during the processing of rubber. Pyrolysis reactions do not normally occur since the maximum temperature of vulcanization is approximately 240°C. During vulcanization the mold contains a reducing atmosphere since air is excluded. Products that could thus be formed during vulcanization and be released from the surface include amines and organic sulfides derived from the accelerators (eg, curing systems containing tetramethylthiuram disulfide may produce carbon disulfide and dimethylamine during curing) (14, 33). The accelerator N-*tert*-butyl-2-benzothiazole sulfenamide can yield *tert*-butylisothiocyanate at curing temperatures (23). Sulfenamide accelerators can yield mercaptobenzothiazole and characteristic amines (2, 14, 16, 17, 21), while thiourea accelerators may decompose to yield isothiocyanates (eg, diethylthiourea produces ethyl isothiocyanate) (8).

A recent study of the mutagenicity of rubber vulcanization gases derived by heating chloroprene rubber, ethylene propylene rubber, styrene-butadiene rubber, and butadiene acrylonitrile rubber indicated a very complex situation with

respect to the number of and properties of substances responsible for the mutagenicity (curing systems, additives, and filling materials from various sources were represented in the material) (10).

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