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Industrial Health Problems in the Rubber Industry

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THE AMERICAN rubber industry is complex and diversified. Its raw materials and products come from, and are used in, many parts of the world. Many of its processes require the use of potentially hazardous materials. Recent years have seen many changes in this industry. One of the most significant of these has been the development of American-made rubbers from domestic raw materials. In 1941 essentially all of the 787,000 long tons of rubber consumed in the U.S.A. were imported natural crude. In 1950, nearly half of the 1,258,000 long tons used came from domestic synthetic production. Many types of American-made rubber are commercially available, but GR-S (Government Rubber-Styrene) is the chief product. Others are butyl, nitrile types, neoprene, and thiokol. In the production of all of them certain health hazards exist. In the processing of them, as well as of natural crude, similar problems arise. A discussion of those relevant to GR-S production, and GR-S and natural crude processing, follows.

I. GR-S Manufacture

THE MANUFACTURE of GR-S rubber consists of copolymerizing two compounds, butadiene and styrene, to form a finely dispersed latex. This is then subsequently coagulated, filtered, dried and baled for processing operations. Various types of GR-S are produced, depending upon the physical properties desired in the final product. This variation requires the use of different operating temperatures and pressures, different butadiene-styrene ratios, various catalysts, modifiers, polymerization accelerators, and anti-oxidants. A flow diagram of the general process is shown in Fig. 1.

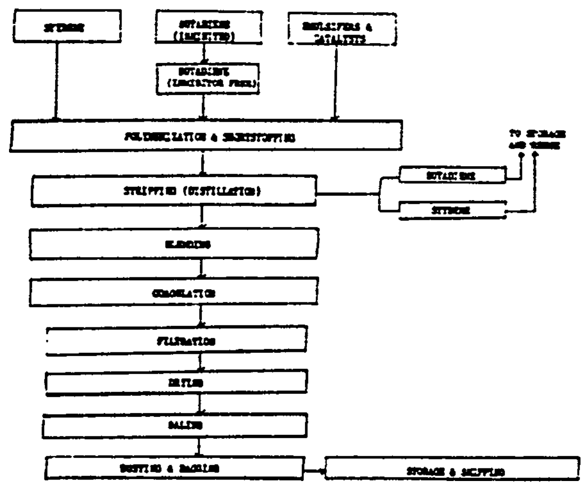

Fig. 1.
Flow Diagram of GR-S Manufacture

BUTADIENE: The butadiene used for GR-S manufacture is the 1,3 isomer, with the formula $CH_2{:}CH.CH{:}CH_2$. It is a gas which liquifies at $-4.4°$ C. It is highly flammable, with an explosive range of 2.0-11.5 percent in air.[1] Because of these physical characteristics, storage and transportation are accomplished under pressure and insulation. Upon its arrival at a GR-S plant, it is handled in a closed system. Necessary precautions must be taken to insure against the possibility of fire and explosion wherever it is used. Butadiene tends to spontaneously form explosive peroxides upon ageing. Hence an inhibitor such as tertiary butyl catechol, must be incorporated into the commercially produced product.[2]

The health hazards of butadiene are mild. It has a narcotic effect at high concentrations, but has little if any cumulative action.[3] Atmospheric concentrations up to at least 1000 p.p.m. can be tolerated for prolonged periods of time without ill effects.

STYRENE: Styrene, $C_6H_5.CH{:}CH_2$ is a liquid, boiling at 145°C. Its limits of flammability are 1.1% (29.3°C) to 6.1% (65.2°C).[4] As in the case of butadiene, rigid precautions are necessary to protect against fire. Physiologically, styrene does not produce the serious effects of the closely related aromatic hydrocarbon, benzene. No significant changes have been found in laboratory animals exposed to vapor concen-

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trations of 650 p.p.m. up to six months[5] but subjective symptoms in humans have been found[3] after several hours' exposure to 800 p.p.m. The vapors become quite irritating above 400 p.p.m. It is therefore desirable to maintain workroom atmospheres below 200 p.p.m.

MINOR COMPONENTS: A large number of substances are used in more or less minor quantities for GR-S manufacturing. Among these are the various catalysts, emulsifiers, polymerization accelerators, short-stopping agents, anti-oxidants, and dusting materials. Fortunately very few of these substances in their specific use present health problems. Exceptions are dinitrochlorobenzene, sodium sulfide, and EFED (triphenyl phosphite).

Dinitrochlorobenzene is a hazardous compound. It is a severe sensitizer and elaborate precautions must be taken to prevent skin contact. If it does occur accidentally, immediate removal from the skin is necessary. In addition to its dermatitis producing potentialities, it is also systemically toxic. The degree of this, however, is not fully established, but is believed to be more severe than nitrobenzene.[6] In the industrial use of this compound, the dermatitis hazard is by far the more important, and because of its severity, more or less controls the systemic hazard automatically.

During the coagulation of the latex, sulfuric acid is used. If sodium sulfide is present, hydrogen sulfide is produced. The high degree of toxicity of this compound is well known. The manufacturing operations at which this evolution occurs are essentially open, and most of them require the installation of process ventilation to satisfactorily control this hazard.

EFED is a relatively new compound industrially. Little is known regarding its toxicity. However, upon hydrolysis phenol is one of the products. This, together with EFED, may be present in the workroom air around the coagulation, filtering, and drying areas in sufficient amounts to require the use of process ventilation.

II. Processing Operations

A LARGE RUBBER industry in its processing of crude rubber into finished products uses a tremendous variety and quantity of different materials. An attempt has been made to list these in the accompanying table. This list is obviously intended to be typical of the industry and is not complete for any one manufacturer. Professional industrial health personnel will recognize here many materials with well-known physiological characteristics, as well as many about which little or nothing is known. It is because of the use of this vast array of substances, as well as the constant introduction of new ones, that industrial hygiene in the rubber industry is a necessity.

It obviously is impossible to discuss in detail the health hazards of any great number of these materials. Many of course, are relatively innocuous and require no discussion. Others present numerous problems. From the standpoints of severity of hazard, number of personnel exposed, and quantity of material used, the solvents as a class are of major importance. These I shall attempt to discuss briefly. It should be realized that in addition to the various systemic problems associated with the use of these solvents, there is always the problem of dermatitis. This in many cases is the more difficult of the two to control.

AROMATIC HYDROCARBONS: Benzol, toluol, and xylol (the names for the commercial grades of benzene, toluene, and xylene) are used quite extensively as solvents for rubber cements and for tackifying purposes. By far the most important of the three from the standpoint of hazards to health is benzol, although the other two are not without danger. The literature contains a large amount of information on physiological effects of these materials, some of which is conflicting, to say the least. The chemical formulas of the three compounds are C_6H_6, $C_6H_5.CH_3$, and $C_6H_5(CH_3)_2$. Their boiling points are 80.2°C, 110.4°C, and 138°C to 144°C respectively. All are flammable, with quite low explosive levels, and with flash points of—12°C, and 4°C, and 18° to 20°C, respectively. The commercial grades of each contain as impurities minor percentages of each of the other two, and xylol contains all three of the xylene isomers (meta, ortho, para).

Acute poisonings rarely result from these solvents, but chronic poisoning is a real probability. This is characterized chiefly

COMPONENTS USED IN THE MANUFACTURE OF RUBBER PRODUCTS

RUBBER

1. *American Made*
   - GR-I
   - GR-S ("Hot" and "Cold")
   - GR-S Latex
   - Hycar Pa
   - Nitriles
   - Neoprene
   - Thiokol
2. *Natural*
   - Fine Para
   - Guayule
   - Natural Latex
   - Pale Crepe
   - Ribbed Smoked Sheets
3. *Reclaim*
   - Inner Tube (Natural Butyl)
   - Mechanical Blend (Black, Light)
   - No. 1 Peel
   - No. 2 Peel
   - Pure Gum
   - Whole Tire

TEXTILES

Chafers (Primarily Cotton)
Hose and Blet Ducks (Rayon, Cotton, Nylon)
Liners (Primarily Cotton)
Tire Cord (Rayon, Cotton, Nylon)

VULCANIZING AGENTS

Ethyl Tuads (Tetraethylthiuram Disulfide)
Methyl Tuads (Aetramethylthiuram Disulfide)
Selenac (Selenium Diethyldithiocarbamate)
Selenium
Sulfur
Tellurac (Tellurium Diethyldithiocarbamate)
Tellurium
Tetramethylthiuram Monosulfide

ACTIVATORS

Barak (Dibutyl Ammonium Oleate)
Para-Amino Phenol
Polyac (Polydinitrosobenzene)
Calcium Hydroxide
Litharge
Sodium Acetate
Stearic Acid
Magnesium Oxide
Triethanolamine
M.O.D.X. (Mixed Organic and Inorganic Acetates)

RETARDERS

Antiscorch Essen (Phthalic Anhydride)
Phthalic Anhydride
Salicylic Acid
Benzoic Acid
Delac J—
Trichloro Melamine
Vultrol—Diphenyl Nitroso Amine

SOLVENTS

Acetone Amyl Acetate Isopropyl Acetate
Benzol Isopropyl Alcohol Kerosene
Butyl Acetate Butyl Alcohol Methyl Alcohol
Carbon Tetrachloride Methyl Ethyl Ketone
Ethyl Acetate Ethyl Alcohol Methyl Isobutyl Ketone
Ethylene Dichloride Monochlorobenzene
Gasoline (Unleaded) Propylene Dichloride Toluol
Heptane Hexane Trichloroethylene Xylol

STIFFENERS AND ANTI SOFTENERS

Glue
Shellac

COLOR PIGMENTS

Aluminum Powder
Antimony Sulfide
Benzidine Orange
Benzidine Yellow
Cadmium Lithopone
Cadmium Selenide
Cadmium Sulfide
Chrome Green
Lead Chromate
Monastral Green
Permanent Green
Permanent Orange
Permanent Red
Red Iron Oxide
Red Lithol Toner
Rubber Green
Titanium Dioxide
Ultramarine Blue
Yellow Iron Oxide

INERT FILLERS

Calcium Silicate Cork Ground Whiting
Hard Clay Precipitated Whiting Soft Clay

ACCELERATORS

Aldehye Ammonia (Ammonia-Acetaldehyde Condensation Product)
Altax (Benzothiazyl Disulfide) Butyl Eight
Butyl Zimate (Zinc Dibutyldithiocarbamate)
Captax (Mercaptobenzothiazole)
Dibenzo GMF (P, P' Dibenzoyl Quinonedioxime)
Diortho Toylyl Guanadine Diphenyl Guanadine
Erie (Bis 4, 5 Dimethyl-Thiazyldisulfide)
Ethyl Tuads (Tetraethylthiuram Disulfide)
Ethyl Zimate (Zinc Diethyldithiocarbamate)
Ethylac (2-Benzothiazyl-N,N-Diehyl Thiocarbamyl Sulfide)
GMF (P-Quinonedioxime)
Guantal (Diphenyl Guanidine Phthalate)
Hepteen, Hepteen Base (Heptaldehyde-Aniline Condensation Product)
Hexa (Hexamethylene Tetramine)
Ledate (Lead Dimethyldithiocarbamate)
Mercaptothiazoline
Methyl Tuads, Monex, Thionex (Tetramethylthiuram Disulfide)
Methyl Zimate (Zinc Dimethyl)
Methylene Para Toluidine
Na-22 Accelerator (2-Mercaptoimidazoline)
Para Nitrosodimethylaniline Polyac
Potassium Pentamethylene Dithiocarbamate
Pullman (Butyraldehyde-Aniline Condensation Product)
Safex (2, 4-Dinitrophenyl Dimethyl-Thiocarbamate)
Santocure (Benzothiazyl-2-Monocyclohexyl-Sulfanamide)
SPDX (Lead Dithiocarbamate)
Tetrone (Cipentamethylene Thiuram Tetrasulfide)
Texas (Mixed Mercapto Alkyl Thiazole)
Thiocarbanilide
Trimene, Trimene Base (Formaldehyde-Monethylamine Condensation Product)
ZBX (Zinc Butyl Zanthate)

FATTY ACIDS

Cottonseed Fatty Acid
Low Acid Palm Oil
Fatty Acid Ester
Stearic Acid
Lauric Acid
Wool Grease

REINFORCING FILLERS

Barytes, Blanc Fixe
Channel Carbon Blacks (Various Types)
Furnace Carbon Blacks (Various Types)
Lithopone
Zinc Oxide
Precipitated or Fumed Silica ("White Carbon Black")

ANTI-OXIDANTS OR AGE RESISTORS

Agerite Alba (Monobenzyl Ether or Hydroquinone)
Agerite Powder (Phenyl Beta Naphthylamine)
Agerite Resin (Polymerized Aldol Alpha Naphthylamine)
Agerite Resin D (Polymerized Trimethyl Dihydroquinoline)
Agerite White (Di-Beta Naphthyl Para Phenylenediamine)
BLE (A Ketone-Amine Reaction Product
Flectol B (Condensation Product of Acetone and Aniline)
Flectol H (Condensation Product of Acetone and Aniline)
Flectol White (1, 1-Di Para Hydroxyphenyl Cyclohexane)
Hoboken (Diphenyl Para Phenylene Diamine)
Iso Proposy Diphenylamine
Neozone D (Phenyl Beta Naphthylamine)
PBNA (Phenyl Beta Naphthylamine)
Santoflex B (Condensation Product of P-Aminodiphenyl and Acetone)
Stalite (Mono and Diheptyl Diamines)

DUSTING MATERIALS

Corn Starch Mica Soapstone Talc
Potato Starch Zinc Stearate

PLASTICIZERS AND SOFTENERS

Asphaltum Oil Bardol Paraffin Wax
Black Petrolatum Paraflux Pine Tar
Coal Tar Base Oil Soft Asphalt Soft Coal Tar
Dibutyl Phthalate Dipentene
Extending Resin Factice Soft Cumar Stabelite
Hydrogenated Rosin Syncera Wax Tergum
Mineral Rubber Tricresyl Phosphate
Paraffin Base Oil
R.P.A. #3 (Xylyl Mercaptan in Inert Oil)

WETTING AGENTS

Alphasol OT Aquarex D Orvus Paste Tergitol #7
Nacconol Turkey Red Oil

MISCELLANEOUS

Ammonia Asbestos Graphite
Calcium Chloride Caustic Soda Hydrochloric Acid
Copper Cyanide Chlorine Pumice Soda Ash
Cobalt Stearate Sodium Bicarbonate
Diatomaceous Earth Sodium Cyanide Sulfuric Acid
Diazo Amino Benzene Tri Sodium Phosphate
Formalin Glycerin Zinc Cyanide Zinc Chloride

by a damage to the blood forming processes, and may be permanently injurious or fatal. The symptomatology and treatment has been adequately discussed previously[7] and will not be repeated here. The working environment of the employee must be so controlled that excessive exposure to any of these solvents will not occur. Suggested maximum vapor concentrations are 50 p.p.m. for benzol and 200 p.p.m. for toluol and xylol. In addition, the personnel so exposed should be examined regularly, with a complete blood count made at two or three month intervals. Any abnormal trend in one or more of the blood values should indicate the need for possible removal of the individual from exposure and correction of operating procedures.

PETROLEUM HYDROCARBONS (DISTILLATES): Members of this group of solvents which find common usage in the rubber industry are gasoline (unleaded), hexane, heptane, and kerosene. Hexane and heptane are chemical compounds, with chemical formulas of $CH_3.(CH_2)_4.CH_3$ and $CH_3.(CH_2)_5.CH_3$ respectively. Gasoline and kerosene are commercial blends of a number of different compounds. Boiling points range from 70°C upwards. All are flammable, with low explosive ranges and with flash points beginning at −45°C.

The physiological action of these solvents is that of a narcotic. They are mildly toxic as compared to the aromatic hydrocarbons. However, some, particularly gasoline, may contain appreciable quantities of benzol, and if so the handling hazard will be proportionately increased. They possess irritant properties to the eyes and respiratory passages, which in most cases will serve as a controlling indicator of excessive exposure. Atmospheric concentrations in the 500-1000 p.p.m. range can be tolerated with safety, unless one or more of the aromatic hydrocarbons as impurities are present in appreciable quantities. In this case a working level based upon the specific aromatic hydrocarbon concentration present should be used.

KETONES: The ketones are excellent rubber solvents, and especially find uses in the processing of the nitrile rubbers. Acetone, methyl ethyl ketone (butanone), and methyl isobutyl ketone are of the most importance. Their chemical formulas are: acetone—$CH_3.CO.CH_3$; methyl ethyl ketone —$CH_3.CO.C_2H_5$; and methyl isobutyl ketone—$CH_3.CO.C_4H_9$. Their boiling points range from 56°C to 118°C, respectively. All are flammable with flash points ranging from —18°C to 23°C.

The toxicities of these compounds are mild. In high concentrations, their effects are those of a narcotic. Chronic intoxication is unknown. Atmospheric concentrations much in excess of 500 p.p.m. for acetone and 200 p.p.m. for methyl ethyl ketone and methyl isobutyl ketone produce uncomfortable eye and respiratory irritation and should be avoided.

CHLORINATED HYDROCARBONS: Of this general class of solvents, carbon tetrachloride, ethylene dichloride, trichloroethylene, perchloroethylene, propylene dichloride, and monochlorobenzene find the most use in the rubber industry. This use varies. Some are used as rubber solvents, others as degreasers, and as fire extinguishing agents. Carbon tetrachloride, trichloroethylene, and perchloroethylene are nonflammable. The three others are. Their chemical formulas and boiling points are as follows:

Carbon tetrachloride—CCl_4. 77°C.

Ethylene dichloride, (1,2 dichloroethane) —$Cl.CH_2.CH_2.Cl$. 84°C.

Trichloroethylene—$CHCl: CCl_2$. 87° C.

Propylene dichloride (1,2 dichloropropane)—$CH_3.CHCl.CH_2Cl$ 97°C.

Perchloroethylene (tetrachloroethylene) —$Cl_2C: C: Cl_2$. 121°C.

Monochlorobenzene—C_6H_5Cl. 132°C.

The chlorinated hydrocarbons possess varying degrees of toxicity. Of the above named, carbon tetrachloride is the most severe. Serious injury and death may result from exposure. Individual susceptibility varies widely. It produces chronic effects, primarily to the kidneys and the liver. It is an insidiously dangerous solvent and requires careful handling. Trichloroethylene and perchloroethylene are considerably less toxic than the others mentioned above, but still need to be handled with discretion. Unfortunately, there are no reliable simple indices useful for clinical evaluations of over-exposure to the chlorinated hydrocarbons. Rigid inspections of the working environment are necessary to maintain atmospheric concentrations at safe levels. These vary with the individual compounds, ranging from 50 p.p.m. for carbon tetrachloride to 200 p.p.m. for perchloroethylene. The treatment of cases of poisoning has been discussed elsewhere.[7]

ALCOHOLS: Alcohols used by the rubber industry are methyl, ethyl, isopropyl, n-butyl, and n-amyl. The chemical formulas and boiling points of these compounds are as follows:

Methyl—CH_3OH. 65°C.
Ethyl—C_2H_5OH. 78°C.
Isopropyl—$(CH_3)_2CHOH$. 83°C.
n-Butyl—$C_2H_5.CH_2.CH_2OH$. 117°C.
n-Amyl—$CH_3.(CH_2)_3.CH_2OH$. 138°C.

All are inflammable, with flash points of 12°C and upwards.

From the standpoint of industrial health hazards, those of most significance are methyl, butyl, and amyl. Methyl alcohol produces its ill-effects primarily on the optic nerve. Accidental and suicidal poisonings from the drinking of methyl alcohol (wood alcohol) frequently occur, but industrial poisonings are rare. Atmospheric concentrations should generally be maintained below 200 p.p.m., and skin contact prevented.

Both n-butyl and n-amyl alcohol are inherently more toxic than their lower homologs.[8] However, because of their lower volatilities, and their irritant properties, little hazard is encountered in their use. Sterner[9] has reported, in a ten year study of workers exposed to butyl alcohol vapors, no ill effects at levels up to 100 p.p.m. Above this level irritation existed. He suggests 100 p.p.m. as a safe working level.

ACETATES: Acetates are useful as general rubber solvents. Those of primary importance are methyl, ethyl, n-propyl, isopropyl, n-butyl and isoamyl. Their chemical formulas and boiling points are as follows:

Methyl—$CH_3CO_2.CH_3$. 57°C.
Ethyl—$CH_3.CO_2.C_2H_5$. 77°C.
N-propyl—$CH_3.CO_2.CH_2.C_2H_5$. 102°C.
Isopropyl—$CH_3.CO_2.CH(CH_3)_2$. 88°C.
N-butyl—$CH_3.CO_2.CH_2.CH_2.C_2H_5$. 125°C.
Isoamyl—$CH_3.CO_2.CH_2.CH_2.CH.(CH_3)_2$. 142°C.

All are flammable with flash points of 9°C and upwards.

As a group these compounds are only mildly toxic, and their industrial health hazards are few. The vapors are irritating in concentrations above 200 p.p.m. The suggested maximum working levels are based largely on this irritating characteristic. They are considered to be among the safest of the solvents.

Summary

THE PRECEDING discussion should not convey an idea of hazardous working conditions existing in the rubber industry. However, it does indicate a few of the problems which may arise if improper handling precautions are used. We believe we have done, and are doing, a good job. However, ours is a rapidly changing industry. It is not only a huge consumer of chemicals, but a large producer as well. New materials, with their unknown hazards, are constantly being developed. Toxicological and industrial hygiene studies for them must likewise be made if they are to be used safety.

This offers a challenging opportunity for industrial health.

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