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CHAPTER 35

Tire and Rubber Manufacturing Industry

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RUBBER INDUSTRY HAZARDS

The production of rubber products involves a mixture of complex chemicals to which workers may be exposed. In addition to the multiple chemicals used in rubber production, there are many by-product chemicals produced by the various processes and reactions.

It was in the early part of the nineteenth century that the rubber industry began in the United States. The vulcanization process discovered by Charles Goodyear in 1839 (using sulfur and heat to cross-link natural rubber molecules), as well as the use of additives to improve processing, led to a demand for rubber products that exceeded supplies. By the end of the nineteenth century, rubber plants were being exported from Brazil to plantations in southeast Asia, Sri Lanka, Indonesia, Liberia, and Zaire. These countries remain the primary producers of natural rubber today.

The growth of the petrochemical industry and advances in polymer technology, coupled with shortages of natural rubber during World War II, led to the creation of the synthetic rubber industry in the 1940s.

Finished rubber products consist of basic elastomers plus a multitude of chemical additives. The increasing demand for natural and synthetic rubber has resulted in an increase in the production of processing chemicals. Today, the demand for synthetic rubber is outpacing the demand for natural rubber. The fastest growing demand will be for ethylene-propylenediene rubber. Demand for styrene-butadiene synthetic rubber (SBR) and SBR-latex is less (1).

Four types of synthetic rubbers have become widely used since 1950: SBR, butyl rubber, nitrile rubber, and polychloroprene. Other synthetic rubbers are polysulfide, polyurethane, and ethylene-propylenediene. SBR is used mainly in tire production and is the most commonly used rubber in the world (1).

In concert with the steady growth in output of the various rubber products, the output of rubber-processing chemicals is expected to continue to increase. These chemicals impart the desirable characteristics for the final rubber product. Tire manufacturing remains the leading consumer of nearly one-half of all natural and synthetic rubber produced annually. This industry employs more than one-half million workers in nearly 400

plants around the world. A single tire may require the use of several hundred raw materials. Workers' exposures may vary, not only with different jobs within a plant, but also with changes in production techniques and material use over time. Many changes have occurred in the industry over the years with regard to the kinds of chemicals used as well as the processes used to manufacture rubber (2).

Natural rubber is obtained from plants, especially the *Hevea brasiliensis* tree, native to the Amazon region of South America. Preliminary processing involves filtering to remove dirt and debris and coagulation with formic and acetic acids. The rubber is then rolled into sheets, cut, and cured with either smoke or sodium bisulfite bleach, then formed into bales for shipping (3).

The production of natural rubber shares many of the occupational health hazards of other agricultural industries. These include use of sharp cutting implements, exposure to pesticides (including sodium arsenite), and risk of tropical diseases in endemic areas. The acids and caustics used in processing are potential respiratory and skin irritants. Increasing use of processing equipment requires careful attention to safety practices to prevent worker injuries.

The basic ingredient of synthetic rubber is polymeric material (elastomer) similar to plastic resin. Rubber in its crude state is lacking in strength and resiliency. Cross-linking using sulfur or sulfur donors during the vulcanization process creates a durable, pliable, thermoset material.

The manufacturing of synthetic rubber involves the use of large volumes of raw materials. Polymerization of rubber ingredients takes place in enclosed vessels. Leaks from these vessels and maintenance operations, such as the cleaning of reaction vessels and maintenance of distribution pipes, were major sources of exposure before implementation of proper venting and respiratory protection measures.

cis-1,4-Polyisoprene is the basic natural rubber. The synthetic SBR is produced through an emulsion polymerization reaction of aqueous styrene and gaseous butadiene. Unreacted monomers are recycled. The latex polymer is coagulated with sulfuric acid and dried before shipping. Other chemicals may be added—such as carbon black, antioxidants, and curing agents—depending on the intended end use of the product (2).

Overexposure to unreacted styrene monomer can result in central nervous system effects of giddiness, loss of coordination, and possible liver damage. Worker exposure to 1,3-butadiene can result in mucous membrane and respiratory irritation at high concentrations; it is also a suspected human carcinogen.

Neoprene (polychloroprene) combines the mechanical properties of natural rubber with increased resistance to aging, oils,

and chemicals. Neoprene is used in belts, hoses, footwear, gloves, and low-voltage insulation. Chloroprene (2-chloro-1,3-butadiene) is flammable, and exposure to high concentrations of unreacted monomers as well as partially polymerized intermediates may produce narcosis, respiratory and skin irritation, alopecia, and liver and kidney damage.

Other synthetic rubbers include butyl (isobutylene-isoprene polymers), nitrile (NBR) copolymers of acrylonitrile and butadiene, and polyurethane. Acrylonitrile is a respiratory and mucous membrane irritant, and overexposure can produce cyanide poisoning. Acrylonitrile is a suspected human carcinogen (2).

INDUSTRY PROCESS AND REACTIONS

The rubber industry work environment is quite diverse with respect to physical and chemical exposures. Hundreds of different chemicals are used as rubber additives in the process of manufacturing rubber products (2). These chemicals are grouped into various functional categories:

- Elastomers (natural or synthetic)
- Fillers
- Antidegradents
- Vulcanizing agents
- Solvents
- Accelerators
- Activators
- Retarders
- Reinforcing agents
- Pigments and dyes
- Antitack agents
- Bonding agents
- Miscellaneous chemicals

The major reinforcement and filler materials are carbon black and amorphous silica, although asbestos-containing materials have been used. Vulcanizing agents include sulfur, zinc oxide, stearic acid, and other sulfide and sulfur compounds. Thiurams, thiocarbamates, and various amine and aldehyde compounds are used as accelerators to increase the rate of rubber curing. Other additives include activators (soaps and fatty acids), extenders (mineral oils), plasticizers (phthalates), antioxidants (amines, quinones), and pigments.

The basic production stages in the manufacturing of rubber tires and tubes are presented in Figure 35-1 and summarized in this chapter. Descriptions for each of these processes are as follows (Table 35-1):

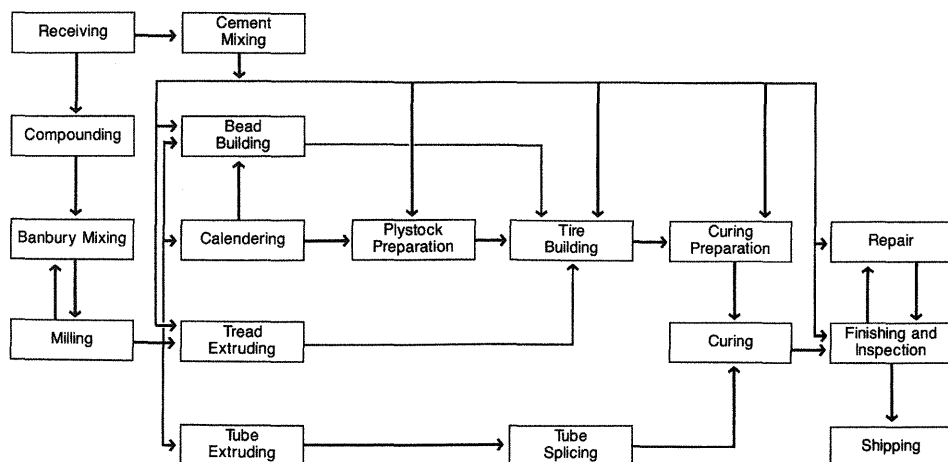


Figure 35-1. Production stages in manufacturing of tires and tubes. (Adapted from ref. 13, with permission.)

TABLE 35-1. Summary description of major work areas (occupational title groups)

1. *Shipping and receiving:* Receiving unloads and stores all incoming ingredients that go into making the final products, e.g., carbon black, pigments, rubber, etc. Shipping stores and loads the final products (e.g., tires) into trucks or boxcars.
2. *Compounding and mixing, cutting and milling:* Cement mixing—raw ingredients (rubber, fillers, oils, pigments) are weighed and mixed together in a Banbury mixer. Environmental exposure to particulates (e.g., carbon black, accelerators, antioxidants, talc) is high. Cements are solvents such as paraffin HC (e.g., hexane), aromatic hydrocarbons (e.g., toluene, xylene), chlorinated HC (e.g., CCl_4 , trichloroethylene), and ketones (e.g., methyl ethyl ketone).
3. *Mill-mixing:* Service to batch preparation—mill-mixing is a largely superseded mixing process. Service jobs are for the compounding and mixing operations. Environmental exposures are similar to compounding and mixing.
4. *Milling:* Rubber mix from Banbury is processed further under heat and pressure, until rubber is in a soft, plastic state. This is probably the first work area where there is substantial exposure to reaction products.
5. *Calender, plystock handling:* The rubber stock from the mill is rolled out into a sheet of controlled thickness, usually covering a fabric. The calender stock (plystock) is then cut and spliced for use in building the ply of the tire. There is some exposure to reaction products and solvents.
6. *Tuber (extrusion), tread cementing:* Rubber stock from a mill is forced through a die forming a tread or tube. The tread is cut in appropriate lengths and cemented with solvents on the cut end so as to be tacky.
7. *Tire building, bead building:* Beads are rubber-and-fabric-covered wire that in a finished tire rest on the rim of the wheel. The treads, beads, and plystock are used to build the tire. The major exposures are to solvents.
8. *Green tire inspection, paint and line:* The green (uncured) tire is inspected and repaired and sprayed with solvents or lined with talc so it will not stick in the curing mold. Solvents—and in some cases, talc—are the major environmental exposures.
9. *Tube and flap building, valves:* The tube from the extruder is cut and valves attached. The inside of the tube is coated with talc and then cured, buffed, and sprayed with solvent to make it tacky.
10. *Curing:* The green uncured product (tire, tube) is cured under heat and pressure. The major environmental exposure is to reaction products, and, in tube curing, to talc.
11. *Inspection, finishing, repair:* The cured product is inspected (repaired if necessary) and made ready for shipping (finishing). Environmental exposures are in repairing (solvents, rubber dust).
12. *Maintenance:* This job group includes mechanics, pipefitters, electricians, welders, painters, and carpenters.
13. *Mechanical and special products:* A variety of products and jobs are included in this group, most of them similar to machine shop types of exposures.
14. *Reclaim operations:* Scrap vulcanized rubber products are shredded, ground up, and devulcanized. By the application of heat and chemicals, the rubber compound is restored to its original plastic state. Exposures are to particulates and chemicals.
15. *Synthetic plant:* This is essentially a chemical plant making elastomers that approximate one or more of the properties of natural rubber. SBR is the most important synthetic rubber. Others include neoprene, nitrile, ethylene-propylene-diene, etc. Exposures are to the gases or liquids that are the ingredients for the particular synthetic rubber being made.
16. *Janitoring, trucking, power plant, etc.:* This is a miscellaneous group with a variety of different jobs and exposures.

SBR, styrene-butadiene rubber.
Adapted from ref. 15, with permission.

- Raw material handling, compounding, and mixing
- Milling
- Extruding and calendering
- Component assembly and building
- Curing or vulcanizing
- Inspection, repair, and finishing
- Storage and dispatch

Raw Materials Handling

The initial step in product fabrication involves weighing and mixing (compounding) various additives with either natural or synthetic rubber. The manual weighing and filling of hoppers results in generation of dust. Additives may be in the form of powders, flakes, or pellets and are supplied in bags or drums.

Carbon black and occasionally zinc oxide arrive in bulk form, either in tankers or metal containers. Antioxidant and other oils are usually received in 55-gallon drums or tank cars. Exposure to dusts or vapors may occur during the handling of these raw materials. Compounding and mixing of materials may be a dusty process, especially when clinical agents stored in open drums and bags are weighed and transferred for mixing in the Banbury units (2).

Raw rubber and other additives are usually fed into a mixer or Banbury unit by conveyor or manual process. These components are mixed together under pressure between the rotors and against the walls of the chamber. The chamber is usually water cooled to reduce heat. However, in some operations, the chamber may be steam heated to reduce the viscosity of the mixture. Retarders, antidegradents, processing oils, reinforcing agents, and fillers are often added to the raw rubber stock at this stage (2).

Milling

The mixer drops its batch of mixed rubber directly onto the rollers of a discharge mill, in which further mixing takes place. This mixture is then cooled to between 65° and 80°C and often transferred to other mills for further processing. Local exhaust ventilation is frequently used to collect fumes and vapors that arise from the process. Workers may be exposed to vapors, aerosols from the hot rubber, and dust from incompletely mixed additives or other compounding agents added on mix mills.

Rubber comes off the mill in a continuous sheet, which is fed by a conveyor to a dip that prevents the rubber from sticking together. Mineral dust (talc and soapstone) slurries are commonly used as antisticking agents. The newly dipped or detackified rubber sheet is dried, folded, placed on pallets, and—in the case of the first-stage rubber—stored. After this stage, rubber is ready for fabrication to the components from which a tire is built.

Rubber stock is heated and remilled to obtain softness and plasticity for further processing. Time and temperature of the milling process govern the chemical reactions within the batch, thus determining the properties of the finished material. During the formation of rubber sheets, the uncured rubber is coated with an antitack agent to reduce sticking. Talc (either in a dry or slurry form) was used extensively for this purpose but has now been replaced by the use of amorphous silica and liquid soaps. The rubber stock is cooled in dip tanks, generating steam.

All of these operations result in potential exposure to reaction products from heated but unvulcanized rubber stock. In addition, there is potential exposure to dust, such as talc or soapstone from the antitack agents.

Extruding and Calendering

The tread and sidewall of a tire are produced by an extrusion process. In the manufacture of tread for tires, the milled rubber sheet is extruded through a die corresponding to specific tread dimensions and weight. It is then cut into specified lengths, and the ends are joined manually or automatically with cement at a tire-building station.

Rubber sheet may also be formed into plystock by calendering. Steel cord and fabrics (nylon, rayon, polyesters, and fiber-glass) may be pretreated using a phenol-formaldehyde solution to improve adhesion.

The tread and sidewalls of a tire can be manufactured separately or in the same operation. The tread-sidewall extruder laminates the two types of strips to form a tire tread and sidewalls. Strips are bonded by heat and pressure generated by a rotating extruder screw. The tread and sidewall may also be formed separately in similar types of production lines. Extrusion temperatures are in the range of 80°C and may result in volatilization of constituents that are applied earlier in the mixing of the rubber. The extruder operator may also be exposed to volatile organic compounds used at the tread-end cement station or other nearby operations. After extrusion, the tread is sometimes cooled in a water bath and dipped in a solvent bath. Solvents typically used in this phase of tire building include naphtha, heptane, hexane, isopropanol, and toluene. The continuous rubber tread is then cut into specified lengths and the tread ends tackified. Tackification usually involves applying a cement containing dissolved rubber and solvents (naphtha and toluene) on the tread ends. Local exhaust ventilation may be available to control solvent vapor exposure.

Calendering is the operation that produces plies and belts, which form the body of the tire and give it strength and stability. Plies and belts are composed of rubber reinforcements of fabric, steel wire, or glass fiber. Plies, belts, and liners are made of a calender, a multiple roll mill that produces stock of carefully controlled thickness. A rolled fabric, normally rayon or some other synthetic fiber, is spliced either by adhesive or a high-speed sewing machine onto the end of a previously processed roll. This continuous sheet of fabric is then dipped under controlled tension into a tank containing latex. Solutions of formaldehyde, caustic soda, and resorcinol—or other synthetic adhesive combinations—may be added to the latex at this point. After dipping, the fabric travels past either rotating meter bars or vacuum suction lines and then through a drying oven to remove excess solvent. The latex-dipped fabric is then passed through a calendering machine, which impregnates it with rubber. Temperature during the calendering operation is 70° to 80°C. Potential toxins emitted from this process are similar in character to those from milling or extrusion.

Tire Building and Component Assembly

Rubber tires represent combinations of many different rubber components. Tires are assembled on a drum combining ply stock, beads, sidewalls, and other components. The surface of the components may be treated with solvent, primarily naphtha, during the tire-building process. Many rubber products, such as hoses, are already formed into their final shape before curing. Tires are sprayed with a mold-release agent and placed into steel molds to impart the final shape and surface characteristics during the curing process.

Passenger car tires are built as cylinders on a collapsible rotating drum. First, the inner liner is wrapped around the drum followed by a variable number of rubber impregnated fabric plies. Next, the edges of the fabric and inner liner are wrapped around the bead assemblies. Then, pressure is applied manually or automatically from the tread center out to the bead to expel air trapped between the assembled components. Belts made of fabric, steel, or glass fiber are laid onto the cord, and finally the tread and sidewall components are wrapped around the assembled components and bonded. Organic solvents, such as naphtha, heptane, hexane, isopropanol, methanol, and toluene, may be used during the building to tackify the rubberized components. Potential sources of human exposure at such stations occur during solvent application and the handling of green (uncured) tire components.

Curing or Vulcanizing

Before curing, the assembled unvulcanized part is inspected and repaired if necessary. The tire is then placed in a ventilated booth, in which it is sprayed on the inside with lubricants and on the outside with release agents, which prevent the tire from sticking to the mold after curing. Either organic-based lubricants or water-based suspensions of silicone solids may be used for outside sprays. Solvent-based lubricants may contain naphtha, hexane, heptane, isopropanol, and toluene. Evaporation of these solvents can contribute to human exposure.

The tire is then molded and vulcanized in a curing press. In this process, the tire is shaped, the tread design created, and chemical cross-linking of the rubber product triggered, allowing the tire to hold its shape. Curing usually takes 20 to 60 minutes at a temperature of 100° to 200°C. All freshly molded tires release substantial volumes of curing fumes into the work area and continue to do so as they are transported—usually by conveyor—to the finishing and storage areas.

Finishing and Inspection

After vulcanization, tires are inspected for faults and may undergo further processing, such as grinding, trimming, repair, painting, and assembly. Potential occupational health hazards in the refinishing operations involve exposure to rubber dust, particularly from trimming, fumes from grinding, and solvent vapors from cleaning, patching, and painting of blemishes.

Storage

Final rubber products can degas a variety of chemicals and chemical by-products during storage, although concentrations are minimal compared with those generated during the cure operation.

CHEMICAL COMPOUNDS USED IN RUBBER COMPOUNDING

Types of Rubber Compounds

A multitude of chemical agents are used to produce the final rubber product. Elastomers, the basic polymers used in rubber manufacturing, are divided into three functional classes:

- General purpose
- Solvent resistant
- Heat resistant

General-purpose elastomers are the SBR type, butyl, natural rubber, and polybutadiene (Fig. 35-2). Chemical- and solvent-resistant elastomers are nitrile, polyurethanes, and polychloro-

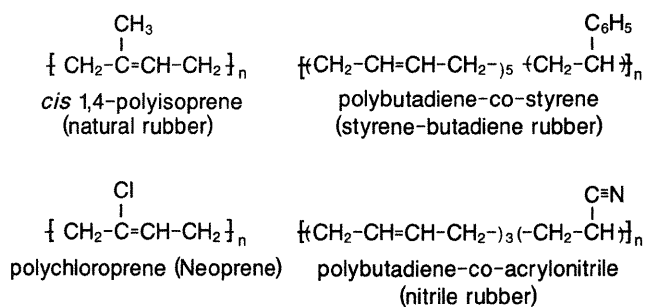


Figure 35-2. Rubber compounds classified by chemical structures. (From ref. 2, with permission.)

TABLE 35-2. Types of synthetic rubbers

Styrene-butadiene rubber (SBR): The major synthetic rubber produced. Makes up 40% of the world's production. Weaker than natural rubber but ages more slowly.

Butyl rubber: Low permeability for air and gases. Used for inner tubes.

Nitrile rubber: Abrasion resistant. Resistant to penetration by chemicals, water, and oils.

Polyisoprene: Used mainly as a blending component with other rubbers. Synthetic polyisoprene rubber contains a high percentage of cis-isoprene.

Polychloroprene: Known as neoprene. Flame resistant and wears longer than SBR. Possesses resistance to oil, solvent, and water penetration. Used mainly in the transportation industry and for sealants, cables, coatings, and adhesives.

Ethylene-propylene: Possesses resistance to ozone, sunlight, weather, and aging.

Silicone rubber: Resists degradation in temperature extremes. Used in aerospace industry and medical-surgical field.

Polyurethane: Used for coatings, insulation, packaging, and in automotive industry.

Poly sulfide: Resistant to solvents and used in sealants in construction and building.

Chlorosulfonated polyethylene rubber: Used in cable covering.

Polyacrylic rubber: Plastic rubber that resists oils and aging. Used as seals and gaskets.

Fluoroelastomers: High thermal stability. Used in aerospace industry.

Thermoplastic elastomers: Melt at high temperatures and resolidify on cooling without loss of elastic property.

Adapted from ref. 2, with permission.

prene (neoprene). Heat-resistant examples are silicone, polyethylene, and polyacrylates. Today, SBR is the major synthetic rubber produced. It makes up approximately 40% of the world production and is the primary component of tires. Examples of synthetic rubber and their properties are shown in Table 35-2.

Vulcanizing Agents

Vulcanizing agents are necessary to induce cross-linking of rubber elastomers during the process of rubber manufacturing. The most common vulcanizing agent in general-purpose use is sulfur, in which cross-links and cyclic structures are formed (2). Other common sulfur donors used are morpholine, dithiocarbamates, dithiophosphates, and tetraethylthiuram disulfide and tetramethylthiuram disulfide.

Other agents used in the vulcanization process are benzoyl peroxide, dicumyl peroxide, aromatic nitrogen compounds, dioximes, phenols, diisocyanates, and dinitroso compounds (3). Silicone rubber, which is fully saturated, cannot be vulcanized with sulfur. Instead, peroxides are necessary to achieve cross-linking by formation of free radicals on the polymer chain (2).

Accelerators

The reaction between sulfur donors and rubber is very slow, and to speed the process a group of chemicals termed *accelerators* is used (Table 35-3).

Accelerators function at curing temperatures of 140° to 200°C. Accelerators can be classified by their chemical structure, their rate of vulcanization, and their sulfur demand. Less active accelerators require large amounts of sulfur donors, whereas more active ones require a smaller quantity.

Slow accelerators are amines and thiourea derivatives. Moderately fast accelerators are sulfonamides, 1,3-diphenylguanidine, and mercaptobenzothiazole (MBT). Very fast accelerators are thiurams, dithiocarbamates, and thiophosphates (Figs. 35-3 through 35-6).

TABLE 35-3. Common rubber accelerators

Thiurams
 Tetramethylthiuram disulfide (TMTD)
 Tetraethylthiuram disulfide (TETD)
 Dipentamethylenethiuram disulfide (PTD)
 Tetramethylthiuram monosulfide (TMTM)

Mercapto group
 2-Mercaptobenzothiazole (MBT)
 Cyclohexylbenzothiazolesulfenamide (CBS)
 Dibenzothiazolodisulfide (MBTS)
 Morpholinomercaptobenzothiazole (MMBT)

PPD group
 Phenylcyclohexyl-PPD (CPPD)
 Isopropylphenyl-PPD
 Isopropylaminodiphenylamine (IPPD)
 Diphenyl-PPD (DPPD)
 Diaminodiphenylmethane (DDM)

Naphthyl group
 Phenyl-β-naphthylamine (PBN)
 Sym-Di-β-naphthyl-PPD (DBNPD)

Carbamates
 Zinc diethyldithiocarbamate (ZDC)
 Zinc dibutyldithiocarbamate (ZBC)

Miscellaneous
 1,3-Diphenylguanidine (DPG)
 Dithiodimorpholine (DOD)
 Monobenzyl ether of hydroquinone
 Butyraldehyde-aniline
 Ethylene thiourea

Adapted from ref. 3, with permission.

The variety of chemical structures ranges from primary, secondary, and tertiary amines; aldehydes; thiophosphates; dithiocarbamates; xanthates; sulfonamides; guanidines; thioureas; and benzothiazoles. The need for better accelerators has led to development of a benzothiazole class of chemicals, particularly 2-MBT, which accounts for 90% of the accelerators in use (2,3). Reacting MBT with amines led to the production of sulfonamide accelerators. Cure rate and scorch safety (scorching devalues a product) are also important factors to consider in the choice of accelerators (2).

Studies have demonstrated that nitrosamines—suspected human carcinogens—are released when compounded rubber is heated, as occurs in milling, calendaring, and curing operations.

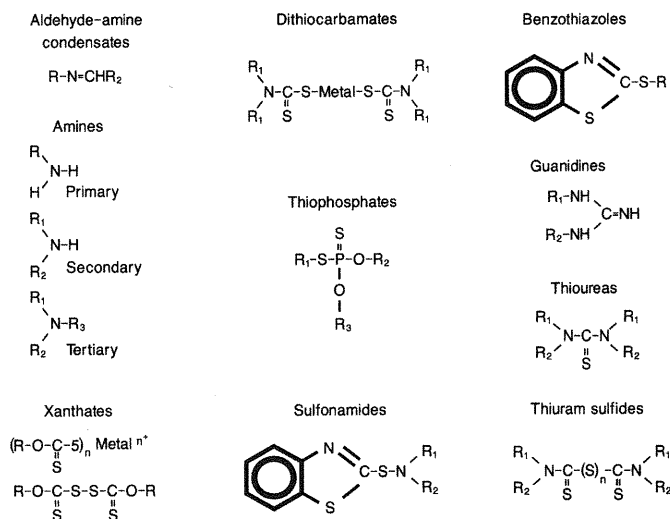


Figure 35-3. Accelerator types classified by chemical structure. (From ref. 2, with permission.)

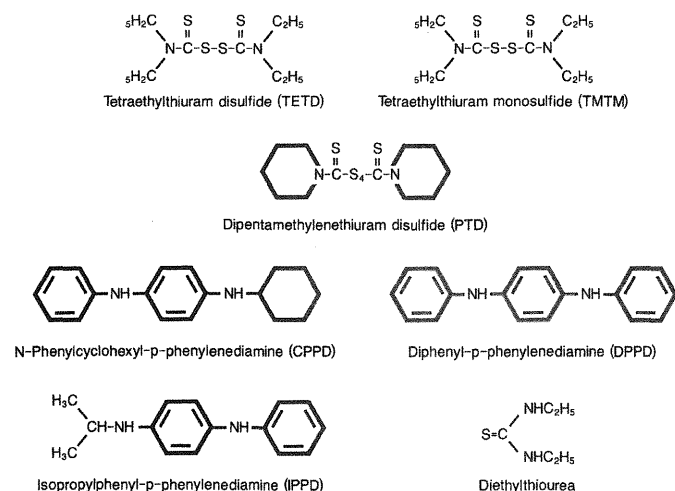


Figure 35-4. Thiurams. (Adapted from ref. 3, with permission.)

Nitrosamines are also present as contaminants in accelerator chemicals (Table 35-4; Fig. 35-7). The highest air concentrations of nitrosamines have been measured in curing areas. Changes in rubber formulations have helped to reduce or even eliminate these by-products. Nitrosamines are the result of the use of amines, which are nitrosated by nitrogen oxides in the manufacturing process.

Activators

Activators are used to make accelerators more effective and speed the process of vulcanization. Activators are usually inorganic compounds and metal oxides such as zinc oxide, lead oxide, magnesium oxide, and sodium carbamate. Organic acids, such as stearic acid or lauric acid, are used to solubilize the metal oxides in the rubber mixture (2). The most common activator is zinc oxide.

Retarders

Retarders are mainly organic acids, anhydrides, and phthalimides; they delay the action of an accelerator. They are sometimes used to slow the vulcanization process. Also, accelerated rubber may cure prematurely, and retarders slow this process. Commonly used retarders are *N*-nitrosodiphenylamine, cyclohexylthiophthalimide, and a sulfonamide (2). Cyclohexylthiophthalimide degrades to phthalimide during the vulcanization process (Fig. 35-8) (2).

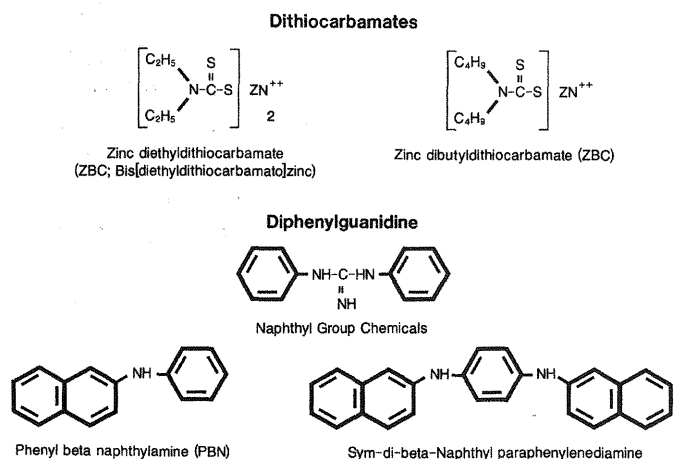


Figure 35-5. Dithiocarbamates and diphenylguanidine. (Adapted from ref. 3, with permission.)

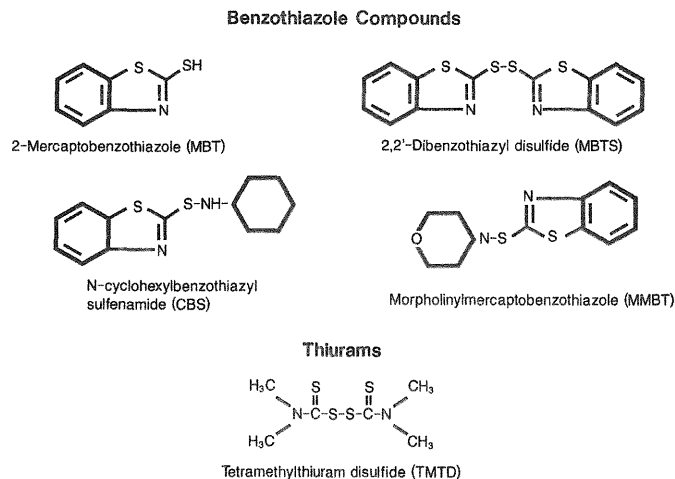


Figure 35-6. Benzothiazole compounds and thiurams. (Adapted from ref. 3, with permission.)

Antidegradants and Antioxidants

Because rubber deteriorates with aging by oxidation, anti-degradants are usually incorporated in the final rubber products to prevent or slow oxidation processes. Oxidation can produce cross-linking of butadiene molecules, resulting in stiffness of rubber products. Antioxidants prevent the polymer chain from degrading. Naphthylamine antioxidants were associated with bladder cancer and have been withdrawn from use. Current antioxidants include phenols, thioesters, and amines. Commonly used antioxidants are diphenylamines and dihydroquinolines. *p*-Phenylenediamine is useful in preventing degradation because of ozone. Antioxidants with phenolic structures fall into five classes: (a) phenols with varying side groups, (b) bisphenols with side groups, (c) thio-bisphenols, (d) polyphenols, and (e) polyhydroxyphenols (3).

Processing Aids

Processing aids are used to make uncured rubber malleable and more easily mixed, extruded, or calendered. In the early years of rubber manufacturing, pine tars were used for this purpose, but they have been replaced by naphthenic and aromatic mineral oils (2). Aromatic processing oils are widespread in the rubber industry. Many rubber formulations contain as much as 20% or more of aromatic mineral oil, with large amounts of polycyclic aromatic hydrocarbons (PAH) present in these oils. Mercaptan derivatives, thiophenols, or MBT may also be used to help soften rubber.

TABLE 35-4. Nitrosamine contamination in commercial rubber chemicals

Accelerator	Nitrosamine present
<i>N</i> -pentamethylene dithiocarbamate, piperidine salt	<i>N</i> -Nitrosopiperidine
Tetramethylthiuram disulfide	<i>N</i> -Nitrosodimethylamine
Tetraethylthiuram disulfide	<i>N</i> -Nitrosodiethylamine
Zinc pentamethylene dithiocarbamate	<i>N</i> -Nitrosopiperidine
Zinc dibutyldithiocarbamate	<i>N</i> -Nitrosodibutylamine
Zinc diethyldithiocarbamate	<i>N</i> -Nitrosodiethylamine
Morpholine derivatives	<i>N</i> -Nitrosomorpholine

Adapted from ref. 18, with permission.

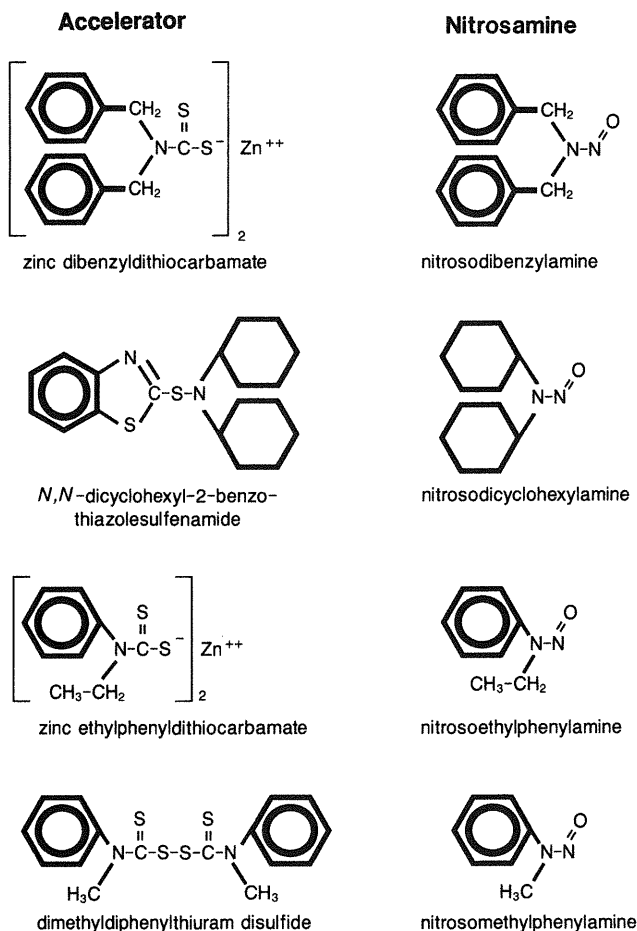


Figure 35-7. Accelerators and corresponding nonvolatile nitrosamines. (Adapted from ref. 2, with permission.)

Reinforcing Agents

Reinforcing agents are very important ingredients in rubber technology and add tensile strength and abrasion resistance to vulcanized rubber (2). The most important reinforcing agents are carbon black and amorphous silicas. Channel black became the carbon black most popular in rubber after 1942. Soon after this, the channel blacks were replaced by furnace blacks. Furnace blacks are manufactured from oil and contain PAHs.

Miscellaneous Agents

A variety of other agents used in the manufacture of rubber products are silicones, fluorinated hydrocarbons, polyethylene glycols, bonding agents, antitack agents, and a variety of organic solvents, including aliphatic hydrocarbons, acetones, 1,1,1-trichloroethane, methyl ethyl ketone, methylene chloride, trichloroethylene, toluene, xylene, tetrahydrofuran, and dimethylformamide. Benzene, employed in the very early history of rubber manufacture, was replaced in the early 1940s with naphtha-type solvents. Flame retardants are added when heat resistance is a required property.

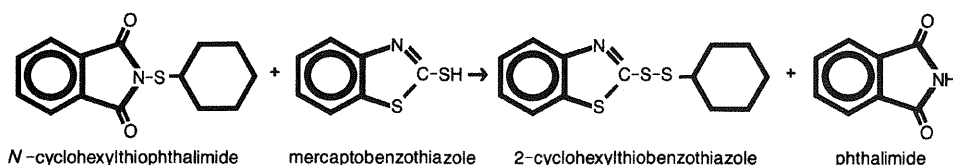


Figure 35-8. Decomposition of the retarder *N*-cyclohexylthiophthalimide during vulcanization. (Adapted from ref. 2, with permission.)

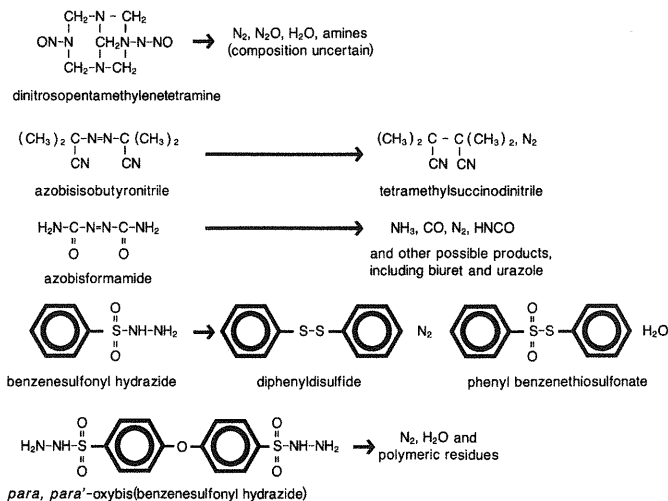


Figure 35-9. Blowing agents and their routes of decomposition. (Adapted from ref. 2, with permission.)

These include clay fillers, ammonium phosphates, magnesium hydroxide, aluminum hydroxide, antimony oxide, chlorinated paraffins, and brominated aromatics, which increase the heat resistance of rubber (3).

Blowing agents are used to produce foam rubber by decomposing at curing temperature to produce gas (Fig. 35-9) (2). Other additive groups are pigments, bonding agents (isocyanates, *p*-dinitrosobenzene, resorcinol-hexamethylenetetramine), antitack agents (mica and talc), and mold release agents (silicones, fluorinated hydrocarbons, polyethylene glycols) (2).

GENERAL HEALTH HAZARDS OF THE RUBBER INDUSTRY

The environmental impacts associated with the disposal of tires is quite substantial and frequently overlooked because of the obvious importance of worker exposure issues. Nevertheless, disposal and potential recycle issues are a major concern to this industry. The most important human health and environmental problem surrounding the treatment, storage, and disposal of tires is associated with their large-scale combustion hazard. The potential and actual impacts of tire fires have been well documented in the United States. The U.S. Environmental Protection Agency (EPA) has published monitoring data from 22 actual tire fire emergencies (4). Previously, the EPA had published detailed characterization data from emission of burning scrap tires in a controlled test experiment (5,6,7). Similar data have been published in standard well-known environmental journals (8,9).

In the United States, tire fires are a relatively common occurrence. More than 240 million vehicle tires are discarded annually in the United States. Less than 25% of this total are reprocessed. Therefore, more than 170 million scrap tires are discarded in landfills, aboveground stock piles, or illegal dumps. Federal legislation has been introduced to address this problem. Proposed legislation has been directed toward reducing the number of

tires permitted in a given location (less than 2,500) and their state of intactness. The latter refers to the need to shred intact tires to below specific size levels.

Tire fires are most commonly associated with arson, although lightning strikes are also a recognized ignition source, as are spontaneous outbreaks that are caused by a combination of heat and vibration. Tire piles are well-known sources of rodent infestations and are common mosquito breeding grounds. Hence, large tire piles pose significant public health risks unreliable to their combination potential.

Tires in landfills do not compact well and tend to rise through a landfill mass to the surface as the dirt around the tires is compressed. As the number of tires below ground increases, this phenomenon tends to be accentuated. The geometry of aboveground piles is such that there are numerous gaps for oxygen transport. This mechanism is a crucial consideration when a tire pile ignites.

The mechanism of tire fires is critical and explains the extreme difficulty in extinguishing these fires. Once ignited, tires produce approximately 18,000 BTUs per second of heat energy, compared with approximately 6,000 BTUs per second for a traditional class A fuel fire. The tires produce tremendous quantities of oil, which also contributes to the fire's persistence. The high heat output severely complicates fire fighting attempts because of the difficulty of working near this extreme thermal source.

Although water may be trapped around and inside disposed tires, this water does not mitigate the inherent fire risk. Water alone has almost always been insufficient to extinguish class A tire fires. Water has strong surface tension and spontaneously rolls off most fuels and rubber surfaces. Therefore, the water moves away too rapidly from the heat to absorb the available heat capacity. Furthermore, extensive water use is associated with substantial environmental impacts because of surface water runoff and subsequent groundwater contamination. Although water alone is insufficient to extinguish the tire fire, it temporarily lowers fire temperatures and increases emissions of particulate and other products of incomplete combustion (PIC).

Water's utility as a tire fire extinguishing material has been enhanced by the use of foams that act by decreasing surface tension. This surface tension reduction allows the water to sheet out, covering the tire surface and penetrating deeper into the fire. This mechanism is different than the use of blanketing foams, which act by a pure oxygen deprivation mechanism. Unfortunately, these types of applied foam blankets are easy to disturb, and their ability to deal with large fires appears to be poor.

Traditionally, the use of sand and large earth-moving equipment has been the mainstay of firefighters with large tire fires. The sand acts as an oxygen deprivation agent and also has the benefit of soaking up some of the produced oil. The earth-moving equipment is used to apply the sand and reconfigure the tire pile into a more favorable geometry.

Toxicologically, tire fires produce tremendous quantities of (a) particulates; (b) heavy metals, particularly zinc and lead; (c) emission of organics, including benzene, toluene, and styrene; (d) volatile PIC; (e) PAHs; and (f) dioxins and furans. Levels of benzene greater than 1 ppm in air have been measured within 300 miles of tire fires. One large tire fire in Hagerstown, Maryland, produced 200,000 gallons (800,000 L) of oil. This oil is itself combustible but frequently is not burned. The water prevents the oil from igniting but does not extinguish the overall fire. In this particular situation, the oil becomes a major source of surface- and groundwater pollution. Hence, if adequate firefighting materials are not available, it is better to let the fire burn at high temperatures until sufficient resources can be used. Otherwise, particulate production and PIC are enhanced without meaningful improvement in fire control.

The ineffective use of water or foams, or both, decreases the overall fire burn rate but paradoxically increases overall emis-

sion. As the temperature of the fire is temporarily lowered, the rubber binds to the cord material. This new material is more difficult to combust at the new, but temporary, lower temperature. The rubber material can be pyrolyzed, which produces volatiles and other PICs, but it does not fully combust. Therefore, overall toxicity and pollution are enhanced rather than mitigated.

As in many other manufacturing industries, noise remains a major concern in the rubber industry. The extensive use of mixing and milling equipment, extruders, calenders, conveyers, and hydraulic tools in the tire industry results in noise levels exceeding 85 dB throughout most operations. Other physical hazards include risk of thermal and chemical burns and heat stress. Besides trauma, dermal and pulmonary exposures from chemicals are common hazard sources. Health hazards are also peculiar to certain sites and processes in the rubber industry because of the variety of chemicals, processes, and reactions that occur.

Dermatitis

Many rubber additives are capable of producing dermatitis (3). Because natural rubber is not considered a contact allergen, people who develop dermatitis after contact with natural rubber products are reacting to persistent additives (3). Rubber additives can produce dermatitis even from cured products by migrating to the surface of the product over time.

A number of accelerators and other compounds used in the rubber industry—including thiurams; amines; guanidines; disulfides; and certain thiazoles, such as MBT—are skin sensitizers causing contact and allergic contact dermatitis in rubber workers. Many of the common rubber sensitizers are included in patch test batteries used by dermatologists and allergists. Cross-reactivity to similar substances may occur, and sensitized individuals generally need to be removed from further exposure to avoid worsening of their condition.

Irritant dermatitis may be precipitated or aggravated by contact with solvents, caustics, and acids. Treatment with topical steroids and emollients is usually effective. Minimizing skin contact with these substances is the best means of prevention. Phenols and hydroquinones can cause focal hypopigmentation (leukoderma).

Respiratory Disease

Several studies have demonstrated an excess of respiratory symptoms and pulmonary function abnormalities in rubber workers. Studies have documented that asthma, chronic lung changes, respiratory problems, and bronchitis have been prevalent in the rubber industry, particularly in dusty areas such as compounding and mixing (10). Findings consistent with mucous hypersecretion and mild airway obstruction have been reported in workers exposed to carbon black, additives, talc, and curing fumes (10). Symptoms reported by these workers have included cough and sputum production, frequent upper respiratory infections, and episodes of bronchitis. Spirometry has shown decrements in flow rates with preservation of lung volumes. In general, the effects of smoking and workplace exposures appear to be additive.

The long-term impact of exposures in the rubber industry on respiratory status is uncertain. Radiographic evidence of pulmonary fibrosis has been reported only rarely in rubber workers and has been related to specific materials and work practices. Mortality studies have not shown excess mortality from these respiratory diseases. If the primary pulmonary insult is the inhalation of particulates and mild irritants, then improved ventilation, material substitution, and better work practices should lessen these effects.

Silicosis and talcosis have also resulted from the substitution of talc for other powder. Talc dust may be of respirable size and contain crystalline silica and fibrous tremolite.

Workers exposed to curing fumes may have a higher prevalence of chronic bronchitis. Respiratory morbidity is related to the intensity and length of exposure to these fumes (10,11). Other studies have shown that employment in the curing departments is associated with shortness of breath, chest tightness, wheezing, and changes in respiratory function tests (10–12).

Chronic lung diseases, such as pneumoconiosis, pulmonary fibrosis, bronchitis, and emphysema, can occur in workers overexposed chemically to carbon black as well as to dusts and particulates (13).

Because of the multitude of chemicals that are either used or formed in the manufacture of rubber products, and the observation that workers are frequently exposed to mixtures of chemical agents, it is often difficult to pinpoint a specific chemical in the etiology of disease. General mortality patterns among rubber industry workers have been investigated in relation to the overall industry as well as to the specific jobs or tasks (14,15).

MEDICAL SURVEILLANCE AND PREVENTION

Health surveillance programs for rubber workers should include periodic audiometry and spirometry. If possible, the information should be standardized to allow assessment of the effectiveness of controls in high-risk areas. Physical examinations should focus on the respiratory system as well as the skin. Despite the many uncertainties regarding the true cancer risks in the rubber industry, screening for gastrointestinal cancer should be considered. This is relatively common in the general population, and early detection can markedly improve outcome, particularly for cancer of the colon.

Reduction in the release of air contaminants into the work environment through the use of proper ventilation and substitution of less toxic materials presents a continuing challenge for the rubber industry. Given the potential risks of respiratory disease and cancer in this industry and that smoking tends to potentiate the effects of some chemicals, workplace smoking restriction policies and smoking cessation programs may be extremely beneficial for rubber workers.

HEALTH HAZARDS BY AREAS

Raw Material Handling, Weighing, and Mixing Areas

Raw material handling, weighing, and mixing exposes the worker to particulate matter (13). In some rubber manufacturing plants, the majority of particulate exposure consists of carbon black, whereas in others, talc and compounding agents may be significant. Cross-contamination of other areas may also occur as a result of ventilation patterns, although the magnitude of such exposures is relatively much less (13).

Mill operators can also be exposed to incompletely mixed compounds from the Banbury mixers and from compounding materials added during mix milling. Talc exposures were common owing to the use of this compound as a detackifier for stored rubber sheets (2,13).

In cement mixing, workers may be exposed to solvents used to prepare cements for use in extrusion, calendering, tire building, repair, and other operations. These solvent mixtures, which often include the addition of dissolved rubber solids, are prepared in the cement house.

Component Assembly and Tire Building

Various organic solvents, including petroleum naphthas, often are used in specific tire-manufacturing operations (2,14). These

TABLE 35-5. Exposure situation for *N*-nitrosamines in the rubber industry

Job description	Chemical	Concentration in the air ($\mu\text{g}/\text{m}^3$)
Raw material handling, weighing, mixing	Nitrosodimethylamine	0.2–0.9
	Nitrosomorpholine	0.1–2.0
Milling, extruding, calendering	Nitrosodimethylamine	0.1–2.0
	Nitrosomorpholine	0.1–9.0
Assembly and building	Nitrosodimethylamine	0.1–1.0
	Nitrosomorpholine	0.5–3.0
Curing or vulcanizing	Nitrosodimethylamine	0.1–2.0
	Nitrosodimethylamine	15–130
	Nitrosodimethylamine	1.0–4.5
	Nitrosomorpholine	0.1–17.0
	Nitrosodimethylamine	1–40
	Nitrosodiethylamine	0.1–5.0
	Nitrosomorpholine	0.1–3.0
	Nitrosodimethylamine	40–90
	Nitrosomorpholine	120–380
	Nitrosodimethylamine	500–1,060
	Nitrosomorpholine	200–4,700
	Nitrosodimethylamine	1
	Nitrosodiethylamine	5
	Nitrosopiperidine	0.3
	Nitrosomorpholine	0.1
Inspection and finishing	Nitrosodimethylamine	1.0–3.5
	Nitrosomorpholine	3–9
	Nitrosodimethylamine	0.2–3.5
	Nitrosodimethylamine	1
	Nitrosodiethylamine	3
	Nitrosodimethylamine	0.1–1.5
Storage and dispatch	Nitrosodiethylamine	0.1–20.0
	Nitrosodimethylamine	1–10
	Nitrosodimethylamine	0.2–10.0
	Nitrosodimethylamine	1–19
	Nitrosomorpholine	0.3–17.0
	Nitrosodimethylamine	0.2–1.0

Adapted from Spiegelhalter B. Carcinogens in the workroom air in the rubber industry. *Scand J Work Environ Health* 1983;9(2):15–25.

include tuber or tread-end cementing, bead building, tire building, and spray booth (doper) operations for green (uncured) tires.

Although petroleum naphtha is a common component of many of the solvents applied to green tire components, other solvents including toluene (tread-end cementing) and *N*-hexane (bead building) are also used (14). Because petroleum naphthas may contain small amounts of aromatics such as toluene, benzene, and xylene, proper evaluation of worker exposure should include monitoring for these chemicals as well.

Repair of cured tires sometimes requires the use of solvents to preclean flawed areas of the tire before application of solvent-rich rubber repair material. Mixtures of toluene and naphtha and other petroleum solvents may be used in such preparations.

Curing or Vulcanization

Before curing, rubber products, including green tires, are frequently sprayed with a solvent-based lubricant in spray booth (doping) operations. This process generates solvent vapors. The subsequent cure cycle generates condensed volatiles, vapors, gases, and reaction products (2,15,16). The curing fume itself consists of a complex array of organic compounds, including nitrosamines, which arise from the actual cure of the tires (2,12,15,17). Nitrosamines—which have been found in curing as well as milling, extrusion, and calendering—include *N*-nitrosodibutylamine, *N*-nitrosodimethylamine (NDMA), *N*-nitrosodiphenylamine, *N*-

TABLE 35-6. Summary of vapor in air concentrations of solvent components from selected work areas

Work area component	Chemical	Range (ppm)
Cement mixing	Pentane	0.91–61.20
	Hexane	0.83–98.50
	Heptane	0.39–90.70
	Octane	0.16–7.64
	Benzene	0.18–16.50
	Toluene	0.37–19.30
	Xylene	0.02–1.50
Tire building	Isopropanol	0.01–28.50
	Pentane	0.29–5.45
	Hexane	0.3–135
	Heptane	0.06–12.20
	Octane	0.19–1.79
	Benzene	0.09–1.52
	Toluene	0.13–3.29
Final inspection	Xylene	0.01–1.38
	Isopropanol	0.07–6.83
	Pentane	0.04–0.82
	Hexane	0.59–6.40
	Heptane	0.09–0.81
	Octane	0.02–0.27
	Benzene	0.01–0.19
Warehouse	Toluene	0.03–0.64
	Xylene	0.02–0.54
	Isopropanol	0.08–0.44
	Pentane	0.03–0.56
	Hexane	0.02–0.45
	Heptane	0.07–0.19
	Octane	0.02–0.21
	Benzene	0.01–0.48
	Toluene	0.01–0.37
	Xylene	0.03–0.51

Adapted from Van Ert M, et al. Worker exposures to chemical agents in the manufacture of rubber tires: solvent vapor studies. *Am Ind Hyg Assoc J* 1980;41:212–219.

nitrosomorpholine (NMOR), *N*-nitrosopiperidine T, and *N*-nitrosopyrrolidine (Table 35-5) (17–19).

Final Inspection and Repair and Finishing Area

Inspection may involve the handling of hot cured rubber products. As a result, workers other than those in curing may be exposed to condensed volatiles, vapors, and gases, although in much lower levels. In final inspection, repair activities may require the use of solvent-based rubber products leading to employee exposure to these vapors (Table 35-6) (14).

Storage and Dispatch Area

Stored rubber products release or degas low concentrations of solvent vapors that were used in the manufacturing process, as well as other less volatile products (see Table 35-6) (14).

CARCINOGENIC AND MUTAGENIC PROPERTIES OF CHEMICALS

Commonly used accelerators and curing agents (thiuram compounds including tetramethylthiuram disulfide, tetraethylthiuram disulfide, and tetramethylthiuram monosulfide) have been demonstrated to be carcinogenic in animal studies (2).

Solvents used in the rubber industry include petroleum naphthas, toluene, hexane, isopropyl alcohol, trichloroethylene, 1,1,1-trichloroethane, and methylene chloride. Occupational

studies suggest some evidence of increased carcinogenesis secondary to solvent exposure (20).

Small amounts of monomers such as acrylonitrile, butadiene, chloroprene, ethylene, propylene, styrene, vinyl acetate, vinyl chloride, and vinylidene chloride remain in solid rubber polymer and could be released into the work environment, but probably at concentrations lower than existing standards. Most of these monomers have not been known to bind directly with cellular macromolecules, but their metabolites might do so (2,16). Sufficient evidence exists to implicate acrylonitrile as a suspected human carcinogen based on animal studies (2,16). Vinyl chloride is a confirmed human carcinogen (2). There is limited animal evidence of the carcinogenicity of styrene (2,16).

Epichlorohydrin is also used in the manufacture of elastomers. It can react directly with macromolecules and serum proteins. Epichlorohydrin is a mutagenic chemical and is also carcinogenic in mice and rats (2,16). No adequate epidemiologic observations are in the literature as to its carcinogenicity in humans.

Talc, widely used as an antitacking agent, is mainly associated with respiratory disease. However, some talcs may contain asbestos fibers and fibrous tremolite.

Carbon blacks contain variable amounts of compounds, some of which have not been identified. The most probable carcinogenic hazard of carbon black is associated with benzene-extractable chemicals, consisting mainly of aromatic hydrocarbons and sulfur compounds (21–23). Among these chemicals are benz(a)anthracene, benzo(a)pyrene, and indeno-pyrene, which are known carcinogens. Chrysene has been described as a tumor-initiating agent, and nitro derivatives of polycyclic hydrocarbons have also been found in extracts of commercial carbon black (21–23). Data indicate that the known carcinogens present in carbon blacks are strongly absorbed but can be eluted by biological fluids (21–23). A 1962 study reported that the polycyclic hydrocarbons, including benzopyrene, present in the furnace and channel blacks were not eluted by human blood, plasma, or gastric juice (22).

Cancer of the bladder has long been recognized as a problem within the rubber industry and has been associated with specific aromatic hydrocarbons. The cause was probably an organic antioxidant added to the rubber mixture— β -naphthylamine—although subsequent concern has focused on α -naphthylamine, benzidine, and 4-aminobiphenyl (xenylamine). Bladder cancer has been associated with three occupational title groups in the rubber industry—receiving and shipping, compounding and mixing, and milling—although the number of bladder cases is small. Reactive metabolic intermediates from aromatic amines and their interaction with cellular macromolecules have been extensively reviewed (2,16,24,25). The carcinogenic or genotoxic activity of aromatic amines and amides is dependent on metabolic activation or *N*-hydroxylation to hydroxylamines. Naphthylamine-acetaldehyde was introduced as an antioxidant in the rubber industry in 1928. It was associated with an increase in incidence of bladder cancer. 4-Aminobiphenyl, benzidine, and β - or 2-naphthylamine are known to be carcinogenic for humans. Their use was discontinued in the early years of the industry. Phenyl β -naphthylamine was used as an antioxidant. Research indicated that phenyl β -naphthylamine is metabolized by the body to β -naphthylamine. There is sufficient evidence for the carcinogenicity of simpler amines—2,4-diaminotoluene and 2-chloroaniline—in experimental animals.

Phthalate Esters

Phthalate esters are plasticizers used in numerous plastic products, including rubber tires. Consequently, they are widely distributed. The two most common plasticizers are diethylhexylphthalate and

di-*n*-butylphthalate. Phthalate esters are not known to be acutely toxic. They contaminate soil and water in wide-ranging areas of the United States. Diethylhexylphthalate and di-*n*-butylphthalate are considered weak animal carcinogens.

Curing Fumes and Other Curing Emissions

During the vulcanization process, fumes and vapors are emitted into the air because of volatilization of rubber ingredients. No experimental data are available concerning the long-term toxicity of curing fumes. Curing fumes from the tire vulcanization process contain a number of chemicals and chemical by-products (2,11,12,15,16). These products are dependent on the temperature, the type or composition of the rubber, and the presence or absence of oxygen. Increased incidence of lung cancer in workers who are in the curing area has been demonstrated in various epidemiologic studies (15,26–27). Many airborne nitrosamines are formed during rubber processing and are found in the work atmosphere (2,17–19,28). No direct evidence yet exists that nitrosamines cause cancer in humans.

Polycyclic Aromatic Hydrocarbons

PAHs are fused benzene ring compounds present in crude oil and generated by burning organic materials. PAHs are found in aromatic oils, which are extensively used in the rubber industry as plasticizers and softeners. A tire may contain as much as 20% aromatic and paraffinic oils (2). These aromatic oils may contain large amounts of PAHs, some of which contain concentrations of carcinogens. Benzo(a)pyrene is a well-known PAH carcinogen (2,21–23).

PAHs in rubber factory atmospheres include

- Fluoranthene
- Pyrene
- Benzo(a)fluorene
- Benz(a)anthracene
- Chrysene
- Benzo(b)fluoranthene
- Benzo(a)pyrene
- Dibenzo(a,j)anthracene
- Dibenzo(a,h)anthracene
- Indenopyrene
- Benzo(g,h,i)perylene
- Anthanthrene
- Perylene

PAHs are potent skin carcinogens in animal models. Normally, in the rubber industry, humans do not frequently come into direct contact with these aromatic oils. However, uncured rubber, with which workers have much contact, contains large amounts of these oils. Thus, PAH transfer to the skin may be facilitated. Carbon black also contains PAHs. Fortunately, only small amounts of PAHs are released into biological fluids by carbon black because of its high absorption feature. Solvent extract of carbon black is carcinogenic, but carbon black itself is not.

PAHs are undoubtedly released during the heating of rubber, but studies have not demonstrated this to be a significant problem in the industry in relation to existing airborne concentrations.

PAHs are metabolized by the P-450 mixed oxidase enzyme system in the liver to carcinogenic compounds. DNA binding studies have shown that several benzo(a)pyrene metabolites bind covalently to DNA.

Mineral oils, such as coal tar oils, petroleum, and other tar products, are widely used in the rubber industry as extenders. The use of mineral oils has increased considerably over the years because they are cheap and impart desirable properties to the finished rubber. These oils contain relatively large quantities of

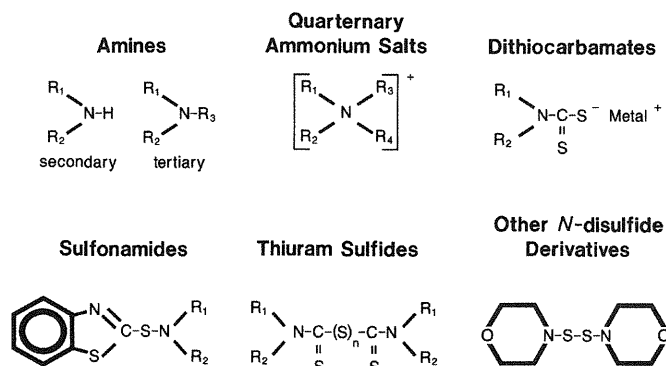


Figure 35-10. Groups of chemicals that can be converted to *N*-nitrosamines. (Adapted from ref. 18, with permission.)

PAHs. PAHs also may be formed when the tars and mineral oils are heated. These mineral oils and tar products vary in composition. They all, however, may induce carcinogenic effects in mammals, including humans. This carcinogenic effect may be due to the presence of the PAHs.

Nitroso Compounds and Nitrosamines

Very little information is available on the health effects of chemical by-products generated during rubber processing. During vulcanization, air is excluded, and the mold contains a reducing atmosphere. Products that can be formed during vulcanization and released from the surface of the rubber include amines and organic sulfides derived from accelerators (Fig. 35-10). There are many reports of these chemicals breaking down at curing temperatures. Because the maximum temperature of the vulcanization or curing of rubber is approximately 240°C, pyrolysis does not normally occur (2). On removal from the mold, the rubber can undergo oxidating reactions in which peroxy-substituted amines and acids can be formed, such as NMOR, NDMA, and *N*-nitrosopyrrolidine (see Table 35-5) (2,24,28). These compounds, demonstrated to be carcinogenic in a number of animal models, have been identified in the extrusion, milling, calendering, curing, and cooling (postcuring) areas of tire factories (15,17–19). The discovery of such compounds in the air of specific areas of tire plants has led to control measures such as improved ventilation and compound substitutions to reduce or eliminate these agents from the workplace environment.

N-Nitroso compounds are produced by acid-catalyzed reactions of nitrites with certain nitrogen-containing amine compounds (24). Nitroso compounds are divided into nitrosamines and nitrosamides. Most of these have been demonstrated to be potent carcinogens. The antidegradant process and curing process involves amines, nitrosamines, and quinolines, which are suspected carcinogens. Possibly, these compounds are precarcinogens that require metabolic activation by the body to become carcinogens (24).

NMOR, a known animal carcinogen, has been quantitated in rubber industry factory air sampling (17). Also, small amounts of another carcinogen, NDMA, have been identified. NDMA was found as an indoor air pollutant at concentrations ranging from 0.07 to 0.14 μg per m^3 . NMOR was also found in the rubber factory as an impurity in morpholine and in the cross-linking accelerator bismorpholinecarbamyldisulfenamide. NMOR was found at all sites sampled in the rubber industries surveyed, including milling, extrusion, calendering, and curing. The lowest level was in the finishing area and the highest levels in the extruding areas (17).

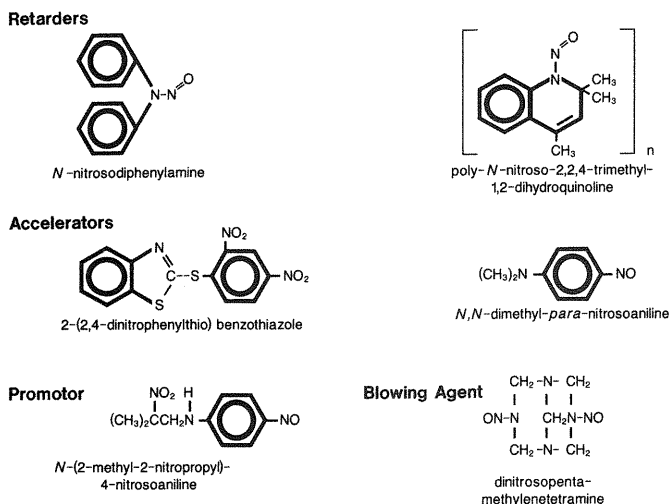


Figure 35-11. Nitro and nitroso compounds used in the rubber industry that can act as precursors of nitrogen oxides. (Adapted from ref. 18, with permission.)

Chemicals containing nitro or nitroso groups can serve as nitrosating agents (18). These chemicals can thermally decompose in hot processes to form nitrogen oxide and directly nitrosate amines contained in rubber (Fig. 35-11) (18). Nitrogen oxides can also be formed as by-products of internal combustion processes secondary to machine use.

Nitrosamines have been reported in numerous worksite air samples in the United States and Germany in breathing zone samples (18). These nitrosamines included NDMA, NMOR, *N*-nitrosobutylamine, *N*-nitrosopiperidine, and *N*-nitrosopyrrolidine. The nitrosatable precursor of each of these compounds is used in the rubber industry, with the exception of *N*-nitrosopyrrolidine.

In addition to the nitrosation of secondary amines, reactions involving tertiary amines or amine derivatives occur in aqueous systems and solid systems, as well as in the gaseous phase. The following two nitrosation reactions are possible:

- Nitrosatable compounds dissolved or dispersed in latex solution can be nitrosated during the production of latex articles. Nitrogen oxide from the air has been proposed as the nitrosating agent in this case. Atmospheric levels of nitrogen oxides can be complemented by other combustion processes, such as open flames and other pollutant sources (17,18,24).
- Chemicals that contain nitro or nitroso groups are potential nitrosating agents, as some of these chemicals may decompose thermally during processing of the rubber to form nitrogen oxides. Direct nitrosation of specific compounds contained in solid rubber is therefore possible. Animal studies have demonstrated that airborne concentrations of nitrosamines, similar to those found in the rubber industry, can induce cancers of the lung, kidney, and liver (18).

The rubber industry as a whole has several hundred different chemicals involved in the manufacture of various rubber products. The choice of chemicals used in different stages of the processing of the rubber varies from company to company, and even within the different departments and factories within the same company.

RUBBER INDUSTRY AND CANCER

Studies of rubber workers in the United States and other countries have demonstrated that the death rate due to all cancers

appears lower than in the general population. But a detailed review of the mortality experience of these cohorts has shown excesses for specific causes of death (26–40). Among U.S. rubber workers, excess malignancies of the lung, lymphatic system, and hematopoietic system—particularly lymphatic leukemia—have been associated with certain jobs in the rubber industry (26–40). Stomach cancers have been associated with jobs in the production line, including compounding and mixing, milling, and extrusion. Lung cancer has been associated with curing jobs in certain rubber industries (26–40).

Establishing causation of these health outcomes with many of the materials and chemicals that occur in the work atmosphere in the rubber industry has been difficult because of the diverse and changing nature of exposures within the rubber industry, the multiple exposures experienced by many workers because of job mobility over a working lifetime, and the lack of historical industrial hygiene data. Most epidemiologic studies of cancer and other diseases in rubber workers have not always been exposure specific, or they have used job descriptions as a substitute for exposure estimates. Consequently, there is sometimes considerable difficulty in identifying etiologic factors in cancer and other disease causation (29). This process is confounded by the need to estimate exposures that occurred several decades ago in relation to cancer occurring more recently. Evidence of human carcinogenicity to either a single chemical or a complex mixture of chemicals in the rubber industry has been derived from the following types of studies (29):

- Reports on individual cancer patients who have a history of exposure to the suspected carcinogen
- Descriptive epidemiologic studies in which the incidence of cancer in human populations is found to vary with exposure to the agent or agents in question
- Analytic epidemiologic evidence—such as case-control or cohort studies—in which individual exposure to the agents is found to be associated with an increased risk of cancer

The first two study types provide only suggestive evidence of causation. The third one, an analytic epidemiologic study, provides better insight if there is no identified bias, error in the design of the study, or confounding factors.

The rubber industry has gone through many evolutionary changes involved with technology and chemicals. To try to define a typical rubber manufacturing operation is difficult in terms of either the process, end product, or environmental controls. Multiple processes in the rubber industry can be associated with different exposure hazards. The variables that arise include variations in production and control technology, variations in process requirements, and variations in work practice (2,15,29).

Assessing exposures of rubber workers is also rather difficult for the following reasons (2,29):

- An individual experiences a large variety of exposures from the multiple chemicals used in a given job and cross-contamination from adjacent work areas.
- Several hundred chemicals, including some complex solvent mixtures, are used in the rubber industry.
- Few workers in the industry remain in the same job during the entire period of their employment, although job mobility for these workers may be minimal. However, they may work at many different jobs over the course of their employment, making it very difficult to track their exposure history.
- Cancer excesses that occur in the industry may have resulted from chemical exposures that occurred within or outside the industry many years before clinical diagnosis of the disease.
- Industrial processes can result in the formation of new materials as by-products of those processes.

Excess mortality from various cancers has been reported in rubber workers, and the International Agency for Research on Cancer has classified specific exposures in the rubber industry as potentially carcinogenic in humans (2). Despite changes in manufacturing materials, operations, work conditions, and worker mobility, epidemiologic investigations have identified excesses of several different cancers in rubber workers, depending on the study population and time frame of interest. Although in some instances specific causes have been suggested, specific factors contributing to cancer excess in rubber workers remain uncertain.

The first cancer identified in rubber workers was an excess in bladder cancer in Great Britain. The cancer excess in workers studied was ultimately attributed to the use of aromatic amines, primarily β -naphthylamine, as an accelerator. The use of this chemical was discontinued by 1950, and excess bladder cancer has not been identified in subsequent studies.

Studies have also shown certain rubber workers to be at an increased risk for developing leukemia (39). Excess has been found in other studies, including a risk of lymphocytic leukemia with exposure to solvents other than benzene (26–40). Limited studies of workers producing SBR have also suggested an excess of leukemia risk (39).

Although rubber workers overall have not been found to be at an increased risk for developing lung cancer, excess lung cancer has been identified in a variety of rubber worker subpopulations. Lung cancer has been associated with exposure to compounding, mixing and milling, and curing fume exposure, but these studies are inconsistent (26–39). Smoking, interactions of smoking with other exposures in the industry, and chance clustering (given the extensive investigation of this industry) all remain possible explanations for the findings related to lung cancer to date.

Most epidemiologic studies of the rubber industry are retrospective follow-up studies of cohorts of rubber workers or case-control studies of people with cancer. Typically, the rate of occurrence or death, or both, from cancer is compared with the rates in a control population. This control may be the general population.

Frequently, in follow-up studies, the rate of death in the study population is less than that in the general population. This difference is termed the *healthy worker effect*. This selection bias occurs because only relatively healthy people enter the employment force, but it usually applies less to cancer than to other causes of death.

In occupational cohort studies, the standardized mortality ratio (SMR) is commonly used. The SMR is the number of deaths observed in a group divided by the number expected in the same group. The quotient is multiplied by 100. The expected numbers, which are customarily based on the mortality experience of the general population, are usually standardized for age and calendar time. In case-control studies, disease rates are not computed because of the small size of the population studied.

The main studies of the rubber industry in the United States consist of those from the Harvard School of Public Health and the University of North Carolina (2,26). Data in the Harvard study included 13,571 male production workers (26). These people were working at a plant on or after January 1, 1940, and worked at least 5 years at the plant between that time and June 1971. They were studied from January 1940 through June 1974. During that period, 980 deaths from cancer were observed; 1,046 were expected. In the second phase of the study, cancer morbidity between 1964 and 1974 was examined by a review of the area tumor registry. The rates of cancer were measured among workers in specific areas of the rubber plant. Lung cancer excesses were noted in the tire-curing area in people who had worked there for at least 5 years, tire-molding people who had worked there for at least 5 years, and in the fuel cell de-icer manufactur-

ing area. In the tire-curing area, there were 31 cases of cancer with 14.1 cases expected; in the fuel cell de-icer area, there were 46 cases of cancer with 29.1 expected (26).

University of North Carolina Studies

In the studies from the University of North Carolina (UNC), 6,678 production workers were studied, and 351 cancer deaths occurred during a 9-year follow-up; 336.9 deaths were expected, based on the U.S. male age and race-specific rate (2,28,29).

McMichael et al. in 1976 detailed job histories of seven specific cancer case groups in this industry (15,40). They found that respiratory cancer excess was found in the following areas: receiving and shipping, compounding and mixing, milling, extrusion, tubing, and reclaim.

Excess mortality from lung cancer was found in one United Kingdom study; an excess of lung cancer was found among workers in many occupations in the tire industry and nontire sectors. Excess cases of lung cancer in U.S. studies were associated with work in compounding and mixing, extrusion, tire curing, and rubber reclaim (2,15,26,32,33,40).

Two populations were defined in the UNC study. The first population consisted of 6,678 men who were alive on January 1, 1964, and had worked for at least 10 years in a large Akron, Ohio, tire plant (40). This population was studied for 9 years, starting from 1964. Overall results of the study demonstrated cancers of other organ systems without excess lung cancer. A parallel study of 1,339 men in a second tire factory in Akron showed essentially the same, with no evidence of increased lung cancer rates (15,40). A case-control study conducted on 61 cases of lung cancer and 61 matched control subjects demonstrated a strong correlation between the rubber curing process and lung cancer. Twenty-five percent of the cases were exposed to curing agents versus 15% of control subjects (15,40).

The second UNC study was conducted on 8,418 white male production workers from 1964 to 1973. Again, lung cancer was not a prominent disease among the cancers observed.

Harvard School of Public Health Studies

This study defined a population of 13,570 white male workers employed in an Akron plant from 1940 to 1971 (2,26). All members of the study had worked for at least 5 years. The number of overall cancer deaths was less than the general population. Bladder cancer appeared in excess. A subsequent cancer study was carried out in this particular plant showing correlations between type of job and excess cancers. The results of this study demonstrated an excess of lung cancer in the curing, molding, and fuel cell area of the plant (32). The mortality of 13,571 white, male rubber employees was studied from 1940 through 1974 as part of the Harvard study. An excess of lung cancer in the tire curing area (observed, 20; expected, 12.4) was identified. In addition, the curing workers had a higher incidence of chronic bronchitis. Of the curing workers with at least 10 years' experience, 25% had chronic obstructive lung disease. Smoking did not account for the difference between the curing versus the control group in terms of increased respiratory disease.

Results of a 5-year analysis from 1967 to 1971 of 40,807 British rubber workers demonstrated an overall 19% increase in the incidence of cancer (34). There was also excess lung cancer in the tire manufacturing area (34).

Smoking habits were not accounted for in this large study; however, the SMR for other smoking and urban-related disease was approximately the same in all sectors. This suggests that smoking is not a primary cause for the excess lung cancer seen in this study (34).

The risk of neoplasms in general was higher for the tire industry as compared with the cable-making industry. No evidence was found to suggest this excess might be due to smoking habits. The death rates for smoking-related causes—in particular, for chronic obstructive lung disease and bronchitis—in the tire industry is approximately the same for the cable-making industry (34). The first prospective study to report on excess lung cancer deaths in the rubber industry was by Mancuso (29).

British Rubber Manufacturer Association/ Birmingham University Study

The British Rubber Manufacturer Association (BRMA) initiated a retrospective study that covered 33,815 men who worked in the rubber industry from 1946 to 1960. Thirteen factories were included: eight tire and five general rubber products. The study population worked for a minimum of 1 year and was divided into three cohorts (28):

- Cohort 1, January 1946 to December 1950
- Cohort 2, January 1951 to December 1955
- Cohort 3, January 1956 to December 1960

The study looked at all causes of death, not just cancer, and was extended until 1975. The final report focused only on cancer cases in the industry.

The initial study analyzed deaths from cancer by studying only members of the population who survived for a minimum for 10 years past beginning employment. This removed all cases of cancer deaths that occurred close to the point of entry into employment. Using this refined 10-year latency technique, an excess of cancer was observed (28).

The lung cancer mortality was analyzed in terms of occupational groups in the rubber industry. The results of this analysis suggested that certain occupations in the rubber industry were associated with higher-than-expected mortality rates for respiratory cancer (28).

Excess lung cancer has been associated with work in the curing, inspection, and mixing areas of the rubber industry in general, as demonstrated by a number of studies. In the BRMA study, the individual environmental exposure of workers was considered to be important in delineation of carcinogenesis. These work environments were identified by obtaining detailed occupational histories as well as job descriptions from workers. For each chemical exposure, the fraction of the subgroup reported to have some exposure to that chemical was recorded and generated data that indicated excess lung cancer with exposure to curing vapors.

A case-control study was conducted with four control subjects being chosen for each case of lung cancer. These control subjects were matched for age, factory, cohort, and duration of service. No single environmental area stands out as a cause of lung cancer; however, curing vapors (vulcanizing) were highlighted.

Extended British Rubber Manufacturer Association Study

Reported in 1982, the extended BRMA study followed the original study population through December 31, 1975, allowing another 5 years of analysis. This study excluded all those workers who died in the 10 years after the beginning of their employment. This restraint reduced the study population from 36,695 participants to 33,815 and removed the healthy worker effect influence (28). The overall results for cancer deaths in the population showed increased SMRs for all cancer types, excess lung cancer, excess leukemia, and excess stomach cancer (28). Lung cancer excess seen in the previous study was reconfirmed by this

extended study data. The extended study also confirmed suspected information regarding occupational site and the excess lung cancer cases. In addition, the results were worse for general rubber goods than for tire industries alone.

The general rubber goods and tire manufacturing rubber industries show excess lung cancer rates in the curing, tire-building, and inspection and finishing areas of the workplace.

CONCLUSION

The rubber industry employs hundreds of chemicals in a variety of processes, and reactions leading to potentially hazardous exposures can occur in multiple environments. Decomposition products from chemical reactions may account for many unknown exposures to potential carcinogens at various sites with excess of lung cancer, leukemia, and lymphomas having been described in certain occupational groups. As a result, control of exposures is an important preventive health issue.

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CHAPTER 36

Automobile Airbag Hazards

J. Michael Hitt

Although the inclusion of automobile airbags in motor vehicles was federally mandated in the 1990s, the concept and research date to the 1960s. Concern for the effectiveness and safety of the device was originally tested by placing a baboon in a cockpit of a simulated aircraft crashing at 120 miles per hour. Research on the safety of the device has continued since that time.

There is no question that airbags perform the function for which they were designed: to protect the driver in moderate- to high-speed frontal crashes. Studies demonstrate that driver fatalities in airbag-equipped cars were reduced by 24% in frontal crashes relative to comparable cars equipped only with manual belts (1). In 1991, nonpedestrian motor vehicle crashes claimed 36,500 lives, with the total cost of all fatal motor vehicle accidents estimated to be \$96.1 billion, excluding the inestimable human loss. Uninjured survivors of fatal crashes were three times more likely to have been restrained. Only 28.9% of fatalities were restrained by either seat belts or airbags or both. I would conservatively estimate that 4,000 lives are saved annually in the United States specifically as a result of the presence and deployment of airbags.

The Federal Motor Vehicle Safety Standard Number 208, *Occupant Crash Protection*, requires that all passenger cars manu-

factured after September 1, 1989, be equipped with automatic crash protection. This requirement has generally been met by providing airbags on all new passenger vehicles since that time. This has opened up a new field of applied toxicology. Thousands of airbag deployments now occur every year. Most generate no toxicologic concern; however, some individuals have reported physical and metabolic injury as the result of these deployments. The popular press has been keenly interested in the subject, as is evidenced by a quotation found in the newspaper *USA Today*: "At least 32 children and 20 adults have been killed by the explosive force of air bags in the USA since mid-1990" (2).

Thousands of workers in the United States and other countries are involved in the production of automobile airbags. Airbag-related industrial injuries occur every year, and some years' fatalities are the direct result of the manufacturing process.

The body of knowledge of the toxicologic effects of automobile airbags and their components on both workers and consumers is rapidly growing. It is increasingly becoming a fascinating topic to physicians, environmental health experts, regulators, lawmakers, and attorneys.

This product will eventually be in the possession of 80% of adult Americans. As with any common product containing chemicals, questions as to potential toxic effects have been and continue to be raised.

The deployment of the airbag requires a controlled rapid generation of gas within centimeters of the driver's face. In newer vehicles, the same scenario is true for the passenger. This results in the release of the products of combustion and creates a unique and potentially hazardous situation within the confines of the passenger compartment. Previously, automotive reactions of this nature had been isolated to the engine compartment and, in the case of the internal combustion engine, shielded by massive metal blocks. The airbag, however, aims a high-speed chemical reaction of similar intensity directly at the automobile occupant. Instead of massive steel shielding, the airbag offers only the protection of a cloth bag, fiber screens, and a thin metal inflator body. The engineering required to protect humans from this protective device is substantial and impressive. The record largely bears out the fruits of the scientific work that went into its development.

AUTOMOBILE AIRBAG MODULE

Figure 36-1 demonstrates the major components of a driver's side automobile airbag module. A passenger side airbag is similar. This system operates by placing the module in the center of the steering wheel. The back side of the inflator is attached to the steering wheel, and the opposite side, facing the driver, contains the airbag, housed within a plastic container and cover. The module is connected to crash sensors at the front, sides, and possibly the passenger compartment of the vehicle (Fig. 36-2). The sensor, which typically consists of an accelerometer, will detect an extremely rapid deceleration and send an electric current to activate the inflator.

The inflator is the heart of the driver's side system. It consists of a lightweight, stainless steel, or aluminum housing, which contains a stack of gas-generating disks or pellets composed primarily of sodium azide and an oxidizer (Fig. 36-3). The gas-generating material is housed within a combustion chamber. The inflator walls are permeated by holes or ports, which allow gas to escape. These holes are screened by a final filter, which serves to cool the gases and protect the airbag itself from particles that might burn or rupture. The entire inflator sits within the circular opening of the airbag. The bag is woven of soft, porous fabric, allowing rapid inflation and deflation.

Clinical Environmental Health and Toxic Exposures

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