

SOURCE ASSESSMENT DOCUMENT

NO. 24

RUBBER PROCESSING

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SECTION I

INTRODUCTION

Rubber must be processed to convert rubber polymers into finished, saleable products. This practice constitutes a source of air pollution. The objective of this work was to assess the environmental impact of rubber processing in the United States and to produce a reliable and timely Source Assessment Document for use by EPA in deciding whether there is a need for additional control technology development.

This document was prepared by acquiring and analyzing information on: (1) the materials used in rubber processing; (2) the basic rubber processing steps; (3) source sites; (4) emissions produced; (5) effects on air quality; (6) the state of the art and future considerations in pollution control technology; and (7) the projected growth and anticipated technological developments in this practice.

[In this document, the effects on air quality resulting from rubber processing were determined using estimated emission factors derived from limited emission data available in the literature. More complete and more reliable data could be obtained by further sampling and analysis of: (1) chemical substance emissions; (2) particulate emissions and (3) other emissions.]^a

^aInformation shown in brackets, [], in this preliminary document may not appear in the final Source Assessment Document.

SECTION II

SUMMARY

Rubber processing is performed to convert rubber (natural and synthetic) into finished, saleable products. It is estimated that approximately 1500 plants perform some type of rubber processing. The products manufactured include: (1) tires and inner tubes; (2) footwear; (3) hose and belting; (4) fabricated rubber products; (5) reclaimed rubber; (6) gaskets and packing; (7) nonferrous wire drawing and insulation; and (8) tire retreading and repairing. Rubber processing plants are concentrated in the industrialized states such as Ohio and California.

Rubber processing involves a number of steps such as: (1) compounding, (2) milling, (3) molding, (4) cementing, (5) spraying, and (6) wiring. These processing steps generate hydrocarbon and particulate emissions. Hydrocarbons consist of rubber chemicals and solvents which are volatilized during the processing. Particulates consist of carbon black, soapstone, zinc oxide, etc., which are generated during compounding and milling operations.

Emissions from rubber processing constitute 0.34% of the national total of hydrocarbon emissions from point sources. Hydrocarbon emissions in the following states exceed 1% of

of the total state hydrocarbon emissions: Alabama, Mississippi, Ohio, and Tennessee.

A severity factor, S, was defined to indicate the hazard potential of each emission source:

$$S = \frac{\bar{x}_{\max}}{F}$$

where \bar{x}_{\max} is the time-averaged maximum ground level concentration of each pollutant emitted from a representative rubber processing source, and F is the primary ambient air quality standard or a "corrected" threshold limit value (TLV \times 8/24 \times 1/100) depending on the type and composition of the pollutant.^a

The representative source was defined as a tire plant with an annual capacity of 1.7 million units. In rubber processing the severity factor equals 1.2 for hydrocarbons, but it is less than 0.1 for all emitted hydrocarbon chemical substances. (This includes only those species for which TLV's have been established.) The population that is affected by the emissions for which S>0.1 is _____ for hydrocarbons.

Control technology for rubber processing consists of absorption, adsorption, condensation, compression, incineration, and fabric filtration of the materials emitted.

^aTLV \times , American Conference of Governmental Industrial Hygienists.

SECTION III

SOURCE DESCRIPTION

A. SOURCE DEFINITION

This source is identified as Rubber Processing and includes the eight industries shown below. The definitions of these industries correspond with their Standard Industrial Classifications (SIC's) as defined by the U.S. Department of Commerce.

- . Tires and Inner Tubes (SIC 3011)

This industry "includes establishments primarily engaged in manufacturing pneumatic casings, inner tubes, and solid and cushion tires for all types of vehicles, airplanes, farm equipment, and children's vehicles; tiring; and camelback and tire repair and retreading materials."¹

¹Preliminary Report, 1972 Census of Manufactures, Industry Series, Tires and Inner Tubes, SIC 3011, U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, Washington, D.C., March 1974.

- Rubber and Plastics Footwear (SIC 3021)
This industry "includes establishments primarily engaged in manufacturing all rubber and plastics footwear, . . . having rubber or plastic soles vulcanized to the uppers."² (Processes specific to the utilization of plastics within the rubber and plastics footwear industry are excluded from further consideration in the assessment of the rubber processing source.)
- Reclaimed Rubber (SIC 3031)
This industry "includes establishments primarily engaged in reclaiming rubber from scrap rubber tires, tubes, and miscellaneous waste rubber articles by processes which result in devulcanized, depolymerized or regenerated replasticized products containing added ingredients. These products are sold for use as a raw material in the manufacture of rubber goods with or without admixture with crude rubber or synthetic rubber."³
- Rubber and Plastics Hose and Belting (SIC 3041)
This industry "includes establishments primarily engaged in manufacturing rubber and plastics

²Preliminary Report, 1972 Census of Manufactures, Industry Series, Rubber and Plastics Footwear, SIC 3021, U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, Washington, D.C., March 1974.

³Preliminary Report, 1972 Census of Manufactures, Industry Series, Reclaimed Rubber, SIC 3031, U.S. Department of Commerce, Social and Economic Statistics Administration Bureau of the Census, Washington, D.C., February 1974.

hose and belting, including garden hose."⁴

(Processes specific to the utilization of plastics within the rubber and plastics hose and belting industry are excluded from further consideration in the assessment of the rubber processing source.)

- Fabricated Rubber Products N.E.C.^a (SIC 3069)
This industry "includes establishments primarily engaged in manufacturing industrial and mechanical rubber goods, rubberized fabrics and vulcanized rubber clothing, and miscellaneous rubber specialties and sundries."⁵
- Gaskets, Packing and Sealing Devices (SIC 3293)
This industry "includes establishments primarily engaged in manufacturing gaskets, gasketing materials, compression packing, molded packings, oil seals, and mechanical seals. Included are gaskets, packing and sealing devices made of leather, rubber, metal, asbestos, and plastics."⁶

^aNot elsewhere classified.

⁴Preliminary Report, 1972 Census of Manufactures, Industry Series, Rubber and Plastics Hose and Belting, SIC 3041, U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, Washington, D.C., February 1974.

⁵Preliminary Report, 1972 Census of Manufactures, Industry Series, Fabricated Rubber Products, N.E.C., SIC 3069, U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, Washington, D.C., March 1974.

⁶Preliminary Report, 1972 Census of Manufactures, Industry Series, Gaskets, Packing and Sealing Devices, SIC 3293, U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, Washington, D.C., March 1974.

- Nonferrous Wiredrawing and Insulating (SIC 3357)
This industry "includes establishments primarily engaged in drawing and insulating, and insulating wire and cable of nonferrous metals from purchased wire bars, rods, or wire."⁷
- Tire Retreading and Repair Shops (SIC 7534)
This industry "includes establishments primarily engaged in repairing and retreading automotive tires. Establishments classified here may either retread customers' tires or retread tires for sale or exchange to the user or the trade."⁸

Consumption of new rubber by the industry is reported in three parts: (1) tires and tire products including pneumatic and solid tires, inner tubes, retread and repair materials, flaps, and sundries; (2) other products including footwear, belts, hose, mechanical goods, foam, sponge, and sundries; and (3) wire and cable. This breakdown permits observation of trends in total new rubber consumption. It also illustrates the dominant position of tires and tire products which consistently use 62% to 66% of all new rubber each year. Wire and cable use a small part of the total which has remained constant in absolute terms but has declined from 3% to 1% over the years from 1958 to 1972. The other products consume the remainder (about

⁷Preliminary Report, 1972 Census of Manufactures, Industry Series, Nonferrous Wiredrawing and Insulating, SIC 3357, U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, Washington, D.C., March, 1974.

⁸Preliminary Report, 1972 Census of Manufactures, Industry Series, Tire Retreading and Repair Shops, SIC 7534, U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, Washington, D.C. (To be published.)

one-third) of total new rubber production in manufacturing a great variety of items.⁹

The tires and inner tubes industry is thus the major industry of this source, accounting for 66% of finished product weight of the entire fabricated rubber products industry. The breakdown of consumption of natural and synthetic rubber by end use as of 1971 is indicated in Table 1.

B. PROCESS DESCRIPTION

1. Feed Material

a. Rubber and Rubber Latex -

(1). Natural rubber - Rubber represents a primary material input to the rubber processing source. Natural rubber is obtained by tapping the tree *Hevea Brasiliensis* and collecting latex from which the rubber is separated by the process known as coagulation. Coagulation occurs when various acids or salts are added. The rubber separates from the rubber serum as a white, doughlike mass, which is then milled and sheeted to remove contaminants and to enable drying. This rubber is known as natural rubber, which chemically is built of 5000 isoprene units in a *cis* (designated herein as cis) configuration.

⁹Pettigrew, R. J., and F. H. Roninger. Rubber Reuse and Solid Waste Management, Solid Waste Management in the Fabricated Rubber Products Industry, 1968. Environmental Protection Agency. Publication SW-22c. 1971. 120 p.

Table 1. U.S. CONSUMPTION OF NATURAL AND SYNTHETIC
RUBBER, 1971¹⁰

Rubber end use	Weight % of total	Cumulative %
Tires and related products	66.0	66.0
Molded goods		
Automotive	4.6	70.6
Other	5.2	75.8
Foam rubber	3.2	79.0
Shoe products	1.9	80.9
Hose, tubing	1.9	82.8
Rubber footwear	1.6	84.4
O-rings, packing gaskets	1.5	85.9
Sponge rubber products	1.4	87.3
Solvent and latex cement	1.3	88.6
Belts and belting	1.1	89.7
Wire and cable	1.1	90.8
Coated fabrics	1.1	91.9
Floor and wall coverings	0.8	92.7
Pressure-sensitive tapes	0.5	93.2
Industrial rolls	0.5	93.7
Athletic goods	0.5	94.2
Military goods	0.5	94.7
Thread (bare)	0.5	95.2
Drugs and medical sundries	0.4	95.6
Toys and balloons	0.4	96.0
All other	4.0	100.0

¹⁰Richardson, J., and M. Herbert. Forecasting in the Rubber Industry. (Paper CMRA 877 presented at joint meeting of the Chemical Marketing Research Association and the Commercial Development Association. New York, May 1974.)

Because natural latex is very sensitive to bacterial action, a preservative must be added to protect it. The most commonly used preservative is dilute ammonia. Ammonia can also be used in combination with formaldehyde (0.15% to 1.30%) or sodium pentachlorophenate (0.3%) Santobrite® based on latex.

Further latex processing consists of concentrating the solids. Centrifuging (90%) and creaming are mostly used for this purpose, with a very small amount of concentration being done by evaporation. In the creaming process, a small quantity of gum, such as ammonium alginate, gum tragacanth or Irish moss, is added. Concentration by evaporation requires the addition of stabilizers, alkalis, and soap to the latex. The evaporation route differs from the other two methods in that all ingredients in the original latex plus any stabilizing additives remain in the finished product. Essentially all latexes are concentrated to 62% to 68% total solids before sale. The latex is transported in its concentrated form for use in the production of foam, latex-dipped goods, adhesives, etc.

Dry rubber is produced by stabilizing the latex with preservatives such as sodium sulfide, diluted to about 15% and coagulated by the addition of dilute formic or acetic acid. The agglomerate is then either washed or dewatered in mills. "Pale crepe," "smoked sheets" and other different grades of rubber including bark, earth scrap and factory salvage are thus produced.

Natural rubber is still used in the United States for truck tires because of its heat-buildup resistance. Other reasons for the use of natural rubber are its excellent

properties, such as a gumstock, and overall balance of desirable properties, and also because rubber making machinery was designed to handle this material.

(2) Synthetic rubber - The first synthetic rubbers to be commercially available in the United States were "thiokol" and "neoprene." These rubbers were introduced in the early 1930's and both of them are still produced commercially because they have special properties that are not matched by natural rubber. Other types of synthetic rubber followed and their chemical formulations, properties, and preferred uses are summarized in Table 2.

Several other elastomers are available. They are considered specialty rubbers, and are mostly limited by their cost to use in areas where specific properties are desired. Examples of these elastomers are listed below:

Thiokol (T) is a polysulfide rubber which has outstanding oil and solvent resistance. However, its other properties are poor.

Silicone rubbers have excellent high and low temperature resistance, good mechanical properties at high temperature, low compression set, and fair oil resistance. Their cost, however, restricts use mainly to aircraft and outer space equipment. Due to their inertness and non-toxicity the silicone rubbers are also used for some food and surgical applications.

EPR (EPM) is ethylene propylene rubber with good aging, abrasion, and heat resistance. It exhibits excellent resistance to oxygen,

Table 2 CLASSIFICATION OF RUBBERS 11-12

ASTM D 1418 designation	Common or trade name	Chemical structure and formula	Monomer	General properties and use
NR	Natural	$\begin{array}{c} \text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{cis-1,4-Polyisoprene} \end{array}$	Isoprene	Excellent physical properties, good resistance to cutting, tearing and abrasion, low heat, ozone, and oil resistance; good resistance to petroleum-based fluids. Its use is still preferred in applications that demand elasticity, resilience, tackiness, and low heat build-up. It is impermeable for the tread of tires for buses, trucks, and racing cars. Resilience properties are still all in units, joints and suspension parts of automobiles. Some unique applications are in building foundations and bridge bearings.
IR	Chloroprene	$\begin{array}{c} \text{---CH}_2\text{---CH}(\text{Cl})\text{---CH}_2\text{---CH}(\text{Cl})\text{---} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{cis-1,4-Polychloroprene} \end{array}$	Chloroprene	Some properties as natural rubber, requires less maintenance than natural rubber. The best replacement for natural rubber.
CR	Isoprene	$\begin{array}{c} \text{---CH}_2\text{---CH}(\text{Cl})\text{---CH}_2\text{---CH}(\text{Cl})\text{---} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{Chloroprene} \end{array}$	Chloroprene	Excellent oxygen, ozone, heat, tearing, and wear resistance; good oil resistance; excellent flame resistance; high tensile strength. Wide and ethyl industries, hoses, extruded automobile parts, low-voltage insulation, and protective clothing and linings.
BR	Butadiene	$\begin{array}{c} \text{---CH}_2\text{---CH}(\text{Cl})\text{---CH}_2\text{---CH}(\text{Cl})\text{---} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{cis-1,4-Polybutadiene} \end{array}$	Butadiene	Excellent abrasion resistance, resistance to film cracking, and high resilience. Used principally as a blend in other rubbers. Used in tire threads, foams, and foot-cure.
SS-	SSP (JF-C)	$\begin{array}{c} \text{---CH}_2\text{---CH}(\text{Cl})\text{---CH}_2\text{---CH}(\text{Cl})\text{---} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{Butadiene-chloroprene} \end{array}$	Butadiene-chloroprene	Good oil and grease resistance, low heat and abrasion and creep resistance, good strength, low resilience, low tear strength, poor ozone, hot oil, ozone, or weather resistance. General purpose rubber used in electrical equipment with natural rubber for tire tread. It is used for tire, chassis, molded goods, shoe soles, flooring, and insulation.
NBR	Nitrile	$\begin{array}{c} \text{---CH}_2\text{---CH}(\text{Cl})\text{---CH}_2\text{---CH}(\text{Cl})\text{---} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{Butadiene-acrylonitrile} \end{array}$	Butadiene-acrylonitrile	Excellent resistance to vegetable, animal, and mineral oils; poor low temperature resistance. Seals, gaskets, rubber rolls, and hoses.
IR	Chloroprene-butadiene	$\begin{array}{c} \text{---CH}_2\text{---CH}(\text{Cl})\text{---CH}_2\text{---CH}(\text{Cl})\text{---} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \text{Chloroprene-butadiene} \end{array}$	Chloroprene-butadiene	Excellent resistance to vegetable, animal, and mineral oils; good resistance to ozone, acids, alkalis, and aging; low tensile strength and resilience, incompatible with natural rubber. Excellent for protection against oil, suitable for use in rubber and leather linings of machine parts. Also, used for many automobile components such as air filter strips. In use resistance to heat, aging, and oil. Part in tire manufacturing, forming, and hot water resistance. Not used as a sealant or in a wide variety of applications of tires. The good heat resistance and low heat build-up make it suitable for wide and stable use in tires, automotive, coating applications, and tank lining.

1. H. J. Cantow, Jr., "Chemical Processes and Properties of Polymers," John Wiley & Sons, Inc., 1957, p. 255.

2. H. J. Cantow, Jr., "Chemical Processes and Properties of Polymers," John Wiley & Sons, Inc., 1957, p. 255.

3. H. J. Cantow, Jr., "Chemical Processes and Properties of Polymers," John Wiley & Sons, Inc., 1957, p. 255.

ozone, acids, alkalis and other chemicals over a wide range of temperatures. It is not oil resistant and its full utilization potential is not fully defined.

Polyurethane rubber (AU) is a polyurethane diisocyanate with exceptional abrasion, cut and tear resistance, high modulus and hardness. It is not suited for normal tire service because abrasion resistance decreases rapidly with increasing temperature. The material is used in some small solid tires, but its main applications are in foams and surface coatings.

Hypalon (CSM) is chlorosulfonated polyethylene with excellent resistance to ozone and strong chemicals like nitric acid, sulfuric acid, chromic acid, hydrogen peroxide and strong bleaching agents. It has good heat resistance and mechanical properties, limited colorability, fair oil resistance and poor low temperature resistance. Uses include conveyor belts, steam hose tubes, o-rings and gaskets in ozone generators, miscellaneous molded goods and coated fabrics for outdoor use.

Fluoroelastomers (FDM) are fluorinated hydrocarbons with excellent high temperature resistance, particularly in air and oil. They are of limited use for cooking utensils.

Synthetic rubbers can be produced either in an emulsion process (butadiene-styrene, polybutadiene, polybutadiene-acrylonitrile, neoprene) or a non-aqueous process (butyl rubber, silicone rubbers, polyisoprene, polybutadiene, polyurethane, polyolefin, solution butadiene-styrene rubbers). In the emulsion polymerization process, the monomer (or the mixture of monomers in copolymerization) is mixed with an appropriate emulsifying solution, catalyst, and modifying agent. When the required conversion of the monomers is achieved the reaction is stopped by the addition of some material such as hydroquinone which destroys the catalyst and arrests further polymerization. At this stage the rubber is contained in a stable milky suspension known as synthetic latex.

The latex is then stripped of unreacted monomers and antioxidant is added. Rubber can be isolated from the latex by coagulation with salt, salt acid, or aluminum sulfate solution. Table 3 shows some mixtures commonly used to prepare synthetic rubbers. The finished product rubber contains fatty acids, rosin acids, antioxidants, moisture, and some inorganic materials (mainly sodium chloride and perhaps some minute quantities of materials used in its preparation).

Non-aqueous processes cover the largest spectrum of methods extending from those which produce an insoluble polymer that separates during polymerization (butyl rubber) to the polymers which remain in solution (bunas). The polymerization reaction takes place in solution with the proper solvent. The solution polymerization for making synthetic rubber has been the source of many varieties of new products. Thus, in the production of butyl rubber, the catalyst (aluminum chloride) is added as a dilute solution in methyl chloride.

Table 3. TYPICAL MIXTURES FOR SYNTHETIC RUBBER PRODUCTION^{1,2}

Rubber	Component	Parts per 100 monomer
SBR (BR, Buna N) ^a (hot polymerization at 50°C)	Butadiene	75.0
	Styrene	25.0
	Water	180.0
	Soap	5.0
	"Lorol" mercaptan (n-C ₁₂ H ₂₅ SH)	0.50
	Potassium persulfate	0.30
SBR (cold polymerization below 30°C)	Butadiene	71.5
	Styrene	28.5
	Water	200.0
	Mixed tert-mercaptans	0.125-0.15
	Potassium fatty acid soap	4.7
	"Daxad-11"	0.1
	KCl	0.5
	FeSO ₄ ·7H ₂ O	0.004
	Sodium formaldehyde sulfoxylate (SFS)	0.0228
	Ethylene diamine tetraacetic acid (Sequestrene AA)	0.0246
	NaOH	0.0024
	Diisopropylbenzene hydroperoxide	0.03 - 0.10
	Sodium dimethyl dithiocarbamate (SDD) stopping agent	0.10
CR (cold polymerization below 30°C) ^b	Chloroprene	100
	N-Wood rosin	4.0
	Sulfur	0.6
	Water	150
	Sodium hydroxide	0.8
	Sodium salt of naphthalene sulfonic condensation product	0.7
	Potassium persulfate	0.2 - 1.0

^a SBR = styrene - butadiene rubber; BR = butadiene rubber; Buna N = butadiene - acrylonitrile rubber. In the recipe for BR, styrene is omitted; for Buna N, styrene is substituted with acrylonitrile.

^b CR = chloroprene rubber.

Produced polymer precipitates out of the solution and is slurried with hot water, whereupon monomer flashes off and is recovered. An antioxidant is added to prevent deterioration during drying and storage and the rubber then is dried. Butyl rubber latex is not produced during the production of this material, but butyl rubber dispersions have been prepared indirectly by dissolving the rubber in a solvent, dispersing the solution, and subsequently removing the solvent to leave a dispersion of butyl rubber in water.

The synthesis of polyisoprene was not successful until 1955. Difficulties were associated with synthesizing *cis*-1,4-polyisoprene and minimizing the formation of *trans*-(designated herein as trans) polyisoprene units. The catalyst used and reported to be specific for synthesis of cis-polymer was lithium metal, melted in petroleum jelly and mixed with pure dry isoprene (0.1 part lithium/100 parts monomer). Alkylaluminum with titanium tetrachloride in hydrocarbon medium, triisobutylaluminum and triethyl aluminum have been used since then. After polymerization is completed the catalyst is deactivated using isopropyl alcohol and an antioxidant is added. The product is dried and cleaned to contain less than 1% volatile material. The synthetic polyisoprene simulates very well the properties of natural rubber. However, it does not contain fatty acid. This is later compensated for in the compounding recipe.

Polybutadiene rubbers utilize organolithium and Ziegler-type catalysts. Alkyl or aryllithium catalysts are reported to produce essentially the same polybutadienes; butyllithium is used most frequently. Ziegler catalysts consist of alkylaluminum compound with titanium tetrachloride or titanium trichloride. Other transition metals such as

vanadium, molybdenum, cobalt, and nickel are also used. Commercial practice seems directed toward the reaction products of TiCl_4 and TiI_4 with alkylaluminum compounds, alkylaluminum halides with cobalt compounds, and aluminum trihalides with cobalt compounds.¹²

Polyurethane is an example of a condensation polymer. In condensation polymerization diisocyanate and dialcohol, react and eliminate simple molecules such as H_2O or ammonia. Some reactions are performed where no compound is eliminated.

Butadiene-styrene rubbers (SBR) can also be polymerized in solution (hexane). Alkyl lithium catalysts have been used in this process. Polyolefin rubbers utilize alkylaluminum catalysts in mixtures of vanadium chlorides (VCl_4 , VCl_3 , VOCl_3 , V-triacetate) or titanium chlorides (TiCl_4 , TiCl_3) in a hydrocarbon solvent.

Silicone rubbers are generally prepared by conversion of dimethyl dichlorosilane by addition of water in the presence of small proportions of iron chloride, sulfuric acid, or sodium hydroxide. These chemicals are later washed out of the polymer.

(3) Reclaimed rubber - The third important feed material in the rubber processing industry is reclaimed rubber, or vulcanized rubber reworked to render it suitable as raw material. Reclaimed rubber is obtained from rubber scrap, natural or synthetic in origin, which is segregated into separate and compatible rubbers and then graded according to quality and intended use. It is not profitable to use

reclaimed rubber unless it costs no more than half as much as virgin rubber. Its utilization therefore fluctuates depending on the costs of virgin rubbers.

Reclaimed rubber is manufactured in various ways, the simplest being digestion of scrap (to which oil has been added) either in caustic soda or zinc chloride to remove non-rubber products. The rubber is then milled. New reclamation involves removal of fabric by mechanical means. The rubber is then ground, mixed with oil and extruded.

The significance of individual rubber feed materials to the rubber processing industry may be demonstrated by percentages of these materials processed in the United States. Of the total 3.4 Tg^a of rubber processed in the United States in 1972, 6% was reclaimed rubber, 76% was synthetic rubber, and the remainder was natural rubber. The total includes imports.

b. Rubber Chemicals - The commercial application of either raw natural dry rubber or raw synthetic rubber is very limited. For the great majority of users, the rubber must be modified, usually by the addition of chemical agents with specific functions. Exceptions include such uses as crepe rubber shoe soles; cement, as in the familiar rubber adhesives; and adhesives in masking tape.

Rubbers in prescribed proportions are blended to obtain rubber of required qualities. The desirable properties achieved by rubber compounding are plasticity, elasticity, toughness, softness, hardness, impermeability, resistance to abrasion, etc. The variety of chemicals added in the

^a 1 Tg = 10¹² grams; other metric system prefixes are shown in Section VIII.

compounding step depends on the type of processing that will follow and on final product use. The following is an example of a rubber compound:

<u>Ingredient</u>	<u>Parts on weight basis</u>
Rubber (such as SBR)	100.0
Sulfur	2.0
Zinc oxide	5.0
Stearic acid	3.0
Accelerator	1.5
Loading or filling pigment	50.0
Reclaim, softeners, extenders, colors, blowing agents, anti-oxidants, antiozonants, odorants, etc.	As required

To identify the materials that are used in the fabrication of rubber products, the following sections present the individual compounds and their functions in rubber processing.

(1) Antioxidants and stabilizers - Antioxidants and stabilizers are needed to protect the rubber during its handling and shipment. Generally, stabilizers are used to protect polymers during their isolation and storage. The antioxidants protect the rubbers both during processing and in the finished product. Most antioxidants give good protection as stabilizers, but not all stabilizers give satisfactory antioxidant activity. Natural rubber needs antioxidants only, but the synthetic polymers require both. Table 4 summarizes the commercially important rubber antioxidants and stabilizers according to the three principal

Table 4. COMMERCIAL ANTIOXIDANTS¹⁴

Chemical name	Trade names or trade-marked names
Aldehyde-amine type	
Aldol-1-naphthylamine	Agerite Resin, Aceto AN
Butyraldehyde-aniline product	Antox
Acetaldehyde-aniline product	Crylene
Aldol-aniline product	Resistox
<u>p,p'</u> -Diaminodiphenylmethane	Tonox
Ketone-amine type	
1,2-Dihydro-2,2,4-trimethyl-quinoline resin	Agerite Resin D, Flectol II, Aceto POD
1,2-Dihydro-2,2,4-trimethyl-6-ethoxyquinoline	Santoflex AW, Polyflex
1,2-Dihydro-2,2,4-trimethyl-6-phenylquinoline	Santoflex B
1,2-Dihydro-2,2,4-trimethyl-6-dodecyl-quinoline	Santoflex DD
Diaryldiamine type	
<u>N,N'</u> -diphenyl- <u>p</u> -phenylene-diamine	Agerite DPPD, JZF
<u>N,N'</u> -di- β -naphthyl- <u>p</u> -phenylenediamine	Agerite White, Aceto DIPP
<u>N,N'</u> -dialkylphenyl- <u>p</u> -phenylenediamine	Wingstay 100, Wingstay 200
Diarylamine type	
Phenyl-1-naphthylamine	Neozone A, Aceto PAN
Phenyl-2-naphthylamine	Neozone D Special, Agerite Powder, PBN, Aceto PBN
Alkylated diphenylamine	Agerite Stalite, Octamine, Pennox A, Wytox ADP, Polylite

¹⁴Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Vol. 17. New York, Interscience Publishers, John Wiley & Sons, Inc., 1968.

Table 4 (continued). COMMERCIAL ANTIOXIDANTS¹⁴

Chemical name	Trade name or trade-marked names
Ketone-diarylamine type	
Diphenylamine-acetone, high-temperature product	AgeRite Superflex, BLE-25, Neozone L, Cyanoflex 100
Diphenylamine-acetone, low-temperature product	Aminox
Phenyl-2-naphthylamine-acetone, low-temperature product	Betanox Special
Diphenylamine-acetone-aldehyde product	BXA
Substituted phenol type	
2,6-Di- <u>t</u> -butyl-4-methylphenol	CAO-1, DBPC, Tenamene 3, Ionol, Amoco 533, Dalpac 4, Deenax, Tenox BHT, CAO-3,
Butylated hydroxyanisole	Tenox BHA, Sustane BHA
2- α -Methylcyclohexyl-4,6-dimethylphenol	Nonox WSL
Styrenated phenol	AgeRite Spar, Wingstay S, Styphen 1
Hindered phenol	Wingstay T, Nevastain A, Cyanox LF, Santowhite 54
Butylated styrenated <u>m,p</u> -cresol	Wingstay V
Bisphenol type	
4,4'-bis(2,6- <u>t</u> -Butylphenol)	Ethyl 712
2,2'-Methylenebis(4-methyl-6- <u>t</u> -butylphenol)	Plastanox 2246, CAO-5
2,2'-Methylenebis(4-ethyl-6- <u>t</u> -butylphenol)	Plastonox 425
4,4'-Methylenebis(6- <u>t</u> -butyl-2-methylphenol)	Ethyl 720
4,4'-Methylenebis(2,6-di- <u>t</u> -butylphenol)	Binox M, Ethyl 702, Ionox 220

Table 4 (continued). COMMERCIAL ANTIOXIDANTS¹⁴

Chemical name	Trade name or trade-marked name
Bisphenol type (continued)	
4,4'-Butylidenebis(6- <u>t</u> -butyl-3-methylphenol)	Santowhite powder
2,2'-Thiobis (4-methyl-6- <u>t</u> -butylphenol)	CAO-4
4,4'-Thiobis(6- <u>t</u> -butyl-2-methylphenol)	Ethyl 736
4,4'-Thiobis(6- <u>t</u> -butyl-3-methylphenol)	Santowhite Crystals
4,4'-Thiobis(3,6-di- <u>sec</u> -amylphenol)	Santowhite L
Hindered bisphenol	AgeRite Superlite, Naugawhite, Pennox D
4,4'-Dioxydiphenyl	Antioxidant DOD
Alkylated polyphenol	Wingstay L
Hydroquinone type	
Hydroquinone	Tecquinol
Monobenzyl ether of hydroquinone	AgeRite Alba
2,5-Di- <u>t</u> -amylhydroquinone	Santovar A
Aminophenols	
<u>N</u> -butyl- <u>p</u> -aminophenol	Tenamene 1
<u>N</u> -lauroyl- <u>p</u> -aminophenol	Suconox 12
2,6-Di- <u>t</u> -butyl- α -dimethyl-amino-4-methylphenol	Ethyl 703
4-Isopropoxy diphenylamine	AgeRite Iso
Phosphite type	
Modified high-molecular-weight hindered phenol phosphite	AgeRite Geltrol
Tri(nonylphenyl)phosphite	Polygard
2-Ethylhexyl octylphenyl-phosphite	VC-1

groups: arylamines, phenols, and phenolphosphides. Trade names of these compounds are also given for easier compound identification. Concentration levels of the stabilizers range from 0.5 to 1.25 parts of stabilizer/100 parts of rubber.

(2) Pigments - Any solid material that is mixed into the rubber, except for vulcanizing agents, may be referred to as a pigment. Dry pigments can be classified as either reinforcing agents or filling materials. The reinforcing agents improve the properties of the vulcanizates while the filling agents serve as diluents. Commonly used pigments and their average particle sizes are given in Table 5.

For example, every pound of rubber used in tire treads may contain 0.23 kg of carbon black; tubes require even more, and carcasses require only slightly less.

In the preparation of colored stocks, a sufficient quantity of a background pigment with high hiding power (e.g., titanium pigments) and organic dye are added to give the desired color. For preparation of less bright shades, inorganic pigments such as iron oxide, antimony sulfide, chromium sulfide, chromium oxide, cadmium selenide and ultramarine blue are used. Basic requirements for colored pigments depend on their stability during product cure and the requirements of the final product itself. Other pigments that may be used for specific purposes include: fibrous asbestos, for its stiffening effect and heat resistance; cotton or other textile fibers for the same purpose at less heat resistance; graphite to produce lower friction coefficient; ground cork for compounds needing low density; glue as a stiffener; litharge or other lead pigments where high

Table 5. PIGMENTS USED IN RUBBER COMPOUNDING¹⁴

Pigment	Grade or trademark and company	Average particle diameter, nm
Carbon black	CC	10-20
	S301 (MPC)	25-30
	S300 (EPC)	30-33
	N440 (FF)	36
	N601 (HMF)	50-60
	N770 (SRF)	70-90
	N880 (FT)	150-200
	N990 (MT)	250-500
	Acetylene	43
Whiting	Witco AA (Witco Chemical Co., Inc.)	3,900
	Micronized (The Glidden Co.)	1,500
	Witcarb R-12 (Witco Chemical Co., Inc.)	145
	Witcarb R (Witco Chemical Co., Inc.)	50
	Purecal V (Wyandotte Chemicals Corp.)	40
	Purecal M (Wyandotte Chemicals Corp.)	1,500
	Atomite (Thompson, Weinman)	1,500
	Calcene TM (PPG Industries)	100
Clay	Catalpo (Freeport Kaolin)	800
	Dixie (R. T. Vanderbilt Co., Inc.)	1,000
Sibica	Hi-Sil (PPG Industries)	25
Calcium silicate	Silene EF (PPG Industries)	30

density is required for opacity to x-rays; and stiffening resins such as polyvinyl chloride, phenolformaldehyde resins, polystyrene, or high-styrene/low-butadiene copolymer resins.

(3) Softeners, extenders and plasticizers - A wide variety of oils, tars, resins, pitches, and synthetic organic materials are used as softeners in rubber compounding. These compounds do not necessarily have any relation to the softness of the compounded material. The softeners are used to: decrease the material viscosity for improved workability, reduce mixing temperature, increase tack and stickiness, aid in dispersion of pigments, reduce shrinkage, provide lubrication, and improve the following extrusion or molding and the like. The term extender is applied to materials that replace a portion of the rubber, usually with some processing advantage. Both of these materials can also be used as diluents.

Plasticizers are primarily used to lower the viscosity of the uncured stock. Usually, they are used in a very low concentration and their effect is a lower Mooney viscosity of the rubber on milling. They should not affect the rate of vulcanization or properties of cured rubber. The ease of plasticization corresponds with the ease of oxidation, which is in the following order: natural rubber > polyisoprene > polybutadiene > polystyrene > polychloroprene > nitrile rubber. The concentration of plasticizers applied to natural and synthetic rubbers may range from 0.25 parts to 1.5 parts/100 parts of rubber material. The plasticizers are effective in natural rubber, polyisoprene, and SBR. The other synthetic rubbers are less affected by the presence of a plasticizer.

The best softeners are those which are good solvents for the rubber. Table 6 lists some softeners and plasticizers used in the processing of natural and synthetic rubber.

(4) Vulcanization and acceleration agents - When rubber is mixed with sulfur and heated, vulcanization (cure) occurs. The terms cure and vulcanization are interchangeable, and may be defined as the chemical reaction which combines the polymer molecules of rubber by crosslinking into larger molecules, restricting their further movement. Vulcanization changes the rubber to a strong elastic substance which is tack free, abrasion resistant, and not readily soluble in common solvents. Sulfur is the vulcanization agent that has been used during the whole period of rubber's existence. Regardless of how little or how much sulfur is used in vulcanizing, some sulfur remains uncombined, and is known as free sulfur. High sulfur materials that liberate sulfur at vulcanizing temperatures, such as organic polysulfides, may substitute for sulfur. Examples of these compounds are: tetramethylthiuram disulfide (Methyl Tuads), tetraethylthiuram disulfide (Ethyl Tuads), dipentamethylenethiuram tetrasulfide (Tetrone A), 4,4'-dithiodimorpholine (Sulfasan R), selenium diethyldithiocarbonate (Selenac), aliphatic polysulfide polymer (Thiokol VA-7), and alkylphenol disulfides (Vultac 2,3).

Because some rubbers contain no unsaturation the vulcanization must be done using different chemicals and techniques such as peroxides or radiation. Another class of curing agents is found among the organic peroxides, such as di-*tert*-(designated herein as tert) butyl and dicumyl peroxides for SBR and silicone rubbers. Terpolymers containing a known nonconjugated diene were developed and can use sulfur for vulcanization. Neoprene rubber is vulcanized using

Table 6. TYPICAL SOFTENERS AND PLASTICIZERS USED
IN RUBBER COMPOUNDING¹⁴

Rubber type	Softener/Plasticizer
Natural rubber (SBR)	<p>All petroleum fractions Pine tars and resins Coal tar fractions Pentachlorothiophenol (RPA-6, Renacit VI) and its activated zinc salt (Endor) Thioxymenols (Pitt-Consol 640) 2,2'-Dibenzamido-diphenyldisulfide (Pepton 22) Zinc 2-benzamidothiophenoxide (Pepton 65)</p>
Neoprene (CR)	<p>Naphthenic petroleum fraction Coal tar fractions Esters Dioctyl sebacate Butyl oleate Monomeric polyether Triethylene glycol caprylatecaprate Trioctyl phosphate</p>
Nitriles (Buna N)	<p>Coal tar fractions Monomeric esters Adipates Sebacates Tributoxyethyl phosphate monomeric fatty acid ester (Synthetics L-1) Di(butoxyethoxyethyl)adipate (TP-95) Triglycol ester of vegetable oil fatty acid (Plasticizer SC) Coumarone - indene resins Rosins Modified phenolics Tetrahydronaphthalene Dibutyl phthalate Dibutyl sebacate</p>
Butyl rubber (IIR)	<p>Mineral oils Paraffin wax Petrolatum Paraffinic and naphthenic oils</p>

zinc oxide and magnesium oxide. Butyl rubber may be vulcanized using alkylphenolformaldehyde resins. Oxides of certain metals such as lead and zinc are used to accelerate the vulcanization.

Depending on the difficulty of obtaining rubber, the amount of sulfur used may range from 1/2 part to 60 parts. Use of elemental sulfur as the vulcanizing agent requires the addition of auxiliary materials to supply the desired properties. The organic accelerator is the most important of these materials. The accelerator has a strong influence on processing safety, the rate of vulcanization, and the physical properties of sulfur vulcanized rubber. Accelerators are listed in Table 7.

(5) Antiozonants - As their name suggests, antiozonants are used to protect rubber from the effects of ozone. Ozone can cause severe cracking in rubber articles, particularly under stress. For example, rubber insulation used around electrical equipment, UV lamps, and neon lights must contain antiozonants because of the high ozone concentrations present. As a result of ozone attack on rubber there is a loss of double bonds. Consequently, highly unsaturated rubbers (natural and styrene-butadiene) are most easily attacked. The antiozonants appear to work by forming a protective film between the rubber and the ozone atmosphere. Commercial antiozonants used for rubber protection are listed in Table 8.

(6) Other rubber chemicals -

(a) Reclaiming agents - Reclaiming agents are used in converting the rubber scrap to plastic processable material.

Table 7. COMMERCIAL ACCELERATORS¹⁴

Chemical name	Trade names or trade-marked names
Aldehyde-amine reaction products	
Acetaldehyde/ammonia	Acetaldehyde Ammonia, Aldehyde Ammonia
Formaldehyde/ethyl chloride/ammonia	Trimene Base
Butyraldehyde/butylamine	Accelerator 833
Butyraldehyde/aniline	Accelerator 808, A-32, Beutene, Goodrite Pullman
Butyraldehyde/acetaldehyde/aniline	A-100
Formaldehyde/p-toluidine	Accelerator 8
Acetaldehyde/aniline	Ethylidene Aniline
Heptaldehyde/aniline	Hepteen Base
2-Ethyl-2-hexenal/aniline	Phenex
Hexamethylenetetramine	Aceto HMT, Methenamine NF
Arylguanidines	
Diphenylguanidine	DPG
Di-o-tolylguanidine	DOTG
Triphenylguanidine	Triphenylguanidine
Mixed diarylguanidines	Accelerator 49
Diphenylguanidine phthalate	Guantal
Di-o-tolylguanidine salt of dicatechol borate	Permalux
Dithiocarbamates	
Copper dimethyl-	Cumate
Lead dimethyl-	Ledate
Bismuth dimethyl-	Bismate
Zinc dimethyl-	Methyl Zimate, Methyl Ziram, Methazate, Accelerator L, Eptac 1, Aceto ZDMD, Vulcacure ZM
Selenium dimethyl-	Methyl Selenac

Table 7 (continued). COMMERCIAL ACCELERATORS¹⁴

Chemical name	Trade names or trade-marked named
Dithiocarbamates (continued)	
Zinc diethyl-	Ethyl Zimate, Aceto ZDED, Cyzate E, Ethazate, Ethyl Ziram
Zinc dibutyl-	Butyl Zimate, Butazate, Butyl Ziram, Cyzate B, Aceto ZDBD
Zinc dibenzyl-	Arazate
Selenium diethyl-	Ethyl Selenac, Ethyl Seleram
Tellurium diethyl-	Tellurac
Piperidinium penta-methylene-	Accelerator 552
Potassium pentamethylene-	Accelerator 89
Zinc pentamethylene-	ZPD-Henley
Cadmium diethyl-	Ethyl Cadmate
Sodium dibutyl-	Butyl Namate, Pennac SDB, Tepidone, Vulcacure NB
Thiuram sulfides	
Tetramethylthiuram mono-sulfide	Thionex, Aceto TMTM, Cyuram MS, Unads, Monex, Mono Thiurad, TMTM-Henley
Tetrabutylthiuram mono-sulfide	Pentex
Tetramethylthiuram di-sulfide	Aceto TMTD, Cyuram DS, Methyl Thiram, Methyl Tuads, Thiurad, Thiuram M, Tuex, Vulcacure TMD, Royal TMTD
Tetraethylthiuram disulfide	Aceto TETD, Ethyl Thiram, Ethyl Thiurad, Ethyl Tuads, Ethyl Tuex, Thiuram E
Dipentamethylenethiuram tetrasulfide	Tetrone A, Sulfads
Dimethyldiphenylthiuram disulfide	Accelerator J

Table 7 (continued). COMMERCIAL ACCELERATORS¹⁴

Chemical name	Trade names or trade-marked names
Thiazoles	
2-Mercaptobenzothiazole	MBT, Captax, Rotax, Mertax, Royal MBT, Thiotax, Akron MBT
Zinc benzothiazolyl mercaptide	Zetax, ZMBT, Pennac ZT, Vulcacure ZT, O-X-A-F, Bantex, Zenite
2,2'-Dithiobis(benzothiazole)	MBTS, Altax, Thiofide, Royal MBTS, Akron MBTS
2-Benzothiazyl-N,N-diethylthiocarbamyl sulfide	Ethylac
Sulfenamides	
N-t-Butyl-2-benzothiazole-	Santocure NS
N-Cyclohexyl-2-benzothiazole-	Cydac, Comac S, Santocure, Delac S, Durax, Royal CBTS
N,N'-Diisopropyl-2-benzothiazole-	DIBS, Dipac
N-oxydiethylene-2-benzothiazole	AMAX, NOBS Special, Santocure MOR
N-(2,6-dimethylmorpholine)-2-benzothiazole-	Santocure 26
N-diethyl-2-benzothiazole-	Accelerator AZ
Miscellaneous	
Trimethylthiourea	Thiate E
Trialkylthiourea	Thiate G
1,3-Diethylthiourea	Pennzone E
1,3-Bis(2-benzothiazolylmercaptomethyl)urea	El-Sixty
2-Mercaptothiazoline	2-MT

Table 8. COMMERCIAL ANTIOZONANTS¹⁴

Chemical name	Trade names or trade-marked names
Symmetrical diamines	
<u>N,N'</u> -di- <u>sec</u> -butyl- <u>p</u> -phenylenediamine	Eastozone 2, Gasoline AO-22
<u>N,N'</u> -dimethyl- <u>N,N'</u> -bis(1-methylpropyl)- <u>p</u> -phenylenediamine	Eastozone 32
<u>N,N'</u> -bis(1-ethyl- <u>e</u> -methyl- <u>p</u> entyl)- <u>p</u> -phenylene-diamine	Eastozone 31, UOP 88, Antozite 2, Santoflex 17
<u>N,N'</u> -bis(1-methylheptyl)- <u>p</u> -phenylenediamine	Eastozone 30, UOP 288, Santoflex 217, Antozite 1
Mixture of dialkylaryl- <u>p</u> -phenylenediamines	Wingstay 100, Wingstay 200
<u>N,N'</u> -bis(1,4-dimethyl- <u>p</u> entyl)- <u>p</u> -phenylene-diamine	Eastozone 33, Antozite MPD, Santoflex 77
Unsymmetrical diamines	
<u>N</u> -isopropyl- <u>N'</u> -phenyl- <u>p</u> -phenylenediamine	Flexzone 3-C, Santoflex 36, Cyzone IP, Eastozone 34, Nonox ZA, A.O. 4010 NA
<u>N</u> -phenyl- <u>N'</u> -cyclohexyl- <u>p</u> -phenylenediamine	Flexzone 6-H, Santoflex 66, A.O. 4010
<u>N</u> -phenyl- <u>N'</u> - <u>sec</u> -butyl- <u>p</u> -phenylenediamine	Flexzone 5-L
<u>N</u> -phenyl- <u>N'</u> -(1,3-dimethyl-butyl)- <u>p</u> -phenylenediamine	Antozite 67, Flexzone 7-L, Santoflex 13, UOP 588, Wingstay 300
<u>N</u> -phenyl- <u>N'</u> - <u>sec</u> -octyl- <u>p</u> -phenylenediamine	UOP 688
Other types	
1,2-Dihydro-2,2,4-trimethyl-6-ethoxyquinoline	Santoflex AW, Polyflex
Nickel dibutyldithiocarbamate	NBC
Nickel isopropylxanthate	KPNI
Waxes	

In this process, the depolymerization of vulcanized rubber occurs in the presence of reclaiming agents and at elevated temperature. Sodium hydroxide and calcium and zinc chlorides are used as the defibering agents, pine oils and plasticizers are used as swelling agents. Many chemicals similar to plasticizers are also good reclaiming agents; e.g., di- and trialkylphenol sulfides and disulfides, thiols, amine compounds, and unsaturated compounds. Preferred amines include aliphatic long-chain, C₁₀-C₁₄, and primary amines.

(b) Blowing agents - Blowing agents are used to produce cellular rubber (foam): They must be finely dispersed and of fine size to give uniform pore product. The cellular structure is formed by gases which are generated within the compound during vulcanization, or dissolved in a compound under pressure. Examples of blowing agents include sodium bicarbonate, sodium carbonate, ammonium bicarbonate, and ammonium carbonate. Some organic materials which release nitrogen are also in use and are summarized in Table 9.

(c) Organic activators - In some cases even the addition of an accelerator results in a slow rate of rubber cure. This rate can be increased by incorporation of organic activators. Examples of these compounds are given in Table 10.

(d) Retarders - Prevention of premature cure during the processing of rubber stock is important if fast accelerators are used to prevent rubber scorching. Some of the retarding agents are listed in Table 11.

Table 9. BLOWING AGENTS WHICH RELEASE NITROGEN¹⁴

Chemical name	Formula	Trade name
Azodicarbonamide	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{H}_2\text{NCN}=\text{NCNH}_2 \end{array}$	Celogen AZ, Genitron AC, Kempore R-125, Porofof K-1074
Azoisobutyronitrile	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{NCC}-\text{N}=\text{N}-\text{CCN} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Genitron AZDN, Porofof N, Accto AZIB, Warecel 70
Diazoaminobenzene	$\text{C}_6\text{H}_5\text{NHN}=\text{NC}_6\text{H}_5$	Porofof DB, diazoaminobenzene
Azocyclohexylnitrile	$\text{C}_6\text{H}_{10}(\text{CN})\text{N}=\text{N}(\text{CN})\text{C}_6\text{H}_{10}$	Genitron CHDN
<u>N,N'</u> -dinitrosopentamethylene-tetramine	$\begin{array}{ccccc} \text{CH}_2 & - & \text{N} & - & \text{CH}_2 \\ & & & & \\ \text{ONN} & & \text{CH}_2 & & \text{NNO} \\ & & & & \\ \text{CH}_2 & - & \text{N} & - & \text{CH}_2 \end{array}$	Unicel ND, DNPT, Opex, Vulcacer
<u>N,N'</u> -dimethyl- <u>N,N'</u> -dinitrosoterephthalamide	$\text{C}_6\text{H}_4(\text{CON}(\text{NO})\text{CH}_3)_2$	Nitrosan
Benzenesulfonyl hydrazide	$\text{C}_6\text{H}_5\text{SO}_2\text{NHNH}_2$	Genitron BSH, Porofof BSH
Benzene-1,3-disulfonyl hydrazide	$\text{C}_6\text{H}_4(\text{SO}_2\text{NHNH}_2)_2$	Porofof B-13
<u>p,p'</u> -Oxybis(benzenesulfonyl hydrazide)	$\text{O}(\text{C}_6\text{H}_4\text{SO}_2\text{NHNH}_2)_2$	Celogen, Genitron OB, Porofof DO-44
Diphenylsulfon-3,3' disulfonyl hydrazide	$\text{SO}_2(\text{C}_6\text{H}_4\text{SO}_2\text{NHNH}_2)_2$	Porofof D-33
4,4'-Diphenyldisulfonyl azide	$(\text{C}_6\text{H}_4\text{SO}_2\text{N}_3)_2$	Nitropore CL-100

Table 10. ORGANIC ACTIVATORS¹⁴

Composition	Trade name
Primary fatty amines	Alamine 7,46
Mono- and dibenzylamines	DBA
Diphenylguanidine phthalate	Guantal
Zinc salts of a mixture of fatty acids	Laurex
Mixture of organic and inorganic acetates	MODX
Dibutyl ammonium oleate	Barak
Normal lead salicylate	Normasal
Fatty acids and metal soaps	

Table 11. COMMONLY USED RETARDERS¹⁴

Chemical name	Trade name
Phtalic anhydride	Retarder E-S-E-N
Benzoic acid	
Salicylic acid	
Maleic acid	
Maleic anhydride	
Terpene-resin acid blend	Turgum S
<u>N</u> -mitrosodiphenylamine	Goodrite Vultrol, Retarder J, Redax

2. Fabrication¹⁴

The basic techniques applied to rubber and rubber latex in the fabrication of rubber products are described in this section. The large number of products made of rubber and rubber latex required the development of many specific approaches to shape the product (hose, belt, molded goods), combine it with other materials (fabric, wire), or produce proper rubber consistency (hard rubber, foam, sponge). These approaches vary based on product specifications. In general, however, all rubber product fabrication processes consist of (1) preparation of a rubber or latex compound, (2) forming the compound into the desired shape (calendering, molding, extrusion, dipping), and (3) product vulcanization or curing. Additional auxiliary operations may include cutting, flash removal, spraying, and product quality control.

Since the tire and inner tube industry is the major industry of this source (see Table 1) processing 66% of the total rubber in the United States, a more detailed description of individual processing steps is given in Section III.B.3. A process diagram is also shown for the production of molded goods that consume 9.8% of the total rubber produced annually. The rest of the rubber processing industry consists of many other types of production, each consuming not more than 4% of the total rubber. Process diagrams are not given for these production categories, but they can be easily constructed based on information presented in this section.

a. Rubber Fabrication Techniques - Once the recipe is selected for a given product type, the individual components must be compounded or weighed, mixed, formed, and vulcanized. As a plastic material, rubber may be spread, calendered,

extruded, molded, cemented, caulked, puttied or wrapped into virtually any shape; coated on cloth, plastic or metal; sandwiched; or forced into cracks. Rubber is an extremely tough material and heavy machinery is needed to work it. Working the rubber generates large amounts of heat which must be properly controlled and dissipated. Rubber fabrication steps include mastication, mixing and forming.

(1) Mastication - Mastication is a preliminary step used in working natural rubber to lower its viscosity prior to the compounding operation. The combination of heat and work on crude natural rubber produces a physical and chemical change. Highly masticated or soft rubber is used in friction compounds, sponge stocks, and rubber solutions or cements. Medium soft rubber is used in calendering compounds, while lightly masticated rubber is used for stiff stocks.

Mastication is carried out at temperatures either below 55°C or higher than 132°C. The intermediate temperatures influence rubber very little. Mastication is performed on a roll mill (low temperature region), internal mixers or screw plasticators (high temperature region of 150°C to 176°C). The roll mill consists of two parallel horizontal rolls rotating in opposite directions at slightly different speeds. The rubber is worked by being pulled through the nip. The temperature in the roll mill is controlled by passing cold or hot water, steam, or hot oil through the hollow rolls. The nip width is adjustable. Rubber comes out of the roll mill as a sheet which is cut to proper size before further use.

The internal mixer such as the Banbury is a more effective device for rubber mastication. It consists of a completely enclosed mixing chamber in which two spiral shaped rotors

operate, as illustrated in Figure 1.

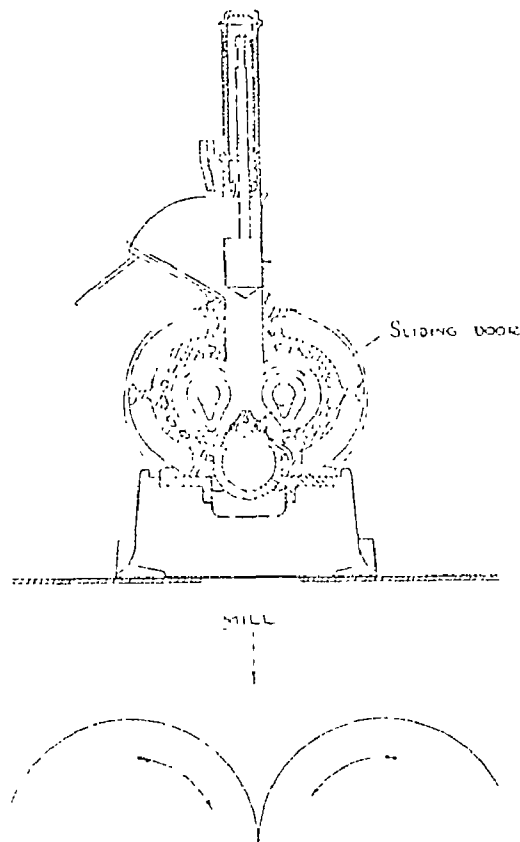


Figure 1. Cross section of a Banbury internal mixer mounted over a rubber mill¹⁵

Rubber is fed through a hopper. The two rotors rotate in opposite directions at slightly different speeds and are hollow to allow circulation of water or steam for temperature control. The product mix from the internal mixer is discharged into a two roll mill, producing rubber sheets.

¹⁵McPherson, A. T., and Klemin, A. Engineering Uses of Rubber, New York, Reinhold Publishing Corporation, Chapman & Hall, Ltd, London, 1956. 490 p.

A plasticator is actually an extruding machine fed by a hopper, with a large screw carrying the material through the machine and extruding it in the form of a cylinder. The rubber cylinder is then cut and opened up to give a continuous ribbon. Rubber sheets of desirable size can then be cut from this ribbon for further processing. The plasticator screw is hollow for circulation of water or steam to allow temperature control. The plasticator cylinder is jacketed for the same purpose.

Since plasticizers function best at elevated temperatures such as those developed in the internal mixer and the plasticator, a chemical plasticizer may be added during the mastication step.

(2) Compounding - One of the most important stages in rubber processing is compounding (mixing). It governs the quality of the final product since all the process steps that follow depend on an adequate and uniform mix. Mixing must provide (1) a uniform blend of all the constituents of the mix; (2) an adequate dispersion of the pigments; and (3) uniformity in consecutive batches for smooth further processing. Mixing can be carried out on a two-roll mixer or an internal mixer such as the Banbury, Intermix, or Bolling mixer. All of these mixers are designed for batch operation.

The batch size processed on a mill can vary depending on mixing equipment capacity. Mills are available in sizes ranging from 0.35 m to 1.07 m with the smaller sizes being more popular due to the better batch control they provide. Mixing equipment capacity is 68 kg to 136 kg for a 2.13-m mill and 454 kg or more for the largest internal mixers.

To obtain good mixing, carefully selected individual ingredients must be added in a specific order because some materials mix with rubber better than do others.

After the raw rubber has been passed between the heated mill rolls a few times it becomes sufficiently soft to adhere to the front, slower moving roll. The distance between rolls is then adjusted so that there is a "bank" of rubber in the "bite" of the rolls. When the rubber is sufficiently soft, additional compounding ingredients are spread on the rubber on the bank. The rubber is cut and covered over to aid in dispersing the individual materials throughout the batch.

Intermix and Bolling mixers are very similar to the Banbury mixer described previously. In the Intermix mixer the shearing action takes place between the rotors rather than between the rotors and the chamber wall. In the operation of the Bolling mixer, the ram pushes the preweighed charge of material down into the mixing chamber where it is forced between helically fluted rotors. Shearing action occurs between the rotors and the chamber walls as in the Banbury. A battery of roll mills is usually placed on the floor below the internal mixers so that the mixed compound may be discharged by gravity to the mills on which it is sheeted.

Internal mixers can handle large batches in relatively short periods of time. However, they are not suitable for the addition of sulfur because their high operating temperature could cause premature vulcanization or scorching. Consequently, even though most of the compound ingredients are added to the internal mixer, the sulfur is added in a subsequent operation on a roll mill.

(3) Forming - The rubber slabs obtained from the mixing mills may be immediately cut into disks or rectangular pieces suitable for charging into a mold. The consistency of the compound often determines how the rubber will be processed and what equipment can be used for building or making up rubber articles. Most of the mixed rubber must be processed into a form suitable for further fabrication. Processes utilized here include calendering, extrusion, frictioning, spreading, slabbing, and cutting.

A calender usually consists of three hollow revolving rolls placed one above the other in such a way that the spacing between them can be accurately adjusted. The temperature on the rolls can be controlled by circulation of steam or cold or hot water through the hollow rolls. The rolls can be driven either at the same or different speeds. A calender which takes the rubber passed through a mill is schematically shown in Figure 2.

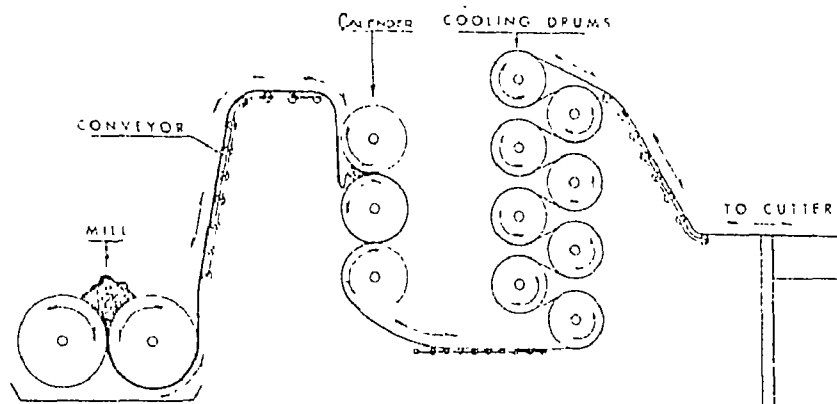


Figure 2. Diagram of the calendering process¹⁵

The purpose of calendering is to form smooth sheets of rubber compound of accurate thickness; it can also be used to coat or impregnate fabric. Coating operations are performed in either three or four roll calenders. The three roll calender applies a coat to one side of the fabric and the four roll calender coats both sides of the fabric.

When the use of fabric is required for reinforcement, as in hose belting, fabric-inserted diaphragms, tires and footwear, the fabric is usually rubberized by passing it through a friction calender along with the rubber compound. In fabric frictioning the center roll of the calender is run hotter and faster than the top and bottom rolls. This forces the rubber into the mesh of the fabric.

Fabric rubberizing is sometimes accomplished by spreading on the fabric surface a heavy dough prepared by blending a suitable rubber compound with gasoline or other solvent. The fabric is stretched and the dough is applied in a thin, uniform layer by means of a knife mounted perpendicular to the fabric. When the spreading is completed the fabric is passed slowly over heating coils to evaporate the solvent. The spreading process is applicable to cases in which either the fabric or the compound is not adaptable to the friction process.

Rubber compound obtained from calendering may be used in a variety of applications in many different shapes. Calendered rubber may be automatically cut into strips as it comes from the cooling drums, die-cut to any desired shape by means of a clicking machine, or cut to desired lengths by means of a water-lubricated circular cutter.

The process of extrusion involves forcing the rubber compound through an extrusion machine. These machines operate with either a cold or a warm rubber feed. Cold feed extruders are longer than the warm feed type in order to permit sufficient breakdown of the rubber compounds for smooth extrusion. Basically, a power driven screw forces the rubber through a cylinder to the front of the machine where it is forced through a die. The extrusion cylinder as well as the screw may be equipped with cooling water or steam for temperature control. Any number of dies are available to provide the desired extruded shapes. Since the rubber expands after being pushed through the die, the die must be smaller in size than the resulting extruded article. The extruder may be fed by hand or by a force-feed system consisting of two feed rollers. Newer extruders operate under vacuum to eliminate trapped air and moisture.

Extrusion is a very economical and widely used method of processing rubber, both for making blanks for molding and for forming rods, tubes, strips, channels, and gaskets in a wide variety of sizes and shapes. The operation sequence in the extrusion process is shown in Figure 3.

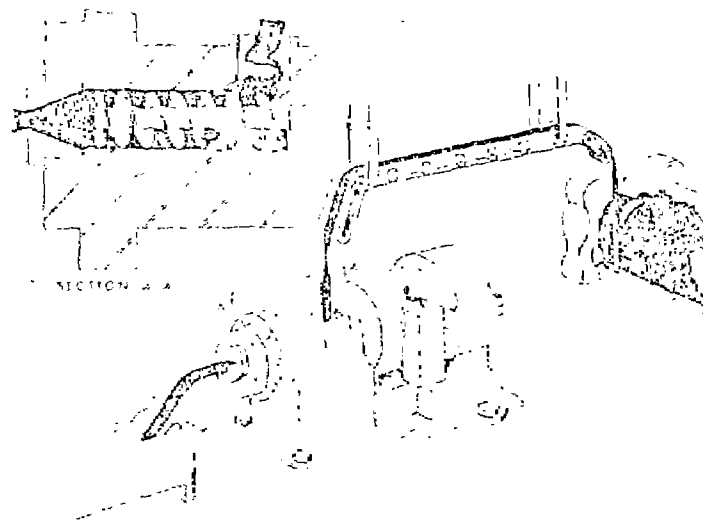


Figure 3. Extrusion processes¹⁵

When it is intended to employ a compound as insulation or jacket on a wire, or as a cover on a previously prepared hose carcass, a side delivery head is used on an extrusion machine. In this case a wire or a hose carcass is fed through the head in a direction perpendicular to the axis of the extruder screw. The head is designed so that the compound is deflected 1.57 radians (90°) and completely surrounds the wire or hose carcass.

Some rubber articles may be produced directly by cutting the milled rubber stock; e.g., if large pieces of heavy gauge rubber stock are needed as blanks for molded rubber articles, they are cut from mixing mill stock (made into a slab of the proper thickness) by means of a knife and a template. Similarly, tubed or extruded compound is cut as needed using cutting machines which may be synchronized with the extruder.

b. Fabrication of Rubber Goods from Latex - The first requirement in production of rubber articles from latex is to bring the rubber latex and all the compounding ingredients into solution or dispersion form. Solution is used when all of the ingredients are water soluble. Frequently, the ingredients are not water soluble and it is necessary to emulsify the liquid ingredients and disperse the solid materials in water.

Dispersions are generally prepared from a coarse slurry of powder with water containing small amounts of dispersing agents and stabilizer. The slurry is then ground on a suitable mill to give the desired particle size. The function of the dispersing agent is to keep the particles suspended. Typical dispersing agents are sodium 2-naphthylene sulfonate and formaldehyde, and an alkyl metal salt of sulfonated

lignin. The amounts of dispersing agents must be determined experimentally. To produce a satisfactory dispersion a wetting agent is usually used in concentrations less than 1% by weight.

Dispersions are prepared using grinding equipment such as colloid mills which break aggregates but do not change the particle size. Colloid mills are used for clay, precipitated whiting, zinc oxide, etc. Grinding equipment that reduces ultimate size and breaks agglomerates is used for solids such as sulfur, antioxidants, and accelerators. Ball and pebble mills, ultrasonic mills and attrition mills are used for this purpose. Typical recipes and directions for antioxidant such as AminoX and ultra accelerator such as zinc dimethyldithiocarbonate (Methazate) are given in Tables 12 and 13.

Emulsions are prepared by first making a coarse suspension of ingredient droplets in water and then exposing this mixture to an intense shearing in a colloid or ultrasonic mill or a homogenizer (a machine that forces the emulsion through a fine orifice under high pressure). Emulsions can be simply prepared by adding the material to a soap solution. Soap can also be prepared quickly in the machine by adding fatty acid or anionic parts such as stearic, oleic, or rosin acid to a solution of potassium hydroxide or an amine in water. Examples of emulsion recipes are presented in Tables 14 and 15.

The preparation of the latex compound is a very simple operation consisting of weighing and mixing the proper amounts of various solutions, emulsions, and dispersions. This is done in a large tank with a mechanical agitator.

Table 12. PREPARATION OF A DISPERSION OF AMINOX
SUITABLE FOR LATEX COMPOUNDING¹⁴

Material	Weight	Procedure
A. Water	68.0	Add A to ball mill
B. Water	22.8	Make up B separately and add to mill
Ammonia (28% NH ₃)	1.0	Add C and D to mill
Blancol ^a	4.0	Ball mill 4 days - keep cooling water on to avoid sintering Aminox
Dowicide A ^b	0.2	
Casein	2.0	
C. KWK bentonite	2.0	
D. Aminox	100.0	
TOTAL ^c	200.0	

^aTrademark of GAF Corporation.

^bTrademark of Dow Chemical Company.

^cTotal solids, 54.2%; active solids, 50%.

Table 13. PREPARATION OF A DISPERSION OF METHAZATE SUITABLE
FOR LATEX COMPOUNDING¹⁴

Material	Weight	Procedure
A. Water	70.0	Add A to ball mill
B. Ammonia (28% NH ₃)	1.0	Make up B and add to ball mill
Blancol	4.0	Add C to ball mill
Dowicide A	2.0	Ball mill 48 hr
Casein	2.0	
Water	22.8	
C. Methazate	100.0	
TOTAL ^a	200.0	

^aTotal solids, 53%; active solids, 50%.

Table 14. PREPARATION OF A NAUGAWHITE EMULSION SUITABLE
FOR LATEX COMPOUNDING¹⁴

Material	Dry parts	Wet parts	Procedure
Water (hot)		19.0	Add Nopco 1444B ^a to hot water with high-speed stirring
Nopco 1444B	5.4	6.0	
Naugawhite	75.0	75.0	Add Naugawhite slowly, allowing a few minutes between additions
TOTAL	80.4	100.0	
			After all the Naugawhite has been stirred in, continue stirring for 15 min

^aNopco 1444B is a highly sulfonated castor oil produced by Nopco Chemical Company.

Table 15. PREPARATION OF AN OIL EMULSION SUITABLE
FOR LATEX COMPOUNDING¹⁴

Material	Parts	Procedure
A. Mineral oil	70	Add A to B using an agitator such as the Eppenbach Homo-mixer
Oleic acid	1.5	
B. Potassium hydroxide	1.5	Put emulsion through a homogenizer to obtain a very small particle size and a high emulsion stability
Water	27.0	
TOTAL	100.0	

Fabrication of rubber articles using compounded latex can be done by a variety of methods. One of the simplest techniques is to dip a form into the latex, and dry the thin film formed on the foam at room temperature or in warm air at 49°C to 60°C while rotating the form to ensure a uniform film thickness. Thicker films are made by multiple dipping.

Another technique for fabricating rubber articles uses porous formers, or porous molds, made of plaster of paris or unglazed porcelain with smaller pore size than the smallest rubber latex particles. The rubber particles are filtered out by this material and latex coagulates due to the presence of calcium ions in the plaster to form a film. The molds are dried in an oven at 60°C for one hour. This can be repeated for 30 minutes after the articles are removed from the mold. For example, dolls and squeeze toys are manufactured using this technique.

Since the rubber particles in latex are negatively charged, electrodeposition has been used to coagulate rubber and make rubber articles. Evolution of oxygen on the anode produced oxidation of the product and caused porosity in the article. Electrodeposition was therefore abandoned but essentially the same coagulation can be attained by using chemical coagulants.

A thin layer of a chemical coagulant is produced by dipping the former in the coagulant solution and evaporating the solvent, preferably alcohol. The thin layer of coagulant can be produced either directly on a clean former or on a former that is coated with a very thin layer of the latex. The former is then dipped in the latex. When the film attains the desired thickness it is washed in hot water at 60°C to 71°C for about an hour to remove the coagulant and

all other water soluble ingredients. The film is then dried in air at room temperature, and the article is cured in a 66°C oven.

Typical coagulants are calcium chloride or calcium nitrate in solution of denatured ethyl alcohol. They are used in mixture with a nonionic surfactant and a release agent (a fine, insoluble powder such as talc, clay or diatomaceous earth) which is suspended in the coagulant. The surfactant and release agent are used to aid in wetting the former and releasing the article from the former, respectively.

Another variety of this process uses a gelling agent (electrolyte with a weak coagulating effect such as ammonium salts and sodium fluorosilicate) in metal molds. This method offers the advantage that latex sets to the gel with no change in volume and without distortion.

Some rubber products may be made by extrusion of the latex. For example, latex thread is produced by extrusion of the latex compound through fine orifices into a coagulant bath which gels the thread. The thread is then toughened, washed, dried and cured. A dilute acetic acid is usually used as the coagulant bath.

The broadest application for both latexes, natural and synthetic, is foam sponge. There are two basic processes available, the Dunlop and the Talalay process, applied in different variations. In the Dunlop process, which is the most commonly used, the latex is whipped to a froth by the mechanical incorporation of air into the latex. The Talalay process produces the froth by chemical rather than mechanical means. Hydrogen peroxide and an enzymic decomposition catalyst are used for this purpose. Oxygen produced by the

decompositon of the peroxide foams the latex mix. The foam is chilled and CO_2 is introduced to gel the latex. Further treatment is the same as in the Dunlop process.

The frothed structure must be set using a coagulant or a gelling agent. Sodium silicofluoride (Na_2SiF_6) is widely used in this application. Zinc oxide is also believed to take an active part in the process. Sodium silicofluoride decomposes and forms sodium fluoride (NaF), silicon tetrahydroxide ($\text{Si}(\text{OH})_4$), and hydrofluoric acid (HF). Zinc apparently reacts with the fatty acid latex stabilizers forming a soluble soap. This destabilizes the latex particles, causing them to coalesce and form a gel. The $\text{Si}(\text{OH})_4$ may also form very fine particles which could adsorb stabilizer and further enhance gelation. In very stable latexes, some secondary gelling agents may be utilized to induce gelation. Cationic soaps, other salts and amines are used for this purpose.

Whipping can be done either continuously or in a batch process. After the gelling agents are added the foam is poured into molds and cured. Additional curing is done after the product is removed from the mold.

Ammonium acetate or ammonium sulfate, in combination with zinc oxide, are employed as the gelling agents in the production of foam backings for various fabrics such as carpets, scatter mats, and upholstery fabrics. Ammonium hydroxide is the product of the reaction. Once gelation occurs the foam is spread directly on the fabric, or it is spread on a belt and transferred wet, to the fabric. The gelling is carried out at elevated temperatures usually by means of infrared lamps.

Latexes are also applied to the undersides of carpets, rugs, and upholstery fabrics. This is done after a film forming adhesive is applied to the underside of the fibrous material. Low-cost latexes that can accept a high loading of pigment and provide desirable anchorage for the fibers are used in this application; e.g., medium styrene-butadiene latexes and self-curing carboxy modified SBR latexes. Pigments utilized here include whiting and soft clays plus some titanium oxide for opacity.

Nitrile latexes and medium styrene-butadiene mixed with beaten paper pulp are used to coat paper and provide excellent strength, elongation, bursting strength, internal bond, and tear strength. Similar application on asbestos fibers produces excellent materials for gaskets, linoleum bases, etc. The pulp coating may also be accomplished by passing the paper web through a latex bath. The amount of coating is controlled by the speed through the bath and by the concentration of the latex bath. Vinyl and acrylic latexes may be applied to paper as a decorative coating to provide a high gloss paper stock. Latexes are also used as adhesives for highly pigmented clay coating and pigment binders applied to paper and paperboard.

c. Vulcanization - Vulcanization of rubber products is done at elevated temperatures and can be carried out under numerous conditions. Some articles are cured in their manufacturing step if sufficient heat is generated in the process (e.g., molded products); other articles require a separate curing step (e.g., latex products and tires).

(1) Mold curing - Molded rubber parts are formed and vulcanized in a single operation by the simultaneous application of pressure and heat. Compression is the oldest type of molding and consists of placing preshaped rubber into a mold and closing the mold under pressure, allowing the rubber to fill out the mold cavity. The heat from the heated platens of the press is conducted through the mold and vulcanizes the rubber. The platens are usually heated by circulating steam through holes drilled in them. Occasionally, electricity or gas burners are used for this purpose.

The rubber overflow or flash must be removed from the article. This operation is labor demanding and expensive because it requires hand labor. If possible the rubber parts are dipped in dry ice where the thin rubber flash becomes brittle and breaks off. This method can be used only if the main body of the part is large enough not to become cool and inflexible and if the rubber is not freeze resistant.

In transfer molding the uncured rubber stock is transferred from one place to another within the mold, allowing the manufacture of complex shapes and articles containing metal inserts. Transfer molding permits closer dimensional control and generally reduces flash. Normally the rubber is placed in a transfer cavity which is fitted with a ram or piston. The force applied to the ram or piston and the heat from the mold cause the rubber to be softened and spread in the molding cavity and cured at the same time.

Injection molding is the same as transfer molding except that the soft rubber compound is injected into the molds. A screw mechanism is utilized to force unvulcanized rubber into a tightly closed mold. Forcing the rubber through

small passages under high pressure increases the temperature of the injected compound and cures the rubber. In order to make injection molding profitable, very short cycles are required, generally in the 45 second to 90 second range. Due to these short times, a curing temperature of 204°C is required.

In molding thick articles long curing times are needed because of the low thermal conductivity of the rubber. This problem is partially overcome by dielectric heating of the blank before it is placed in the mold. This heating also improves the flow of the compound in the mold.

The processing steps involved in the production of molded goods are shown schematically in Figure 4.

An example of more complicated molding is that of the pneumatic tire in which a steel mold shapes the exterior surface of the tire from bead to bead, and the pressure during cure is supplied from a flexible bag acting as a diaphragm that forces the uncured tire against the mold surface. The diaphragm, an integral part of the press, is made of a resin cured butyl stock which has extremely good heat resistance. Steam or hot circulating water is introduced to the inside of the diaphragm to cure the tire from the inside. (Tire vulcanization is further described in Section III.B.3.)

(2) Curing of other rubber articles - Extruded and some molded articles may require additional curing. The most common method of vulcanizing these articles is to place them in pans that are set on a truck and rolled into a large steam chamber or heater for vulcanization. Varnish or lacquer may be applied before vulcanization to produce a smooth, glossy product finish.

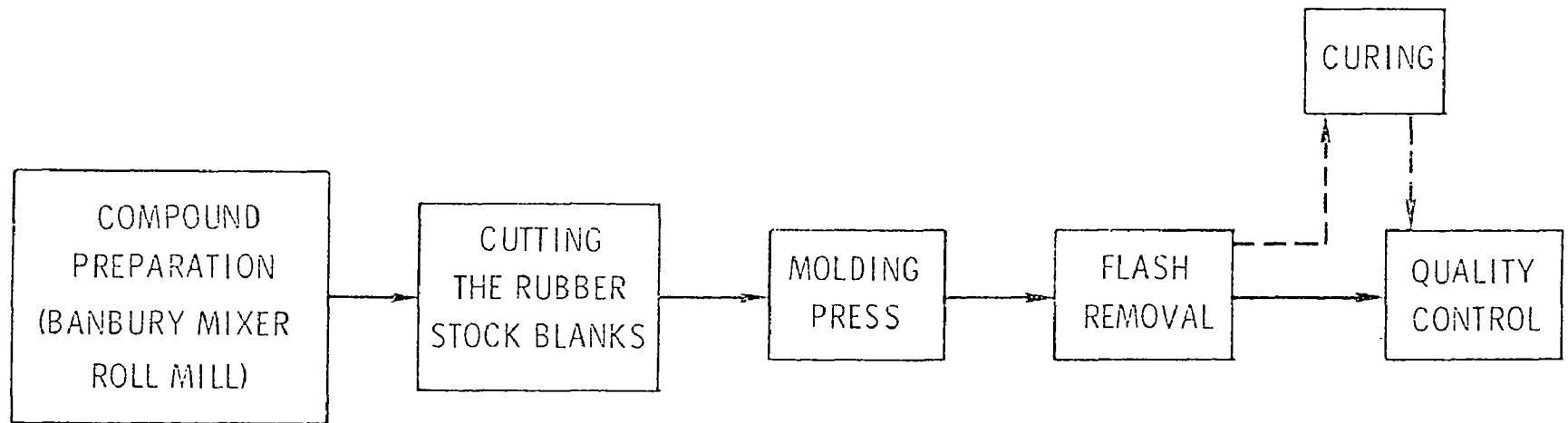


Figure 4. Processing steps in the production of molded goods

Rubber articles that would sag or flatten under their own weight before they could completely set up must be supported during vulcanization. In most cases such articles are embedded in talc or powdered soapstone. Gum rubber tubing is placed on a mandrel or rod and wrapped with fabric which is subsequently removed. Hose and insulated wires and cables may be supported during vulcanization by means of a lead sheath that is extruded over them. The vulcanization step takes about 30 minutes at 140°C to 150°C.

The continuous vulcanization of insulated wire represents a special case in which the wire is rubber covered while passing through an extruder (as described in Section III.B.2. a(3)), then run directly into a tube containing steam at 1.38 MPa to 1.72 MPa. Such a tube may be 30.5 m to 61 m long and the wire resides in it for approximately 15 seconds. Large cables are usually processed in vertical machines but horizontal and catenary types are also available.

Hose cured in lead is another special case, involving a combined mold and hydrolytic cure. In this process, the prepared construction is surrounded with a lead wall extruded through a die. The inside surface of the lead casing gives the desired design (usually ribbed). Long lengths of the leaded hose are wound on drums, and fittings are applied to the two ends to permit circulation of heated water under pressure. The drum is then placed in a steam autoclave and steam is applied externally. Thus, the lead casing is in effect the mold, and the hose is forced firmly against the mold by hot water circulating through the inside under pressure. After cure, the lead jacket is split and removed.

Continuous curing is utilized in the production of belting or floor matting. A continuous length of belt is made without splices or overlapping and cured in a "Roto-Cure." This press consists of a rotating vulcanizing drum about 1.5 m in diameter. A belt of highly polished steel is pressed tightly against this curing drum around a large portion of its circumference. The compound is fed into the space between the curing drum and the belt and vulcanizes during its trip around the drum.

Sponge rug underlay and sheet sponge are made by placing a compound containing a chemical blowing agent between two mesh or cloth belts that travel between two long platens. The blowing agent decomposes before the curing progresses significantly and expansion takes place to the desired thickness, governed by the spacing between the platens. At the end of the platens, the cure has been completed and the sponge is rolled up.

Continuous curing in a liquid is utilized in the production of both solid and cellular extruded goods. In this case, the uncured stock passes directly from the extruder into a liquid heat transfer medium which is maintained at temperatures from 204°C to 316°C. Eutectic mixtures of metals (e.g., 58% bismuth - 42% tin) or salts and heat stable organic liquids such as polyalkylene glycol are used in these applications. Some techniques utilize a fluidized bed for the heat transfer medium. For travel through the curing tank the product either passes through a series of driven rollers or is submerged in a lighter density organic liquid and floated on the bottom layer of molten metal. The latter method is satisfactory for solid extrusions. Hollow sponge extrusions float on the organic liquid and these have to be driven through the curing bath.

If curing at elevated pressure is desired, water is used in place of steam. Rubber lined vessels are steam cured unless they are too large to fit in a steam autoclave. Boiling water is used in such cases.

Air is sometimes preferred over steam in the vulcanization step, especially when moisture must be avoided, or staining or water spotting must be prevented. Hot air at either atmospheric or elevated pressure, 103.4 kPa to 275.8 kPa, is usually used, but ammonia gas is sometimes applied to produce a glossy surface on footwear. The air is circulated at a rapid rate to provide even heating of the article and avoid bad spots in the vulcanizates. Waterproof goods, boots and shoes are vulcanized in hot air ovens.

Articles made from rubber latexes are vulcanized using the same principle as those for dry rubber compounds. Low temperature curing is completed at about 104°C whereas hard rubber latex compounds require about 149°C. Hot air, steam or hot water cures are most frequently used.

3. Tire Manufacture

As shown in Table 1, the tire industry processes 66% of the total rubber processed in the U.S. and is the most important industry of the rubber processing source discussed in this document.

Tires are built from several parts as illustrated in Figure 5. There are three variations in tire construction: conventional, belted bias, and radial ply tires, as shown in Figure 6. Different rubber compounds are used in making the several tire parts because each part performs a different function. The carcass (made of body fabric or cord plies),

the impact plies (which are placed between the body plies and the tread to provide extra impact resistance), the bead assembly, the tread, and the tire wall are all made from different rubber compounds. Tire manufacturers use both synthetic and natural rubber, the latter mainly for steel belted and large size tires. The basic recipes for rubber compounds are generally very similar except that synthetic compounds require different black loadings, somewhat more softener, less sulfur, and more accelerator.

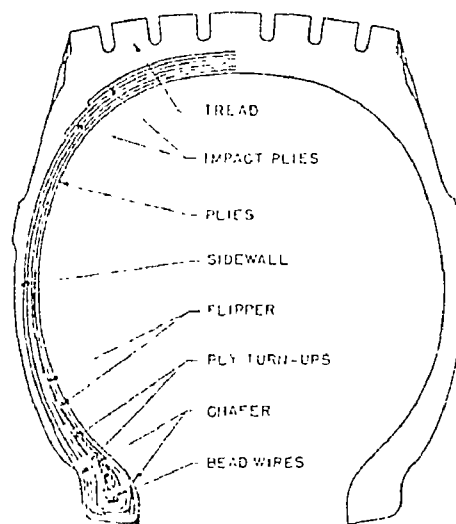
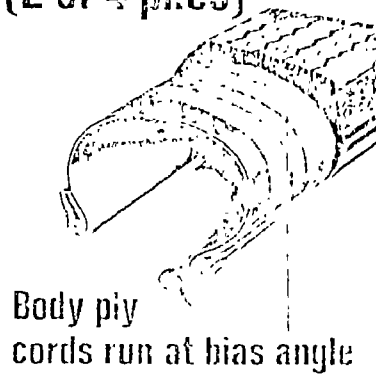
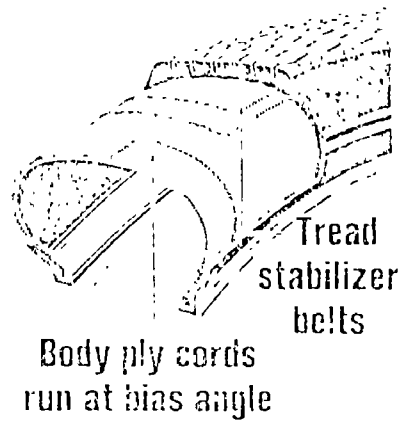


Figure 5. Cross section of a tire¹⁵

CONVENTIONAL TIRE (2 or 4 plies)



BELTED BIAS TIRE



RADIAL PLY TIRE

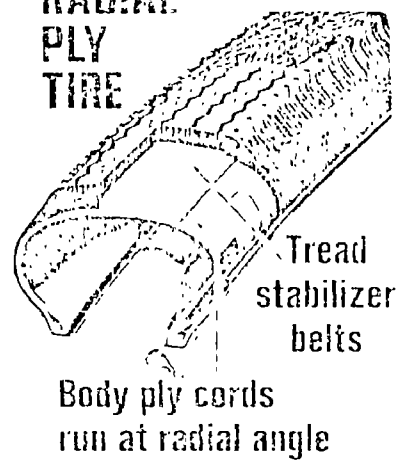


Figure 6. Variations of tire construction¹²

The basic steps involved in tire manufacturing are schematically shown in Figure 7. Recipes for each specific part of the tire are selected and the compounds are prepared using roll mills and Banbury mixers. Table 16 lists typical compositions of the rubber compounds for different tire parts. All ingredients except sulfur and the accelerator are added to the rubber in a Banbury mixer. The batch is then dumped on a roll mill, shown earlier in Figure 1, located below the mixer for addition of the curing ingredients. Compounded rubber is made into standard sheets which are then used to manufacture the individual tire parts.

Carcass plies are made of cord fabric insulated with rubber compounds. A variety of carcass materials are available to the tire manufacturer including cotton, rayon, nylon, polyester, steel wire, and glass fiber; the last two materials are used in radial tires. Today, very little cotton cord is used in pneumatic tires. Cotton has been replaced by rayon and more recently by nylon. The increasing popularity of radial tires has increased the use of steel wiring and glass fiber in tire manufacture. Selection of the cord fabric depends primarily on cost because tire cords represent a large portion of the cost of tires.

Rubber compound used to manufacture tire plies must adhere to the cord fabric and have enough tack to hold together while the green (unvulcanized) tire is being assembled and cured. Impact plies are built somewhat tougher than inner plies since they must remain intact to divert road shocks and bind the rigid carcass of the tire to the tire tread. Both sides of cord plies for the tire carcass are coated at once on a four roll calender.

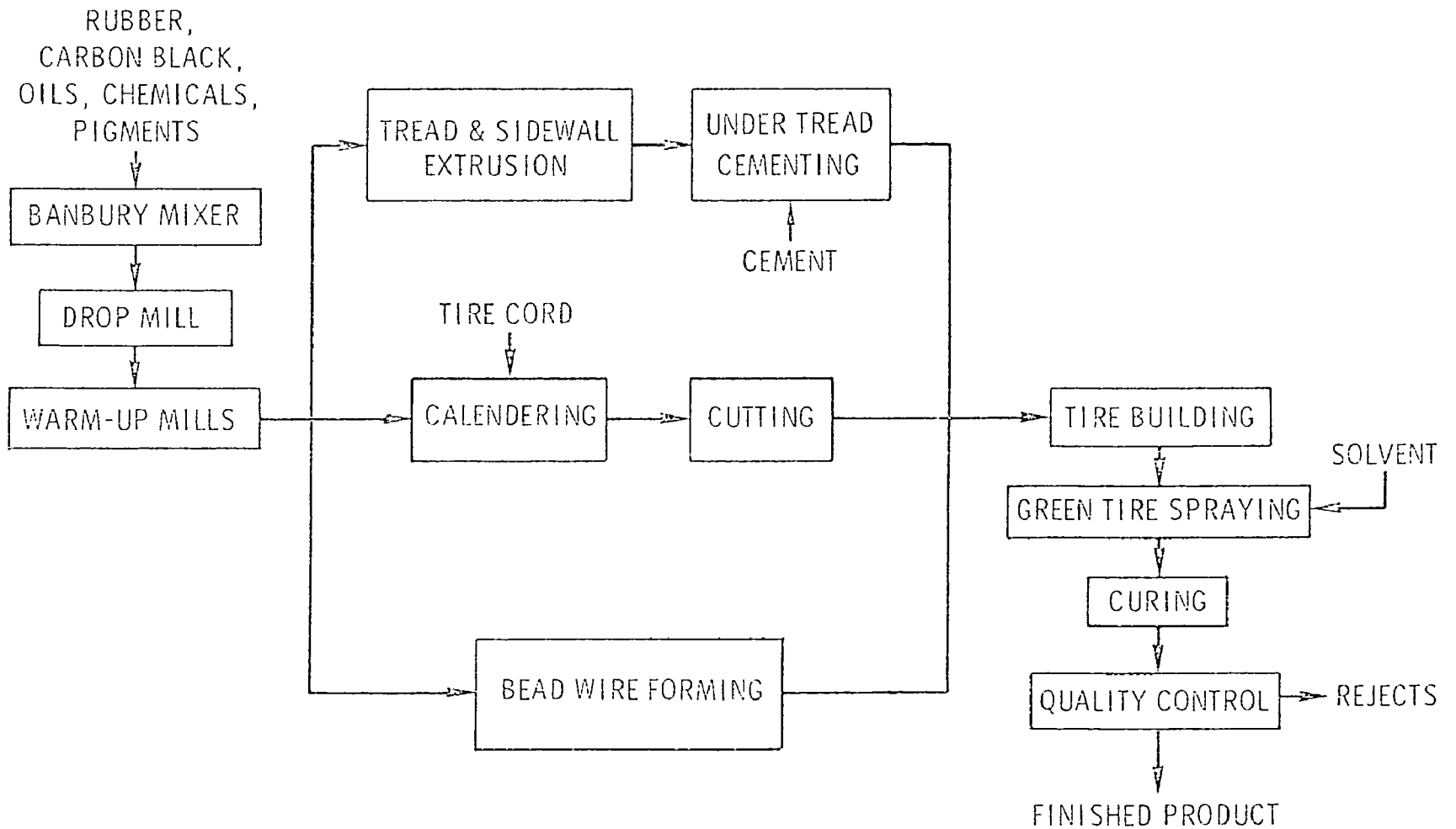


Figure 7. Tire plant process flow diagram

Table 16. TYPICAL COMPOUND COMPOSITIONS FOR
TIRE PARTS¹⁵

Tire part	Component	Parts by weight
Inner carcass or body plies (truck tires)	Natural rubber	100
	SRF black	25
	Zinc oxide	3
	Stearic acid	2
	Softener	5
	Antioxidant	1
	Sulfur	2.8
	Primary accelerator	0.75
	Secondary accelerator	0.15
Outer carcass or body plies (truck tires)	Natural rubber	100
	SRF black	15
	EPC black	20
	Zinc oxide	3
	Stearic acid	2
	Softener	5
	Antioxidant	1
	Sulfur	2.8
	Primary accelerator	0.75
	Secondary accelerator	0.15
Impact plies	Natural rubber	100
	EPC black	40
	Zinc oxide	3
	Stearic acid	2
	Softener	5
	Antioxidant	1
	Sulfur	2.80
	Primary accelerator	0.80
	Secondary accelerator	0.20

Table 16 (continued). TYPICAL COMPOUND COMPOSITIONS
FOR TIRE PARTS¹⁵

Tire part	Component	Parts by weight
Beads	Natural rubber	100
	SRF black	120
	Zinc oxide	8
	Precipitated whiting	15
	Softener	11
	Stearic acid	5
	Sulfur	3
	Accelerator	1.5
Treads	Natural rubber	100
	EPC black	45
	Zinc oxide	3
	Stearic acid	2
	Softener	3
	Antioxidant	1.50
	Sulfur	2.75
	Accelerator	0.90
Inner tubes	Natural rubber smoked sheets	100
	Peptizer	1
	Zinc oxide	4
	Fine thermal carbon black	40
	Antioxidant	2
	Paraffin	1
	Sulfur	1.5
	Primary accelerator	1.4
	Secondary accelerator	0.2

Its relatively rough surface texture allowed natural rubber stocks to be applied directly to cotton cord. This is not quite feasible with rayon and nylon cords which must be coated with an adhesive before the cord fabric can be coated with rubber compound in the calender. Medium styrene-butadiene and butadiene-styrene vinyl pyridiene latexes are usually used in this application. Vinyl pyridine latexes are universally used for nylon tire cord. A typical tire cord dip solution is given in Table 17.

Table 17. TYPICAL TIRE CORD DIP SOLUTION¹⁴

Material	Dry parts	Wet parts
SBR type 2000 latex at 40%	80	200
Vinylpyridine latex at 47%	20	43
Stabilizer (20% Dresinate 731)	1	5
Water to 20% solids		78
Resin solution (6.5%)	17.3	266
Total	118.3	592
Resin solution formula		
Water to 6.5%		238.5
NaOH	0.3	0.3
Resorcinol	11.0	11.0
Formaldehyde (37%)	6.0	16.2
Total	17.3	266.0

In the normal sequence of operations, ply fabric is passed through the adhesive dip solution, the excess dip is removed, the coated fabric is dried to a moisture level less than 1%, the rubber compound is calendered on both sides of the cord fabric, and rubber cement is applied to the carcass. The last step is necessary only for carcass plies with a high

percentage of synthetic rubber compounds because the tack of synthetic rubber is insufficient to stick properly to the vulcanized rubber. Finally, the fabric is cut to a specific angle and the required width on a bias cutting machine.

Wire bead, made of several strings of high carbon steel is used to keep the tire on the rim. Each strand is coated with rubber compound while passing through an extruder. Several strands are passed simultaneously through the die of the extruder, then rolled together to make the bead. The bead is wrapped with rubberized square woven fabric, then rewrapped with the same fabric, the edges of which extend upward into the sidewall where they can be anchored into the lower sidewall of the tire.

The tread and sidewall of the tire are formed by extrusion through dies. The extruded profile is designed to provide sufficient rubber to fill in the tread and sidewall pattern in the mold.

Tire tread is made of two sections: the cap, which contacts the road; and the base, the section next to the carcass. Since the two sections are made of different rubber compounds, dual extruding units have been developed. Good adhesion between the cap and the base is important, and in dual extrusion these two parts are plied together hot. Some extruding machines produce the cap and base already joined. Passage through a water bath cools and shrinks the continuous tread slab, which is then cut to the correct length for tire assembly.

Tires are assembled on rotating drums of a diameter slightly larger than that of the tire. Individual tire parts are

supplied to the builder in a form that allows the fastest assembly of the tire. Carcass plies are cut to the proper angle, width, and length, and may be delivered in rolls that allow unreeling of the fabric without strain (to avoid angle distortion), or in bands of two to four plies. The treads and sidewalls are also delivered precut to length. Synthetic rubber tread is delivered with crude rubber cement on its underside and ends to ensure proper adhesion to the tire carcass.

Four to eight cord plies are applied to the drum without stretching; each is tied under and over the bead in a manner which securely locks the bead. Natural rubber plies should have enough tackiness to adhere to themselves. Synthetic rubber plies are coated with a rubber cement to provide sufficient tackiness. If impact plies are used, they are added next, followed by the sidewall and tread sections. At this point the assembled tire is cylindrical in shape.

Usually, the whole tire is assembled on the drum by one man, but machines have been developed that automatically rotate the drum through several stations for addition of the successive parts. The drum is then collapsed to release the tire, which gains its final shape during vulcanization in the mold. The inside contour of the tire is formed by a curing bag placed inside the tire. The bag fulfills two functions: it gives the tire the proper shape and it provides a container into which heat and pressure can be applied to vulcanize the inside of the tire. Heat and pressure are supplied by various combinations of steam, air, and water.

Tire shaping and curing equipment have undergone several developments. The curing bladder is an integral part of a

new curing press. This combines the forming and curing operations in a single machine and eliminates the labor of inserting and removing the curing bag. Because the bladder is a part of the press and also is thinner than the separate bags, more effective use of internal heat in curing the tire and a significant reduction in curing time are achieved. Tires are vulcanized at 100°C to 200°C for 20 to 60 minutes. Longer times are required to cure large truck tires.

C. GEOGRAPHICAL DISTRIBUTION

Two states, Ohio and California, contain over 25% of the 1500 rubber product plants in the United States. In contrast, 33 other states account for 25% of the total, while the remaining 50% of the plants are found in 15 states with 25 to 85 plants per state. The largest number of tire and inner tube plants are found in cities such as Akron, Ohio and Los Angeles, California (with population densities exceeding 500 persons/km²).

Table 18 is a summary of the product type and number of rubber producing plants in the United States, by state. Figure 8 is a graphic representation of the total number of plants on a state by state basis.

Rubber product plants are located in the population and manufacturing centers of the country, particularly in the East North Central (Great Lakes) region. In individual categories, states with 25 or more total plants per state contain approximately 75% of the plants in the category rubber products, N.E.C. Nine states (Ohio, California, Tennessee, Alabama, Pennsylvania, Illinois, Texas, North Carolina, and Oklahoma) contain 50% of the tire and inner tube manufacturing plants.

Table 18. SUMMARY OF RUBBER PRODUCING PLANTS BY PRODUCT TYPE¹⁻⁵

State	Tires and inner tubes	Rubber and plastics footwear	Rubber and plastic hose and belting	Fabricated rubber products N.E.C. ^a	Reclaimed rubber ^b	Total
Alabama	10	4	3	8	1	25
Alaska	0	0	1	2	0	3
Arizona	1	0	1	2	0	4
Arkansas	5	2	1	5	1	14
California	15	3	5	144	2	169
Colorado	1	0	1	2	0	4
Connecticut	3	4	1	60	0	68
Delaware	1	0	0	5	0	6
Florida	2	2	1	17	0	22
Georgia	3	1	1	15	0	20
Hawaii	0	0	1	3	0	4
Idaho	1	1	1	3	0	6
Illinois	9	4	4	61	2	80
Indiana	4	3	3	55	2	67
Iowa	4	0	2	9	0	15
Kansas	2	0	2	8	0	12
Kentucky	3	1	1	4	0	9
Louisiana	4	1	1	6	0	12
Maine	3	6	2	25	0	36
Maryland	4	1	1	16	0	22
Massachusetts	4	5	2	20	0	31
Michigan	5	2	4	44	1	57
Minnesota	1	0	1	8	0	10
Mississippi	3	1	1	11	0	16
Missouri	2	4	2	8	0	16
Montana	1	1	1	2	0	5

^a Not elsewhere classified.^b Estimate.

Table 18 (continued). SUMMARY OF RUBBER PRODUCING PLANTS BY PRODUCT TYPE¹⁻⁵

State	Tires and inner tubes	Rubber and plastics footwear	Rubber and plastic hose and belting	Fabricated rubber products N.E.C. ^a	Reclaimed ^b rubber	Total
Nebraska	1	0	1	7	0	9
Nevada	3	0	1	2	0	6
New Hampshire	2	5	2	10	0	19
New Jersey	3	7	2	68	0	80
New Mexico	1	0	1	2	0	4
New York	4	7	4	67	1	83
North Carolina	7	2	2	17	1	29
North Dakota	1	0	0	5	0	6
Ohio	27	5	12	169	4	217
Oklahoma	7	2	1	7	1	18
Oregon	3	2	1	4	0	10
Pennsylvania	8	9	4	48	1	70
Rhode Island	1	3	1	5	0	10
South Carolina	4	1	1	14	0	20
South Dakota	1	0	0	5	0	6
Tennessee	11	4	2	13	1	31
Texas	7	2	2	36	1	48
Utah	1	0	1	2	0	4
Vermont	2	5	2	10	0	19
Virginia	5	2	1	17	1	26
Washington	4	2	1	4	0	11
West Virginia	2	1	1	11	0	15
Wisconsin	4	1	2	35	1	43
Wyoming	1	0	1	2	0	4
TOTALS	202	106	90	1,103	21	1,522

^aNot elsewhere classified.^bEstimate.

Figure 8. Geographic distribution of rubber product plants in the U.S.

Table 19 gives a summary of production capacities by state for three categories: tires and tubes, rubber and plastics footwear, and rubber and plastic hose and belting. Seventy-five percent of the tire and tube production is located in 13 states: Ohio, California, Tennessee, Pennsylvania, Michigan, Alabama, Mississippi, Massachusetts, Iowa, Wisconsin, Texas, Illinois and Kansas.

Table 19. STATE BY STATE PRODUCTION OF RUBBER GOODS^{1, 2, 4, 9}

State	Tire and tube production, millions of units/yr	Rubber and plastics footwear, ^a millions of units/yr	Rubber and plastic hose and belting, ^a Gg/yr
Alabama	31	11	12
Alaska	--	--	4
Arizona	--	--	4
Arkansas	4	6	4
California	33	2	20
Colorado	2	--	4
Connecticut	6	11	4
Delaware	--	--	--
Florida	--	5	4
Georgia	6	3	4
Hawaii	--	--	--
Idaho	--	--	1
Illinois	10	4	14
Indiana	7	3	1
Iowa	15	--	11
Kansas	11	--	11
Kentucky	8	3	4
Louisiana	1	6	4
Maine	1	17	8
Maryland	9	3	4
Massachusetts	15	14	8
Michigan	23	2	14
Minnesota	--	--	5
Mississippi	15	3	4
Missouri	--	2	11
Montana	--	--	4
Nebraska	--	--	5

^aEstimates.

Table 19 (continued). STATE BY STATE PRODUCTION OF RUBBER GOODS

State	Tire and tube production, millions of units/yr	Rubber and plastics footwear, ^a millions of units/yr	Rubber and plastic hose, ^a and belting, ^a Gg/yr
Nevada	--	--	2
New Hampshire	--	14	8
New Jersey	1	7	8
New Mexico	--	--	4
New York	1	7	16
North Carolina	6	6	8
North Dakota	--	--	--
Ohio	53	5	87
Oklahoma	2	6	5
Oregon	1	--	4
Pennsylvania	24	10	16
Rhode Island	--	8	4
South Carolina	2	3	4
South Dakota	--	--	--
Tennessee	24	11	8
Texas	12	6	9
Utah	--	--	2
Vermont	--	14	8
Virginia	4	5	4
Washington	1	1	4
West Virginia	--	3	4
Wisconsin	12	1	7
Wyoming	--	-	2
TOTALS	340	200	390

^aEstimates.

SECTION IV

EMISSIONS

A. LOCATIONS AND DESCRIPTIONS

Emissions from rubber processing plants are a function of the unit operations performed and the chemical substances used during processing. The materials emitted include particulates (carbon black, zinc oxide, soapstone, oil mists, etc.) and hydrocarbons (volatilized rubber chemicals, rubber impurities, etc.). These materials are emitted from the following unit operations: compounding, forming, building, and curing. The emissions from each of the unit operations, specifically for tire manufacturing are discussed below.

1. Compounding

The blending of ingredients used in rubber processing is performed in batchwise operations using rubber mills or internal (Banbury) mixers.¹⁶ These units typically handle 68 kg to 136 kg per hour of blended rubber stock. The ingredients which are compounded (blended) in this operation are:¹⁶

¹⁶Danielson, J. A. Air Pollution Engineering Manual, 2nd Edition. Air Pollution Control District, County of Los Angeles. U.S. Environmental Protection Agency, May 1973.

- Base polymer or blend
- Vulcanizing agents; e.g., sulfur, sulfur monochloride, selenium, tellurium
- Vulcanizing accelerators; e.g., aldehyde amines, guanidines, and thiuram sulfides
- Accelerator modifiers; e.g., activators and retarders
- Antidegradants; e.g., antioxidants, antiozonants, protective waxes, inhibitors of metal-catalyzed oxidation
- Reinforcing fillers; e.g., carbon blacks, minerals
- Processing aids; e.g., chemical peptisers for polymers, softeners, plasticizers, dispersing aids, tackifiers, Factice®, and lubricants
- Coloring agents, both organic and inorganic
- Diluents; e.g., inert mineral fillers, organic materials, extending oils
- Specific additives; e.g., blowing agents, fungicides, fibrous materials
- Reclaimed or vulcanized rubber

In the compounding operation, the various materials must be added in a specified order to provide the desired rubber stock physical properties. The rubber is added to the mixer first, followed by accelerators, plasticizers, reinforcing pigments, antioxidants, and any inert fillers or coloring agents. The vulcanizing agent is always added last to prevent vulcanization of the rubber during compounding. The order of addition of materials to the compounding unit determines the order in which materials are emitted.¹⁵

Emissions from compounding consist of particulates and hydrocarbons. The particulates are solids (carbon black, zinc oxide, soapstone, etc.) and liquid aerosols (organic additives).¹⁶ The hydrocarbon vapors originate from impurities in the rubber and from the organic additives. Particulate emissions occur when the additives are introduced into the batch. The resultant cloud has an opacity

of 5% to 50% (per EPA Method No. 9). This cloud persists for a few seconds to several minutes and the particulates have diameters less than 15 μ m. Hydrocarbon emissions occur as a result of the heat generated during the mechanical mixing of the batch.¹⁶

Compounding units are equipped with exhaust hoods that remove the heat generated by the mixing action. They also remove particulate and hydrocarbon emissions from the work area. Bag filters are employed to recover the solid particulates for recycle within the plant.¹⁶ where H₂

2. Curing

Curing (vulcanization) is a batch process for molded products (tires, mechanical goods, etc.) and can be a continuous process for extruded goods (sheets, strips, etc.). Curing temperatures typically range from 100°C to 200°C but may be as low as 25°C or as high as 300°C for specialized stocks and processes. Curing times typically range from 20 minutes to 60 minutes but can be several days. The time required for vulcanization is a function of temperature and stock thickness.¹⁷

Vulcanization temperatures (100°C to 200°C) result in the emission of organic materials from the rubber stock. Theoretically, these emissions can occur via two distinct mechanisms, which are: (1) the volatilization of species present in the stock; and (2) the formation of new com-

¹⁷Rappaport, S. M. The Identification of Effluents from Rubber Vulcanization. University of North Carolina. Chapel Hill. Ph.D. Thesis. 1974.

pounds by chemical reactions. In the case of tire manufacturing, it has been shown that the discharges are the result of volatilization rather than chemical reaction products.¹⁷ In addition, the emission of low boiling compounds (C₅ to C₈) has been shown to be one to two orders of magnitude greater than the discharge of high boiling compounds (C₁₀ and above).⁽¹⁷⁾ The materials volatilized, the source of each material in the stock, and the relative concentrations of the materials emitted are presented in Table 20. The raw data used to generate the relative concentrations for six of the compounds are presented in Table 21.

The available literature indicates that emissions occur primarily among ingredients which are either liquids at room temperature or solids with melting points at or below curing temperatures. On this basis, the possible species emitted can be determined as indicated below.¹⁷

(a) Polymer or Blend Volatiles - General purpose polymers do not decompose until pyrolysis temperatures (300°C to 400°C) are reached. Depolymerization reactions have been indicated only upon continued heating at 175°C to 225°C for several hours. Curing operations of much shorter duration result in little or no breakdown. Hence, polymer emissions will be the result of residual monomer and impurities from the manufacturing process and should represent less than 1% of total polymer by weight. However, monomers are sufficiently volatile that appreciable amounts may be lost in precuring operations such as milling and calendaring. Typical boiling points are 145°C for styrene, 78°C for acrylonitrile, and 59.4°C for chloroprene.

(b) Antioxidants and Antiozonants - In most cases, emissions of phenolic compounds are higher than those of amines. Total

Table 20. MATERIALS EMITTED DURING RUBBER VULCANIZATION¹⁷

Material emitted	Source in rubber stock	Relative concentration, ^a , ^b ppb by volume
Toluene	Polybutadiene rubber	1,120
4-Vinyl-1-cyclohexene	Polybutadiene rubber	71
Ethyl benzene	Aromatic oil extender	78
<u>m</u> -Xylene	Aromatic oil extender	(35)
<u>p</u> -Xylene	Aromatic oil extender	(35)
Styrene	Styrene-butadiene rubber	84
<u>t</u> -Butylisothiocyanate		(90)
1,5-Cyclooctadiene	Polybutadiene rubber	6.3
Benzothiazole	Accelerator	(80)
<u>N</u> -sec-butylaniline	Antiozonant	(30)
1,5,9-Cyclododecatriene	Polybutadiene rubber	15.8
Methyl naphthalenes	Aromatic oil extender	(90)
Butadiene trimer	Polybutadiene rubber	(15)
Ethyl naphthalene	Aromatic oil extender	(10)
Dimethyl naphthalene	Aromatic oil extender	(10)
Diphenyl guanidine	Accelerator	(100)

^a Relative concentrations were obtained by sampling the atmosphere within the curing room. The values reported indicate concentrations of the individual compounds within the curing room.

^b Parentheses around data indicate estimates of concentrations made by Monsanto Research Corporation from Rappaport's published raw data.

Table 21 CURING CONCENTRATIONS OF SELECTED COMPOUNDS^{a,17}

Compound	Concentrations for each measurement, ppb by volume									Mean	Standard deviation	Relative error, %
	1	2	3	4	5	6	7	8	9			
Toluene	1,500	1,290	1,190	887	927	1,530	1,249	832	660	1,120	301	20.7
4-Vinyl-1-cyclohexene	84.5	97.7	66.1	56.0	70.6	77.7	71.6	60.6	54.4	71.0	8.42	9.1
Ethyl benzene	81.6	126	69.0	53.4	82.8	90.0	96.6	60.5	53.8	73.2	22.7	22.3
Styrene	96.3	130	79.4	61.5	83.22	86.7	95.6	67.5	61.6	84.6	21.5	19.5
1,5-Cyclooctadiene	8.19	7.71	5.95	4.88	7.08	6.39	7.37	4.61	4.27	6.27	1.44	17.7
1,5,9-Cyclododecatriene	8.68	8.64	5.68	5.86	8.37	7.13	9.22	5.61	5.70	7.21	1.52	16.2

^a All samples were collected in the center of the passenger tire curing area.

emissions are greater in black stocks than in gum. The total emissions from curing molds may range as high as 5% to 20% for thin stocks and the more volatile antidegradants. However, normal vaporization losses amount to only 0.5% to 1.0% by weight of the antidegradant present in the stock. The melting points of the common antioxidants are given in Table 22.

Table 22. MELTING POINTS OF COMMON ANTIOXIDANTS

Antioxidant type	Compound	m.p., °C
Phenol	2,6-Di- <u>t</u> -butyl-4-methylphenol	69 to 70
"	2,4-Di- <u>t</u> -amylphenol	Liquid
"	3- <u>t</u> -Butyl-4-hydroxyanisole	Liquid
"	2,2'-Methylen-bis(4-methyl-6- <u>t</u> -butyl phenol)	125 to 130
Amine	Phenyl- β -naphthylamine	105 to 106
"	<u>N</u> - <u>N</u> '-diphenyl- <u>p</u> -phenylenediamine	144 to 152
"	<u>N</u> - <u>N</u> '-diphenylethylenediamine	60 to 65

(c) Accelerators - As with the antidegradants, the common accelerators have melting points between 70°C and 200°C. Hence, emissions of these components are to be expected at normal curing temperatures. Average total emissions of 0.5% to 1.0% by weight of accelerator present can be anticipated.¹⁸ The melting points of the common accelerators are given in Table 23.

¹⁸Angert, I. G., et al. Volatilization of Phenyl-2-Naphthylamine from Rubber, Rubber Chemistry and Technology, 34:807, July-September 1961.

Table 23. MELTING POINTS OF COMMON ACCELERATORS

Accelerator type	Compound	m.p., °C
Dithiocarbamate	Zinc diethyldithiocarbamate	171 to 180
"	Zinc dibutyldithiocarbamate	98 to 108
"	Sodium dibutyldithiocarbamate	liquid
"	Selenium dimethyldithiocarbamate	140 to 172
Thiuram	Tetramethylthiuram monosulfide	103 to 108
"	Tetramethylthiuram disulfide	140 to 148
"	Tetraethylthiuram disulfide	62 to 75
Sulfenamide	<u>N,N</u> -diethyl-2-benzothiazylsulfenamide	liquid
"	<u>N</u> -cyclohexyl-2-benzothiazylsulfenamide	93 to 108
"	<u>N</u> -oxydiethylene-2-benzothiazylsulfenamide	70 to 90
Thiazole	2-Mercaptobenzothiazole	164 to 176
"	Benzothiazyl disulfide	160 to 176
"	2-Benzothiazyl- <u>N,N</u> -diethylthiocarbamylsulfide	69
Guanidine	Diphenylguanidine	145 to 147
"	Di- <u>o</u> -tolylguanidine	167 to 173

(d) Processing Aids, Diluents - Processing aids are generally in the form of oils, usually paraffinic, and function as lubricants, plasticizers, and softeners. Diluents are primarily aromatic extender oils used to improve overall performance of synthetic rubbers. Volatilization from these mixtures is expected to vary considerably depending on their composition. Available data show that the total emissions in 3 hours at 167°C range from 0.05% to 1.0% by weight.¹⁹

(e) Miscellaneous Compounding Ingredients - The materials in this category which are most likely to be volatilized are the vulcanizing agents and retarders. These substances include amines, esters, and organic acids, most of which are either liquids at room temperature or solids with melting points between 70°C and 200°C. Emissions of the order of 1% by weight can be expected.

In nearly all cases, the materials used in rubber blends are of technical grade. Hence, the purity of the principal component is low (60% to 95%), and some of the impurities will be sufficiently volatile to be emitted during curing. The wide melting point ranges of many of the compounds given above are indicative of high impurity levels. Gas chromatographic analysis of commercial antioxidants has confirmed the high impurity levels in these compounds.²⁰ As a result, there are hundreds of compounds which may be emitted in trace amounts during the curing operation.

¹⁹Duke, J., et al. Oil Types in the Program for Oil Extended Rubber. Industrial and Engineering Chemistry. 47:1077, May 1955.

²⁰Caeta, L. J., et al. Antioxidant Analysis. Rubber Age. 101:47, March 1967.

(f) Volatilized Components - The volatilization of components from rubber stock during cure has been shown to follow the theoretical equation:¹⁸

$$C = C_0 (1 - e^{-mt/R}) \quad (1)$$

where C = amount of component lost in time t, percent by weight of rubber

C_0 = initial weight percent of component

m = a constant which depends on the diffusion coefficient of the species at the curing temperature

R = thickness of rubber stock

t = time

Thus, physical losses of particular ingredients are related exponentially to the temperature and duration of cure, stock thickness, and individual diffusion coefficients.

G. G. Winspear used Equation 1 to estimate the loss of various components from two typical tread stocks, black sidewalls, and white sidewalls.¹⁵ The formulations for each of the tire parts used to calculate the loss of materials from typical tires are given in Tables 24, 25 and 26 (tire tread, black sidewall and white sidewall, respectively). Table 27 defines the commercial ingredients of the various formulations. The estimated emission factors using Equation 1 and Tables 24-26 are presented in Table 28 which lists the emission factors by material emitted for each tire part with the source of the material identified by ingredient.

Table 28 shows that the total amount of volatile material released is between 5 g/kg and 7 g/kg, or 0.5% to 0.7% by weight, or 50 to 70 grams per tire. Of this amount, 90%

Low 15,000 tires/day
50 g./tire

750,000 g./day
750 kg/day (1.30 lb/day)
6.75 tons/day (0.26 tons/day)

High 15,000 tires/day
70 g./tire

83

1,050,000 g./day
1,050 kg/day (2.30 lb/day)
1.05 tons/day (1.15 tons/day)

Table 24. PASSENGER TIRE TREAD FORMULATIONS¹³

Ingredient	Rubber type			
	Natural rubber		SBR/ <u>cis</u> -Polybutadiene	
	Parts by weight	Weight, %	Parts by weight	Weight, %
Smoked sheet	100	44.8	-	-
SBR 1712	-	-	103.1	66.3
<u>cis</u> -Polybutadiene	-	-	25	16.1
REOGEN	2	0.9	-	-
K-STAY G	-	-	5	3.2
Stearic acid	2.5	1.1	2	1.3
Zinc oxide	3.5	1.6	3	1.9
AGERITE RESIN D	1.5	0.7	1.5	1.0
AGERITE HP	0.5	0.2	0.5	0.3
ANTOZITE 67 S	4	1.8	4	2.6
Microcrystalline wax	1	0.5	1	0.6
Philrich 5	5	2.2	7	4.5
HAF	50	22.4	-	-
ISAF	50	22.4	-	-
Sulfur	2.5	1.2	1.8	1.2
AMAX NO. 1	-	-	1.5	1.0
REDAX	0.5	0.2	-	-
Totals	223.0	100.0	155.4	100.0

Table 25. PASSENGER TIRE FORMULATIONS FOR BLACK SIDEWALLS¹⁸

Ingredient	Rubber type			
	Natural rubber		SBR	
	Parts by weight	Weight, %	Parts by weight	Weight, %
Smoked sheet	100	55.6	-	-
SBR 1500	-	-	50	25.8
SBR 1712	-	-	50	25.8
REOGEN	1	0.6	1	0.5
Stearic acid	3	1.7	1.5	0.8
Zinc oxide	5	2.8	3	1.6
ANTOZITE 67 S	4	2.2	4	2.1
Microcrystalline wax	1.8	1.0	2	1.0
AGERITE SUPERFLEX SOLID	2	1.1	2	1.0
Philrich 5	-	-	12	6.2
THERMAX	10	5.6	-	-
GPF Black	50	27.7	65	33.6
Sulfur	2.5	1.4	2.1	1.1
AMAX	0.5	0.3	1.1	0.5
Totals	179.8	100.0	193.7	100.0

Table 26. PASSENGER TIRE FORMULATIONS FOR WHITE SIDEWALLS¹⁸

Ingredient	Rubber type			
	Natural rubber/ neoprene/hypalon		Natural rubber/ SBR	
	Parts by weight	Weight, %	Parts by weight	Weight, %
High modulus crepe	40	20.1	70	37.7
Neoprene W	40	20.1	-	-
Hypalon 20	20	10.0	-	-
SBR 1502	-	-	30	16.1
Stearic acid	1	0.5	1.5	0.8
Zinc oxide	35	17.6	20	10.8
AGERITE SUPERLITE	1.5	0.8	1.5	0.8
Titanium dioxide	40	20.1	37	19.9
Whiting (ppt)	7.5	-	7.5	-
McNamee clay	4	2.0	20	10.8
Light process oil	15	7.5	1	0.5
Ultramarine blue	0.3	0.1	0.3	0.2
Sulfur	1.3	0.7	2.8	1.5
ALTAX	0.9	0.4	1.5	0.8
METHYL TUADS	0.3	0.1	-	-
Diphenyl guanidine	-	-	0.2	0.1
Totals	199.3	100.0	185.8	100.0

Table 27. DEFINITIONS OF COMMERCIAL INGREDIENTS¹⁸

Ingredient	Definition
REOGEN	A mixture of an oil soluble sulfonic acid of high molecular weight with a high boiling alcohol and a paraffin oil. Used as a peptizing agent and strong plasticizer for all elastomers. Functions as a scorch retarder.
K-STAY G	Mixtures of an oil soluble sulfonic acid of high molecular weight and selected petroleum base oils.
AGERITE RESIN D	Polymerized 1,2-dihydro-2,2,4-tetramethyl-quinoline antioxidant, melting point = 74°C minimum.
AGERITE HP	A blend of approximately 65 parts phenyl- β -naphthylamine and approximately 35 parts of diphenyl-p-phenylenediamine antioxidants, melting range = 89-96°C.
ANTOZITE 67 S	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene-diamine antiozonant, 50% active, semi-liquid.
HAF	High abrasion furnace black.
ISAF	Furnace black.
AMAX	N-oxydiethylene benzothiazole-2-sulfenamide accelerator, melting range = 70-80°C.
AMAX NO. 1	AMAX plus a percentage of benzothiazyl disulfide (MBTS).
REDAX	N-nitrosodiphenylamine retarder, melting range = 63-68°C.
Philrich 5	Aromatic petroleum oil, extender and plasticizer.
AGERITE SUPER-FLEX SOLID	A diphenylamine-acetone reaction product, 75% active antioxidant.
THERMAX	Medium thermal carbon.
ALTAX	Benzothiazyl disulfide (MBTS), melting range = 159-170°C.
METHYL TUADS	Tetramethylthiuram disulfide (TMTD), melting range = 142-156°C.

Table 28. ESTIMATED EMISSIONS OF VOLATILE COMPOUNDS FROM HYPOTHETICAL PASSENGER TIRE WITH
10 kg COMBINED WEIGHT OF TREAD AND SIDEWALL STOCKS¹⁹

Tread = 9 kg; Sidewalls = 1 kg

Ingredient	Emission factors, g/kg					
	Tire tread		White sidewall		Black sidewall	
	Natural rubber	SBR/cis-Polybutadiene	Natural rubber/neoprene/hypalon	Natural rubber/SBR	Natural rubber	SBR
Polymer						
Smoked sheet	5.19				0.55	
SBR 1712		4.12				0.26
High modulus crepe			0.19	0.36		
Polybutadiene		1.02				
Neoprene W			0.19			
Hypalon 20			0.01			
SBR 1500						0.26
SBR 1502				0.16		
Antidegradant						
AGERITE PESIN D	0.08	0.06				
AGERITE HP	0.03	0.02				
AGERITE SUPERLITE			0.005	0.003		
AGERITE S.S.					0.01	0.01
ANTOZITE 67 S	0.21	0.16			0.02	0.02
Accelerator						
AMAX NO. 1	0.03					
AMAX		0.06			0.002	0.006
ALTAX			0.004	0.008		
METHYL TUADS			0.001			
DPG				0.001		
Oil						
Philrich 5	0.26	0.29				0.06
Light process			0.07	0.005		
Miscellaneous						
REOGEN	0.11				0.006	0.005
K-STAY-G		0.21				
REDAX	0.03					
Totals	5.94	5.94	0.470	0.542	0.588	0.621
Average	5.94		0.505		0.605	
Percent of total	84.2		7.2		8.6	

is derived from the polymer blend. Antidegradants contribute approximately 5% to the losses and accelerators roughly 1%. Note that synthetic rubbers discharge approximately three times as much accelerator as does natural rubber. The remaining 3% of the emissions stem from a mixture of oils and special additive ingredients.¹⁷

To appreciate the number of emitted materials represented by this 50 to 70 grams per tire, the following assessment might be helpful. Each of the two stocks per tire considered are assumed to contain an average of 10 ingredients which could be volatilized. Rappaport states that since technical grade ingredients are used, there are as many as 1000 different compounds which may conceivably be released.¹⁷

Since rubber vulcanization is performed over a range of processing temperatures, Rappaport measured the total loss of hydrocarbons from tread stock during vulcanization. His experiments were performed on 6.4 mm thick tread stock at curing temperatures ranging from 160°C to 200°C and a curing time of 20 minutes. Table 29 summarizes the tire formulation used in Rappaport's research. Table 30 summarizes the results he obtained and the empirical correlation presented below shows the loss of volatile hydrocarbons as a function of temperature:¹⁷

$$C = 0.00212 T - 0.15328 \quad (2)$$

where C = amount of total hydrocarbon lost, weight
fraction of rubber

T = curing temperature, °C

Table 29. TREAD STOCK FORMULATION USED BY RAPPAPORT¹⁷

Ingredient	Weight percent (approximate)
Polymer	
Styrene-butadiene rubber (1)	25
Styrene-butadiene rubber (2)	25
Polybutadiene(<u>cis</u>) rubber	10
Antidegradant	
<u>N</u> -phenyl- <u>N</u> - <u>sec</u> -butyl- <u>p</u> -phenylenediamine	0.5
Accelerator	
<u>N</u> - <u>t</u> -butyl-2-benzothiozole sulfenamides	0.5
Diphenyl guanidine	0.1
Carbon black	
Furnace black	30
Oil	
Aromatic ^a	20
Miscellaneous	
Sulfur	0.5
Activated zinc oxide	0.5
Stearic acid	0.5
Sunproof wax	0.5
Total	113

^a Since some oil is used to extend styrene-butadiene rubbers, the figures shown here are the total weight percent for all oils; this brings the total to 113%.

Table 30. VOLATILIZATION OF GREEN TREAD STOCK DURING
VULCANIZATION AT TEMPERATURES BETWEEN
160°C and 200°C¹⁷

Vulcanization temperature, °C	Weight loss, %	Total hydrocarbon emission factor, ^a g/kg
160	0.189	1.89
170	0.196	1.96
160	0.176	1.76
180	0.268	2.68
190	0.259	2.59
190	0.232	2.32
170	0.201	2.01
160	0.195	1.95
200	0.261	2.61
180	0.235	2.35
170	0.202	2.02
170	0.204	2.04
200	0.273	2.73
180	0.231	2.31

^aStatistical analysis of total hydrocarbon emission factors
for temperatures ranging from 160°C to 200°C:

mean = 2.23 g/kg

standard deviation = 0.32 g/kg

relative error = 0.19 g/kg or 8.41%

3. Under Tread Cementing

Under tread cementing, which is one of the forming operations, is a spreading operation used to apply a glue or cement to the underside of a tire tread to facilitate its application to the green tire. Solvent is used as the vehicle for application of the glue. The solvents used evaporate and become hydrocarbon emissions within the tire plant.²¹

Van Lierop and Kolika have published data on the measurement of hydrocarbons from an under cementing operation.²¹ The solvent used as the vehicle in these studies was Texol®, a low-boiling naphtha type of solvent. The amount of solvent (as C₆) which evaporates from under tread cementing was measured as 83 g/m². This amounts to 23 g/tire assuming that the average tire tread has a cemented surface area of 0.28 m². A total of 8 tests was performed to obtain this emission factor which has a standard deviation of 7.8 g/m². These data can be manipulated to yield an emission factor of 1.88 g/kg by assuming that the average tire weighs 12.25 kg.

4. Green Tire Spraying

Green tire spraying, which is one of the building operations, utilizes two distinct solvent based sprays (one internally and one externally) to act as mold release agents and rubber flow promoters during cure.²¹ The solvents used in this operation evaporate both inside and outside of the spray booth used.

²¹Van Lierop, G., et al. Measurement of Hydrocarbon Emissions and Process Ventilation Requirements at a Tire Plant. Armstrong Rubber Co. (Paper presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston. June 15-20, 1975.) 23 p.

Van Lierop and Kalika published emissions data on the solvent evaporation from green tire spray operations. The solvent used was Texol, a low-boiling naphtha. The amount of solvent (as C₅) which evaporates from green tire spraying was found to be 0.14 kg/tire which corresponds to 11.4 g/kg, assuming the average tire weighs 12.25 kg. Average solvent consumption is 0.15 kg/tire which shows that 88% of the solvent applied to green tires evaporates from the tire. The fugitive emissions (i.e., those to the workroom) accounted for 27% to 35% of the total hydrocarbon emissions.

5. Other Processing Emission Points

Other emission points within the tire plant that result from rubber processing are calendering and extrusion operations. The mechanical work performed on the rubber compound in these operations generates a considerable amount of heat. The materials emitted during such operations are similar to the hydrocarbons from compounding operations.²¹

B. EMISSION FACTORS

The quantities of materials emitted per unit of rubber processed have been reported by several authors as discussed in Section IV.A. Table 31 is a compilation of the information gathered from the literature and contains information from only those articles that present emission factors or data that could be used to calculate emission factors. (Blanks in Table 31 indicate that the particular data are not reported in the cited references, while dashes indicate no emissions of the criteria pollutant for the operation.)

The emission factors presented in Tables 32 and 33 were obtained by sampling a representative tire manufacturing

Table 31. SUMMARY OF EMISSIONS DATA REPORTED IN THE LITERATURE FOR RUBBER PROCESSING

Processing step	Criteria pollutant emission factor, ^a g/kg				
	Particulates	Sulfur oxides	Nitrogen oxides	Hydrocarbons	Carbon monoxide
Compounding		-	-		-
Curing	-	-	-	7.05	-
Calendering	-	-	-		-
Extrusion	-	-	-		-
Under tread cementing	-	-	-	1.88	-
Green tire spraying	-	-	-	11.4	-
Whole incineration					
Totals					

^aBlanks in the above table indicate that specific data are not reported in the cited references; dashes (-) indicate no emissions of the criteria pollutant for the processing step.

Table 32. EMISSION FACTORS FOR COMPOUNDING IN A TIRE PLANT

Material emitted	Emission factors, ^a	
	kg/tire	g/kg ^a
Particulates		
Carbon black		
Zinc oxide		
Sulfur		
Others		
Hydrocarbons		
Toluene		
4-Vinyl-1-cyclohexene		
Ethyl benzene		
Styrene		
1,5-Cyclooctadiene		
1,5,9-Cyclododecatriene		
m-Xylene		
p-Xylene		
t-Butylisothiocyanate		
Benzothiazole		
N-sec-butylaniline		
Methyl naphthalenes		
Butadiene trimer		
Ethyl naphthalene		
Dimethyl naphthalene		
Diphenyl guanidine		
Others		

^aAssuming the average tire weighs 12.25 kg.

Table 33. EMISSION FACTORS FOR CURING IN A TIRE PLANT

Material emitted	Emission factors,	
	kg/tire	g/kg
Hydrocarbons		
Toluene		
4-Vinyl-1-cyclohexene		
Ethyl benzene		
Styrene		
1,5-Cyclooctadiene		
1,5,9-Cyclododecatriene		
m-Xylene		
p-Xylene		
t-Butylisothiocyanate		
Benzothiazole		
N-sec-butylaniline		
Methyl naphthalenes		
Butadiene trimer		
Ethyl naphthalene		
Dimethyl naphthalene		
Diphenyl guanidine		
Others		

plant. These data were used to calculate the ground level concentrations, mass emissions, and affected population in Section IV.D.

C. DEFINITION OF A REPRESENTATIVE SOURCE

In order to determine the source severity, which is described in Section IV.D., a representative source for rubber processing was defined as follows:

- 1) The representative source is limited to the manufacture of tires since this area of rubber processing constitutes 66% of the industry. The emissions from other branches of the industry will be the same in materials emitted and approximately the same in mass of emissions because the emissions are a function of the rate of volatilization of ingredients used in the rubber (Section IV.A.).
- 2) The plant capacity for this representative source is the mean production capacity of all tire plants, which is 1.7 million units per year. (See Section III.C.) Assuming that the average tire weighs 12.25 kg, the mean plant capacity also equals 20.1 Gg.
- 3) The composition of the representative tire is given in Tables 24, 25 and 26.
- 4) The representative source is located in the state with the largest number of plants; i.e., Ohio (Section III.C.).

Table 34. MAXIMUM GROUND LEVEL CONCENTRATIONS OF DIFFERENT EMISSIONS
FROM RUBBER PROCESSING^a

Material emitted	Mass emission rate, g/sec	X _{max} ['] µg/m ³	TLV, mg/m ³	Ambient air quality standard, mg/m ³
Criteria pollutants				
Particulates			10	0.26 ^b
Hydrocarbons	1.36	310	NA	0.16 ^c
Sulfur oxides			13	0.365 ^d
Nitrogen oxides			9	0.1 ^e
Carbon monoxide			55	40 ^f
Chemical substances				
Carbon black			3.5	NA ^g
Soapstone			6.7	NA
Zinc oxide			5	NA
Toluene	0.39	88	375	NA
4-Vinyl-1-cyclohexene	0.02	4.5	NA	NA
Ethyl benzene	0.03	6.8	435	NA
Styrene	0.03	6.8	420	NA
1,5-Cyclooctadiene	0.002	0.45	NA	NA
1,5,9-Cyclododecatriene	0.003	0.68	NA	NA
Naphtha	0.89	200	400	NA
Others				

^a Calculations based on estimated emission.

^b 24-Hour average.

^c 3-Hour average.

^d 24-Hour average.

^e Annual average.

^f 1-Hour average.

^g NA - not applicable.

where Q_{in} = mass emission rate, g/sec
 \bar{u} = average wind speed = 4.5 m/sec
 H = average height of emissions = 15.2 m
 $e = 2.72$
 $\pi = 3.14159$

2. Severity Factor

To obtain an indication of the health hazard potential of the emission source, a severity factor, S , was defined as:

$$S = \frac{\bar{x}_{max}}{F} \quad (4)$$

where \bar{x}_{max} = time-averaged maximum ground level concentration

F = hazard factor; equal to the primary air quality standard for particulate, sulfur oxides, nitrogen oxides, carbon monoxide and hydrocarbons, and equal to $TLV \times 8/24 \times 1/100$ for all chemical substances

This severity factor represents the ratio of the time-averaged maximum ground level exposure to the potential hazard level of exposure for an emitted material.

x_{max} was calculated using the formula:

$$\bar{x}_{max} = x_{max} \left(\frac{t_{max}}{t_1} \right)^{0.17} \quad (5)$$

where $t_{max} = 3$ minutes

t_1 = appropriate averaging time, minutes

The appropriate averaging time was 24 hours for all other pollutants.

For particulate, sulfur oxides, nitrogen oxides, carbon monoxide and hydrocarbons, the averaging times are the same as those used in the primary ambient air quality standards.

\bar{x}_{\max} and severity factors for each material emitted from the representative rubber processing plant are presented in Table 35. [These calculations were based on emission factors obtained from the literature and do not necessarily represent the values that might be obtained from a sampling program.]

3. Contribution to Total Air Emissions

The contribution of rubber processing to statewide and nationwide air emissions was measured by the ratio of mass emissions from this source to the total emissions from all sources.

The mass emissions of hydrocarbons and particulates resulting from rubber processing were calculated by multiplying the emission factors by the total processing done in the state. The mass emission for each pollutant is shown in Table 36 for the states where rubber processing is performed, along with the nationwide emissions. [There are no figures for sulfur oxides, carbon monoxide, and nitrogen oxides in Table 36 because the emission of these from rubber processing is presently unknown.]

Table 37 gives the ratios of hydrocarbon and particulate emissions resulting from rubber processing to the total emissions of these materials in each corresponding state and the nation. The total pollutant emissions for each state were obtained from the 1972 National Emission Report. On a nationwide basis, the emissions from rubber processing constitute 0.3% or more of the total hydrocarbon emissions.

Table 35. TIME-AVERAGED MAXIMUM GROUND LEVEL CONCENTRATIONS
AND SEVERITY FACTORS FOR EMISSIONS
FROM RUBBER PROCESSING

Material emitted	\bar{x}_{\max} , $\mu\text{g}/\text{m}^3$	Severity factor, S
Criteria pollutants		
Particulates	190	1.2
Hydrocarbons		
Sulfur oxides		
Nitrogen oxides		
Carbon monoxide		
Chemical substances		
Carbon black	31	0.087
Soapstone		
Zinc oxide		
Toluene		
4-Vinyl-1-cyclohexene		
Ethyl benzene		
Styrene		
1,5-Cyclooctadiene		
1,5,9-Cyclododecatriene		
Naphtha		
Others	70	0.018

^a Indeterminate, since TLV for species has not been established.

Table 36. TOTAL EMISSIONS OF HYDROCARBONS AND
PARTICULATES RESULTING FROM RUBBER
PROCESSING OPERATIONS BY STATE

State	Hydrocarbons, Cg/yr	Particulates, Mg/yr
Alabama	7.7	
Alaska	-	
Arizona	-	
Arkansas	1.0	
California	8.2	
Colorado	0.5	
Connecticut	1.5	
Delaware	-	
Florida	-	
Georgia	1.5	
Hawaii	-	
Idaho	-	
Illinois	2.5	
Indiana	1.7	
Iowa	3.7	
Kansas	2.7	
Kentucky	2.0	
Louisiana	0.25	
Maine	0.25	
Maryland	2.2	
Massachusetts	3.7	
Michigan	5.7	
Minnesota	-	
Mississippi	3.7	
Missouri	-	
Montana	-	
Nebraska	-	
Nevada	-	
New Hampshire	-	

Table 36 (continued). TOTAL EMISSIONS OF HYDROCARBONS AND
PARTICULATES RESULTING FROM RUBBER
PROCESSING OPERATIONS BY STATE

State	Hydrocarbons, Gg/yr	Particulates, Mg/yr
New Jersey	0.25	
New Mexico	-	
New York	0.25	
North Carolina	1.5	
North Dakota	-	
Ohio	13.0	
Oklahoma	0.5	
Oregon	0.25	
Pennsylvania	6.0	
Rhode Island	-	
South Carolina	0.5	
South Dakota	-	
Tennessee	6.0	
Texas	3.0	
Utah	-	
Vermont	-	
Virginia	1.0	
Washington	0.25	
West Virginia	-	
Wisconsin	3.0	
Wyoming	-	
U.S. Totals	84.3	

Table 37. PERCENT CONTRIBUTION OF EMISSIONS OF
HYDROCARBONS AND PARTICULATES FROM RUBBER
PROCESSING TO CORRESPONDING STATE
EMISSIONS FROM POINT SOURCES

State	Hydrocarbons	Particulates
Alabama	1.2	
Alaska	-	
Arizona	-	
Arkansas	0.51	
California	0.38	
Colorado	0.26	
Connecticut	0.68	
Delaware	-	
Florida	-	
Georgia	0.33	
Hawaii	-	
Idaho	-	
Illinois	0.14	
Indiana	0.12	
Iowa	1.2	
Kansas	0.87	
Kentucky	0.61	
Louisiana	0.01	
Maine	0.20	
Maryland	0.74	
Massachusetts	0.84	
Michigan	0.79	
Minnesota	-	
Mississippi	1.89	
Missouri	-	
Montana	-	
Nebraska	-	
Nevada	-	
New Hampshire	-	

Table 37 (continued). PERCENT CONTRIBUTION OF EMISSIONS OF
HYDROCARBONS AND PARTICULATES FROM RUBBER
PROCESSING TO CORRESPONDING STATE
EMISSIONS FROM POINT SOURCES

State	Hydrocarbons	Particulates
New Jersey	0.03	
New Mexico	-	
New York	0.02	
North Carolina	0.34	
North Dakota	-	
Ohio	1.13	
Oklahoma	0.15	
Oregon	0.11	
Pennsylvania	0.67	
Rhode Island	-	
South Carolina	0.06	
South Dakota	-	
Tennessee	1.65	
Texas	0.14	
Utah	-	
Vermont	-	
Virginia	0.27	
Washington	0.07	
West Virginia	-	
Wisconsin	0.57	
Wyoming	-	
U.S. Totals	0.34	

4. Population Exposed to High Pollutant Concentrations

To obtain a quantitative evaluation of the population influenced by a high concentration of emissions resulting from a typical rubber processing plant, the areas exposed to the time-averaged ground level concentration, \bar{x} , for which $\bar{x}/F \geq 1$ and $\bar{x}/F \geq 0.1$ were obtained by determining the area within the isopleth for \bar{x} , and the number of people within the exposed area was then calculated by using a proper population density.

The representative population density used in the calculation of affected population was the average state population density, weighted by the amount of rubber processing in each state. For each of the pollutants with a severity factor greater than or equal to 1, the area and population exposed to a time-averaged ground level concentration for which $\bar{x}/F \geq 1$ and $\bar{x}/F \geq 0.1$ are shown in Table 38. For each of the pollutants with $0.1 < S < 1$, numbers are shown only for $\bar{x}/F \geq 0.1$. In addition to the average exposed population, two extreme cases were also examined and these are listed in the same table.

It can be seen from Table 38 that for the average case, the population influenced by high ground level concentration is _____ for the pollutants with $S > 0.1$. [However, it should be noted again that there may be some other compounds emitted but not reported in the literature.]

Table 38. AREA AND POPULATION EXPOSED TO POLLUTANTS FOR WHICH
 $\bar{X}/F \geq 1$ AND $\bar{X}/F \geq 0.1$ ^a

Pollutant	Affected area, km ²		Exposed population					
			Best case		Worst case		Average	
	$\bar{X}/F \geq 1$	$\bar{X}/F \geq 0.1$	$\bar{X}/F \geq 1$	$\bar{X}/F \geq 0.1$	$\bar{X}/F \geq 1$	$\bar{X}/F \geq 0.1$	$\bar{X}/F \geq 1$	$\bar{X}/F \geq 0.1$
Hydrocarbons								
Particulates								
Others								

^aBased on assumed emission factors.

SECTION V

CONTROL TECHNOLOGY

Emissions from the rubber processing industry consist of hydrocarbons and particulates. Each type has its own control technology.

A. HYDROCARBONS

1. Adsorption

Adsorption is the process for removing molecules from a fluid by contacting them with a solid. Gases, liquids, or solids can be selectively removed from airstreams with materials known as adsorbents. The material which adheres to the adsorbent is called the adsorbate.²²

The mechanism by which components are adsorbed is complex, and although adsorption occurs at all solid interfaces, it is minimal unless the adsorbent has a large surface area, is porous, and possesses capillaries. The important characteristics of solid adsorbents are their large surface-to-volume ratio and preferential affinity for individual components.²²

²²Hughes, T. W., et al. Source Assessment: Prioritization of Air Pollution for Industrial Surface Coating Operations. EPA-650/2-75-019-a, Contract No. 68-02-1320 (Task 14). February 1975.

The adsorption process includes three steps. The adsorbent is first contacted with the fluid, and adsorption results. Second, the unadsorbed portion of the fluid is separated from the adsorbent. For gases, this operation is completed when the gases leave the adsorbent bed. Third, the adsorbent is regenerated by removal of the adsorbate. Low pressure steam is used to regenerate the adsorbent, and the condensed vapors are separated from the water by decantation, distillation, or both.²²

Activated carbon is capable of adsorbing 95% to 98% of the organic vapor from air at ambient temperature in the presence of water in the gas stream.²³ Because the adsorbed compounds have low vapor pressure at ambient temperatures, the recovery of organic materials present in air in small concentrations is low. The adsorption system can be operated without hazard because the vapor concentration is below the flammable range.²²

When an organic vapor in air mixture starts to pass over activated carbon complete adsorption of the organic vapor takes place. As the adsorptive capacity of the activated carbon is approached, traces of vapor appear in the exit air, indicating that the breakpoint of the activated carbon has been reached. As the air flow is continued, and although additional amounts of organic materials are adsorbed, the concentration of organic vapor in the exit air continues to increase until it equals that in the inlet air. The adsorbent is saturated under these operating conditions.²²

²³Hydrocarbon Pollutant System's Study. Vol. I. Stationary Sources, Effects, and Control. MSA Research Corporation. (PB-219 073.) October 1972.

The adsorption of a mixture of adsorbable organic vapors in air is not uniform, and the more easily adsorbed components are those with the higher boiling points. When air containing a mixture of organic vapors is passed over activated carbon, the vapors are equally adsorbed at the start. However, as the amount of the higher boiling component in the adsorbent increases, the more volatile component revaporizes. The exit vapor consists primarily of the more volatile component after the breakpoint has been reached. This process continues for each organic mixture component, until the highest boiling component is present in the exit gas. In the control of organic vapor mixtures, the adsorption cycle should be stopped when the first breakpoint occurs as determined by detection of vapors in the exit gas. Many theories have been advanced to explain the selective adsorption of certain vapors or gases. These theories are presented in Perry and Chilton²⁴ and will not be discussed here.

The quantities of organic vapors adsorbed by activated carbon are a function of the particular vapor in question, the adsorbent, the adsorbent temperature, and the vapor concentration. Removal of gaseous vapors by physical adsorption is practical for gases with molecular weight over 45.²⁴ Each type of activated carbon has its own adsorbent properties for a given vapor and the quantity of vapor adsorbed for a particular vapor concentration in the gas and at a particular temperature is best determined experimentally. The quantity of vapor adsorbed increases when the vapor concentration increases and the adsorbent temperature decreases.²²

²⁴Perry, J. H., and C. H. Chilton. Chemical Engineers' Handbook. New York, McGraw-Hill, 1973.

After breakthrough has occurred, the adsorbent is regenerated by heating the solids until the adsorbate has been removed. A carrier gas must also be used to remove the vapors released. Low-pressure saturated steam is used as the heat source for activated carbon and also acts as the carrier gas. Superheated steam at 350°C may be necessary to remove high boiling compounds and return the carbon to its original condition when high boiling compounds have reduced the carbon capacity to the point where complete regeneration is necessary.²²

Steam requirements for regeneration are a function of external heat losses and the nature of the organic material. The amount of steam adsorbed per kilogram of adsorbate, as a function of elapsed time, passes through a minimum. The carbon should be regenerated for this length of time to permit the minimum use of steam.²⁴ After regeneration, the carbon is hot and saturated with water. Cooling and drying are done by blowing organic-free air through the carbon bed. Evaporation of the water aids cooling of the carbon. If high temperature steam has been used, other means of cooling the carbon are required.

Fixed bed adsorbers arrayed in two or more parallel bed arrangements are used to remove organic vapors from air (See Figure 6). These are batch-type arrangements, where a bed is used until breakthrough occurs and is then regenerated. The simplest adsorber design of this type is a two bed system where one carbon bed is being regenerated as the other is adsorbing organic vapors. In a three bed arrangement a greater quantity of material can be adsorbed per unit of carbon because the effluent passes through two beds in series while the third bed is being regenerated. This permits the activated carbon to be used after breakthrough since the second bed in the series removes organic vapors

in the exit gas from first bed. When the first bed is saturated, it is removed from the stream for regeneration; the bed which was used to remove the final traces of organic vapors from the effluent then becomes the new first bed; and the bed which has been regenerated becomes the new second bed.²²

Heat is released in the adsorption process, which causes the temperature of the adsorbent to increase. If the concentration of organic vapors is not high, as in the case of room ventilators, the temperature rise is typically 10°C.^{22,25}

The pressure drop through a carbon bed is a function of the gas velocity, bed depth, and carbon particle size. Activated carbon manufacturers supply empirical correlations for pressure drop in terms of these quantities. These correlations usually include pressure drop resulting from directional change of the gas stream at inlet and outlet.²²

Activated carbon adsorption systems installed in rubber processing plants have been reported in the literature. One system was installed in a latex based operation for the manufacture of gloves. The gloves were dried in a drying room to remove traces of solvent and the air from the drying room was vented into a solvent recovery system operated on 1-hour adsorbency cycles. The efficiency of the system was 72% to 73%, including collection of the vapor-laden air.²⁵

²⁵Air Pollution Engineering Manual, Second Edition. U.S. Environmental Protection Agency, Research Triangle Park. Publication No. AP-40. May 1973. 987 p.

²⁶Solvent Recovery System Proves a Speedy Payout. Rubber World. 105(5):44, February 1972.

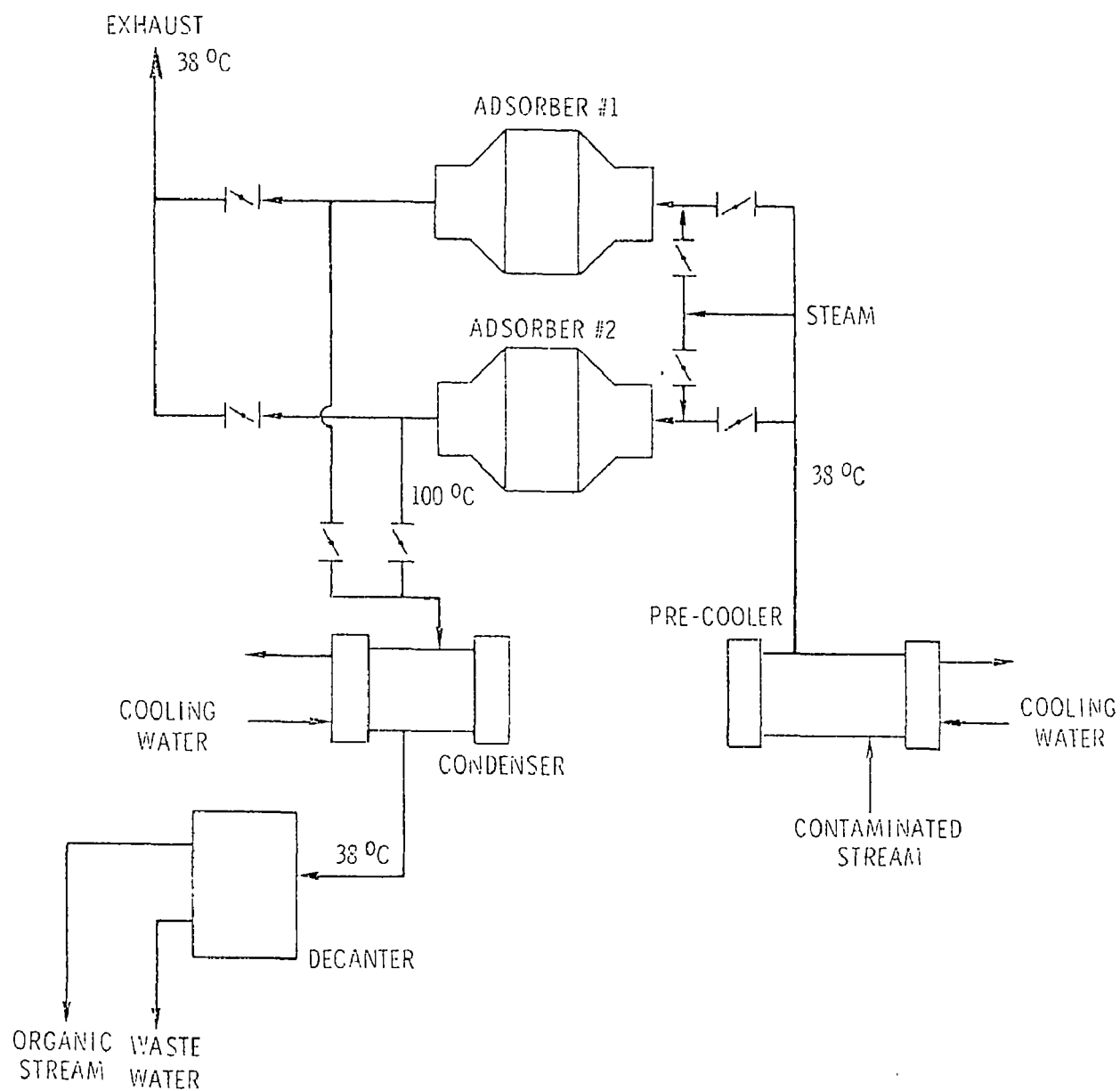


Figure 9. Carbon adsorption system²³

2. Absorption

Absorption is the process by which one or more soluble components are removed from a gas mixture by dissolution in a liquid. The absorption process may consist of dissolving the component in a liquid followed by reaction with a reagent, or of solution without reaction.²²

The equipment used for continuous absorption can be a tower filled with a solid packing material, an enclosure through which the gas flows and into which the liquid is sprayed, or a tower which contains a number of bubble-cap, sieve, or valve-type plates. Absorption operations are carried out in a wetted-wall column (a tubular column in which the gas flows vertically through the tube and the liquid flows down over the column wall), a stirred vessel, or other type of equipment.²²

The design of absorbers has been discussed by Treyball²⁷ and Perry and Chilton.²⁴ The problems which arise in designing absorbers can be attributed to variation of solubilities because of non-isothermal operating conditions, semi-ideal liquid solutions, and the change in the gas and liquid flow rates caused by transfer of the solute from the gas phase to the liquid phase.

3. Incineration

a. Thermal Incineration - Direct-flame afterburners depend upon flame contact and high temperatures to burn

²⁷Treybal, R. E. Mass Transfer Operations. New York, McGraw-Hill, 1968. 666 p.

the combustible material in gaseous effluents to form carbon dioxide and water.²⁸ The combustible materials may be gases, vapors, or entrained particulate matter which contributes opacity, odor, irritants, photochemical reactivity, and toxicity to the effluent. Direct-flame afterburners consist of a refractory-lined chamber, one or more burner temperature indicator-controllers, safety equipment, and, sometimes, heat recovery equipment.²⁸

The afterburner chamber consists of a mixing section and a combustion section. The mixing section provides contact between the contaminated gases and the burner flame. Good mixing is provided by high velocity flow which creates turbulence. The combustion section is designed to provide a retention time of 0.3 sec to 0.5 sec for completion of the combustion process. Afterburner discharge temperatures range from 540°C to 800°C, depending on the air pollution problem. Higher temperatures result in higher afterburner efficiencies.²⁸

The gas burners used in afterburners are of the nozzle-mixing, premixing, multiport, or mixing plates type. Burner placement varies depending on burner type and on the design objective of providing intimate contact of the contaminated air with the burner flames. When all the contaminated air passes through the burner, maximum afterburner efficiency is obtained.²⁸

Nozzle-mixing and premixing burners are arranged to fire tangentially into a cylindrical afterburner. Several

²⁸Rolke, R. W., et al. Afterburner Systems Study. Shell Development Company, (PB-212 560). August 1972.

burners or nozzles are required to ensure complete flame coverage, and additional burners or nozzles may be arranged to fire along the length of the burner. Air for fuel combustion is taken from the outside air or from the contaminated air stream, which is introduced tangentially or along the major axis of the cylinders.²⁸

Multiport burners are installed across a section of the afterburner separate from the main chamber. Although all air for combustion is taken from the contaminated air stream, multiport burners are not capable of handling all of the contaminated air stream. Contaminated air in excess of that used for fuel combustion must be passed around the burner and mixed with the burner flames in a restricted and baffled area.²⁸

Mixing plate burners were developed for afterburner applications, and are placed across the inlet section of the afterburner. The contaminated air and the burner flames are mixed by profile plates installed around the burner between the burner and afterburner walls. The high velocities (1 m/sec) provided by the burner and profile plate design ensure mixing of the burner flames and the contaminated air not flowing through the burner. The contaminated air stream provides air for fuel combustion.²⁸

The efficiency of an afterburner is a function of retention time, operating temperatures, flame contact, and gas velocity. No quantitative mathematical relationship between these variables exists because the kinetics of the combustion process are complex and flow inside afterburners is not defined. However, for good design, the following observations can be made with respect to afterburner efficiency:²⁸

- Efficiency increases with increasing afterburner operating temperature.
- Efficiency decreases if the contaminated gases entering the afterburner are excessively preheated.
- Efficiency increases with increasing contact between the contaminated gases and the burner flame.
- Efficiency increases with increasing retention time for retention times less than one second.
- Efficiency is a function of the afterburner design and the inlet concentration of organic materials.
- Ninety percent afterburner efficiency is difficult to reach below a 700°C operating temperature if the generation of carbon monoxide in the afterburner is included.

An example of the application of direct-flame incineration to a rubber processing plant is reported in the literature.²⁹ B. F. Goodrich Sponge Products operated a curing oven which was exhausted to the atmosphere. The exhaust stream contained an oil aerosol and also presented an odor problem. A direct-flame incinerator with heat recovery equipment was installed. The incinerator used No. 2 fuel oil as a supplementary fuel. At a system flow of 14 Mg/hr and an incineration temperature of 600°C, total hydrocarbons were reduced from 1,305 ppm (by weight) to 207 ppm, an efficiency of 84%. Allowing for the contribution of fuel oil, the efficiency becomes 89%. In another run at a temperature of 640°C, total hydrocarbons were reduced from 1,055 ppm (by weight), to 89 ppm for an efficiency of 92%. Again allowing for the contribution of the fuel oil, the efficiency becomes 97%.

²⁹Sandomirsky, A. G., et al. Fume Control in Rubber Processing by Direct-Flame Incineration. Journal of the Air Pollution Control Association. 16(12):673-676, December 1966.

b. Catalytic Incineration - A catalytic afterburner contains a preheat burner section, a chamber containing a catalyst, temperature indicators, and controllers, safety equipment, and heat recovery equipment. The catalyst in such an afterburner promotes combustion by increasing the rate of the oxidation reactions without itself appearing to change chemically.²² (See Figure 10).

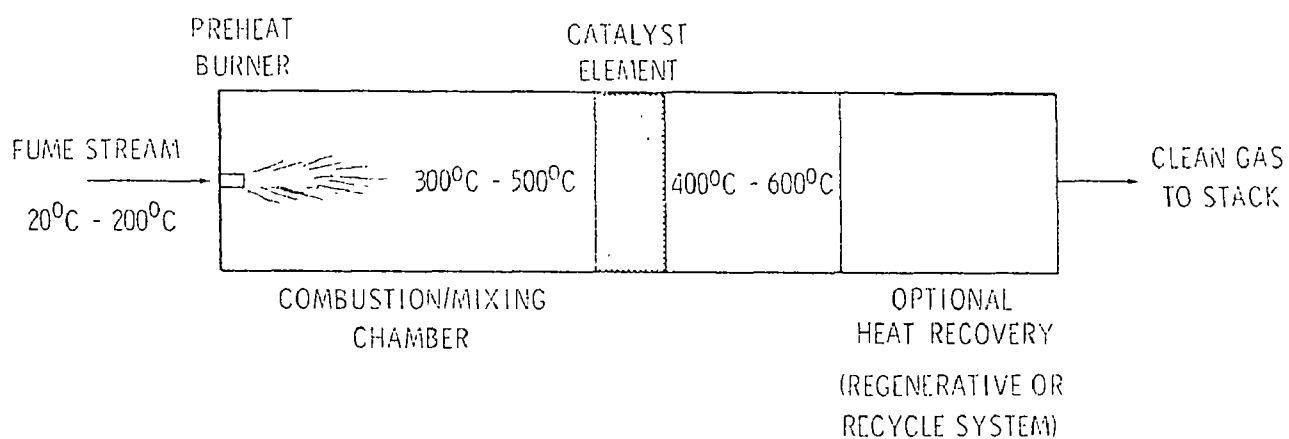


Figure 10. Catalytic afterburner²⁸

The contaminated air entering a catalytic afterburner is heated to the temperature necessary for carrying out the catalytic combustion. The preheat zone temperature, in the range of 340°C to 600°C, varies with the combustion and type of contaminants. Because of thermal incineration in the preheat zone, the preheat burner can contribute to the efficiency of a catalytic afterburner.²²

Catalysts used for catalytic afterburners may be platinum-family metals supported on metal or matrix elements made of

ceramic honeycombs. Catalyst supports should have high geometric surface area, low pressure drop, structural integrity and durability, and should permit uniform distribution of the flow of the waste stream through the catalyst.

Catalysts can be poisoned by phosphorus, bismuth, arsenic, antimony, mercury, lead, zinc, and tin, which are thought to form alloys with the metal catalyst. Catalysts are deactivated by materials which form coatings on them, such as particulate material, resins, and carbon formed during organic material breakdown. High temperatures will also deactivate catalysts. Because the combustion reaction is exothermic, the catalyst bed temperature is above the inlet temperature. The temperature increase depends on the concentration of organic material burned and the heat of combustion of that material. Compensation for decreased catalyst activity can be made by: (1) initial overdesign in specifying the quantity of catalyst required to attain required performance; (2) increasing preheat temperature as chemical activity decreases; (3) regenerating the catalyst; and (4) replacing the catalyst.²¹

The quantity of catalyst required for 85% to 95% conversion of hydrocarbons ranges from 0.5 m³ to 2 m³ of catalyst per 1000 m³/min of waste stream. Although the catalyst temperature depends on the hydrocarbon burned and the condition of the catalyst, the operating temperature of catalytic afterburners ranges from 260°C to 540°C.²²

4. Vapor Condensation

Organic compounds can be removed from an air stream by condensation. A vapor will condense when, at a given temperature, the partial pressure of the compound is equal to or greater than its vapor pressure. Similarly, if the temperature of

a gaseous mixture is reduced to the saturation temperature (i.e., the temperature at which the vapor pressure equals the partial pressure of one of the constituents), the material will condense. Thus, either increasing the system pressure or lowering the temperature can cause condensation. In most air pollution control applications, decreased temperature is used to condense organic materials, since increased pressure is usually impractical.³⁰

The equilibrium partial pressure limits the control of organic emissions by condensation. As condensation occurs, the partial pressure of material remaining in the gas decreases rapidly, preventing complete condensation. For example, at 0°C and atmospheric pressure, a gas stream saturated with toluene would still contain about 8,000 ppm of that gas. Thus, a condenser must usually be followed by a secondary air pollution control device such as an afterburner.³⁰

B. PARTICULATE

1. Wet Scrubbing

Wet scrubbers use a liquid (e.g., water) either to remove particulate matter directly from the gas stream by contact or to improve collection efficiency by preventing re-entrainment. The mechanisms for particle removal are: (1) fine particles are conditioned to increase their effective size, enabling them to be collected more easily; and (2) the

³⁰Control Techniques for Hydrocarbons and Organic Solvent Emissions from Stationary Sources. U.S. Department of Health, Education, and Welfare. AP-68, March 1970.

collected particles are trapped in a liquid film and washed away, reducing reentrainment.³¹

The effective particle size may be increased in two ways. First, fine particles can act as condensation nuclei when the vapor passes through its dew point. Condensation can remove only a relatively small amount of dust, since the amount of condensation required to remove high concentrations is usually prohibitive. Second, particles can be trapped on liquid droplets by impact using inertial forces. The following six mechanisms bring particulate matter into contact with liquid droplets:³¹

Interception occurs when particles are carried by a gas in streamlines around an obstacle at distances which are less than the radius of the particles.

Gravitational force causes a particle, as it passes an obstacle, to fall from the streamline and settle on the surface of the obstacle.

Impingement occurs when an object, placed in the path of a particle containing gas stream causes the gas to flow around it. The larger particles tend to continue in a straight path because of inertia and may impinge on the obstacle and be collected.

Diffusion results from molecular collisions and, hence, plays little part in the separation of particles from a gas stream.

Electrostatic forces occur when particles and liquid droplets become electrically charged.

Thermal gradients are important to the removal of matter from a particle containing gas stream because particulate matter will move from a hot area to a cold area. This motion is caused by unequal gas molecular collision energy on the hot and cold surfaces of the particles and is directly proportional to the temperature gradient.

³¹Control Techniques for Particulate Air Pollutants. U.S. Department of Health, Education, and Welfare, (PB 190 253). January 1969.

Wet scrubber efficiencies are compared on the bases of contacting power and transfer units. Contacting power is the useful energy expended in producing contact of the particulate matter with the scrubbing liquid. The contacting power represents pressure head loss across the scrubber, head loss of the scrubbing liquid, sonic energy or energy supplied by a mechanical rotor. The transfer unit (the numerical value of the natural logarithm of the reciprocal of the fraction of the dust passing through the scrubber) is a measure of the difficulty of separation of the particulate matter.³¹

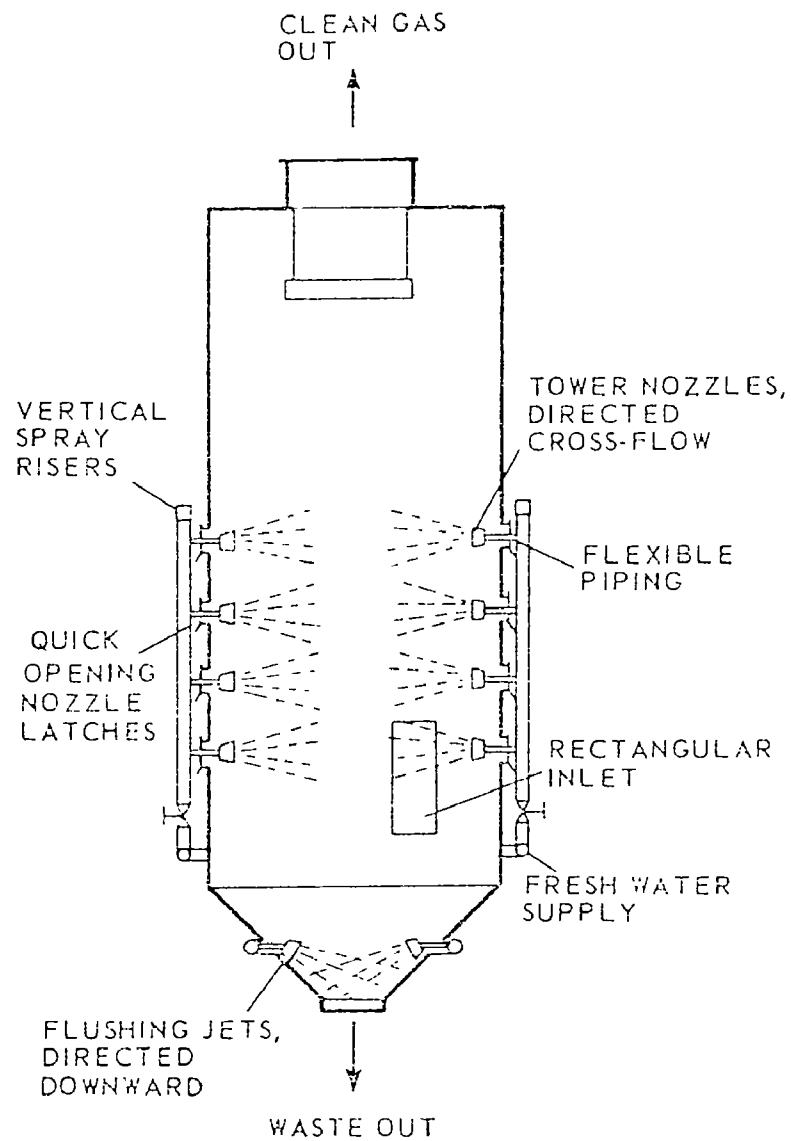
a. Spray Chamber - The simplest type of wet scrubber is the spray chamber, a round or rectangular chamber into which water is sprayed either cocurrently, countercurrently, or crosscurrently to the gas stream. Liquid droplets travel in the direction of liquid flow until inertial forces are overcome by air resistance. Large droplets settle under the influence of gravity, while smaller droplets are swept along by the gas stream. These droplets and particulate matter may then be separated from the gas stream by gravitational settling, impaction on baffles, filtration through shallow packed beds, or by cyclonic action.³¹

b. Gravity spray tower - Another simple type of wet scrubber is the gravity spray tower in which liquid droplets fall downward through a countercurrent gas stream containing particulate matter. To avoid droplet entrainment, the terminal settling velocity of the droplets is greater than the velocity of the gas stream. Collection efficiency increases with decreasing droplet size and with increasing relative velocity between the droplets and air stream. Since these two conditions are mutually exclusive, there is an optimum droplet size for maximum efficiency: from 500 μm to 1,000 μm .³¹

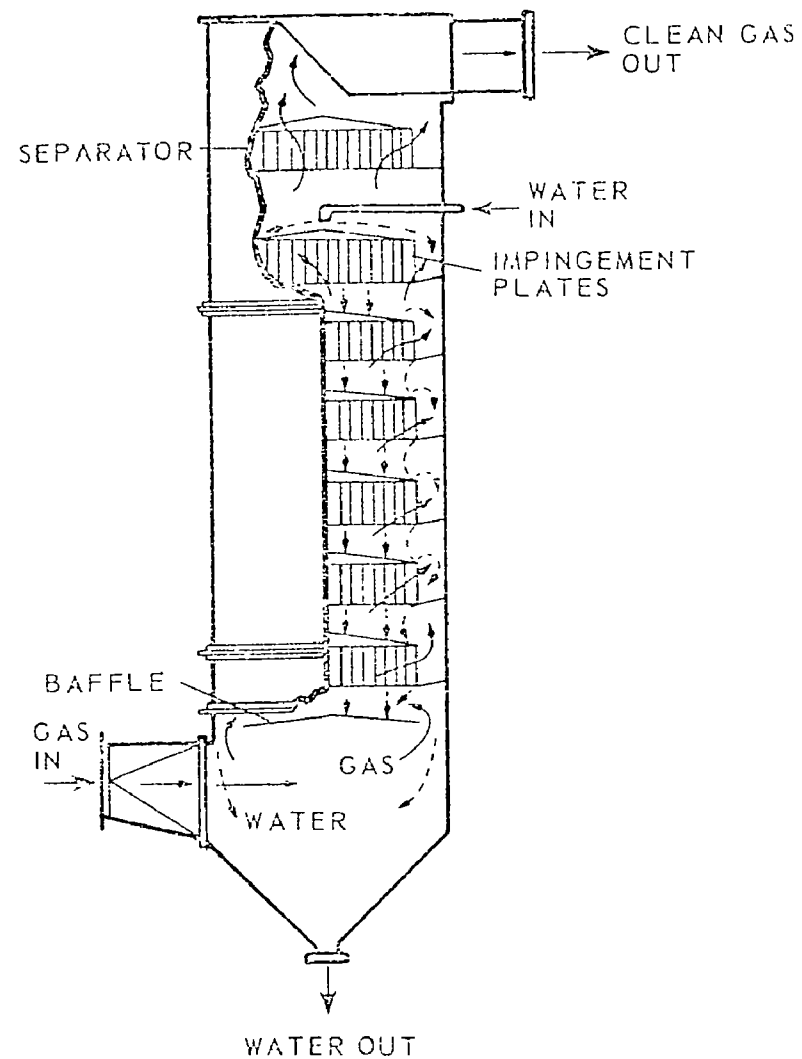
c. Centrifugal Spray Scrubbers - An improvement on the gravity spray tower is the centrifugal spray scrubber. (Figure 11). This type of wet scrubber increases the relative velocity between the droplets and gas stream by using the centrifugal force of a spinning gas stream. The spinning motion may be imparted by tangential entry of either the liquid or gas streams or by the use of fixed vanes and impellers.³¹

d. Impingement Plate Scrubbers - An impingement plate scrubber (Figure 12) consists of a tower equipped with one or more impingement stages, mist removal baffles, and spray chambers. The impingement stage consists of a perforated plate that has from 6,500 to 32,000 holes per square meter and a set of impingement baffles arranged so that a baffle is located above every hole. The perforated plate has a weir for control of its liquid level. The liquid flows over the plate and through a downcomer to a sump or lower stage. The gas enters in the lower sector of the scrubber and passes up through a spray zone created by a series of low pressure sprays. As the gas passes through the impingement stage, the high gas and particle velocity (2.25 to 3 m/sec) atomizes the liquid at the edges of perforations. The spray droplets, about 10 μm in diameter, increase fine dust collection.³¹

e. Venturi Scrubbers - High collection efficiency of fine particles by impingement requires small obstacle diameter and high relative velocity of the particle as it impinges on the obstacle. Venturi scrubbers (Figure 13) accomplish this by introducing the scrubbing liquid at right angles to a high velocity gas flow in the throat of a venturi where the velocity of the gas alone causes the disintegration of the liquid. Another factor which affects the efficiency of a



CYCLONIC SPRAY SCRUBBER.



MULTI-WASH SCRUBBER.

Figure 11. Centrifugal spray scrubbers³¹

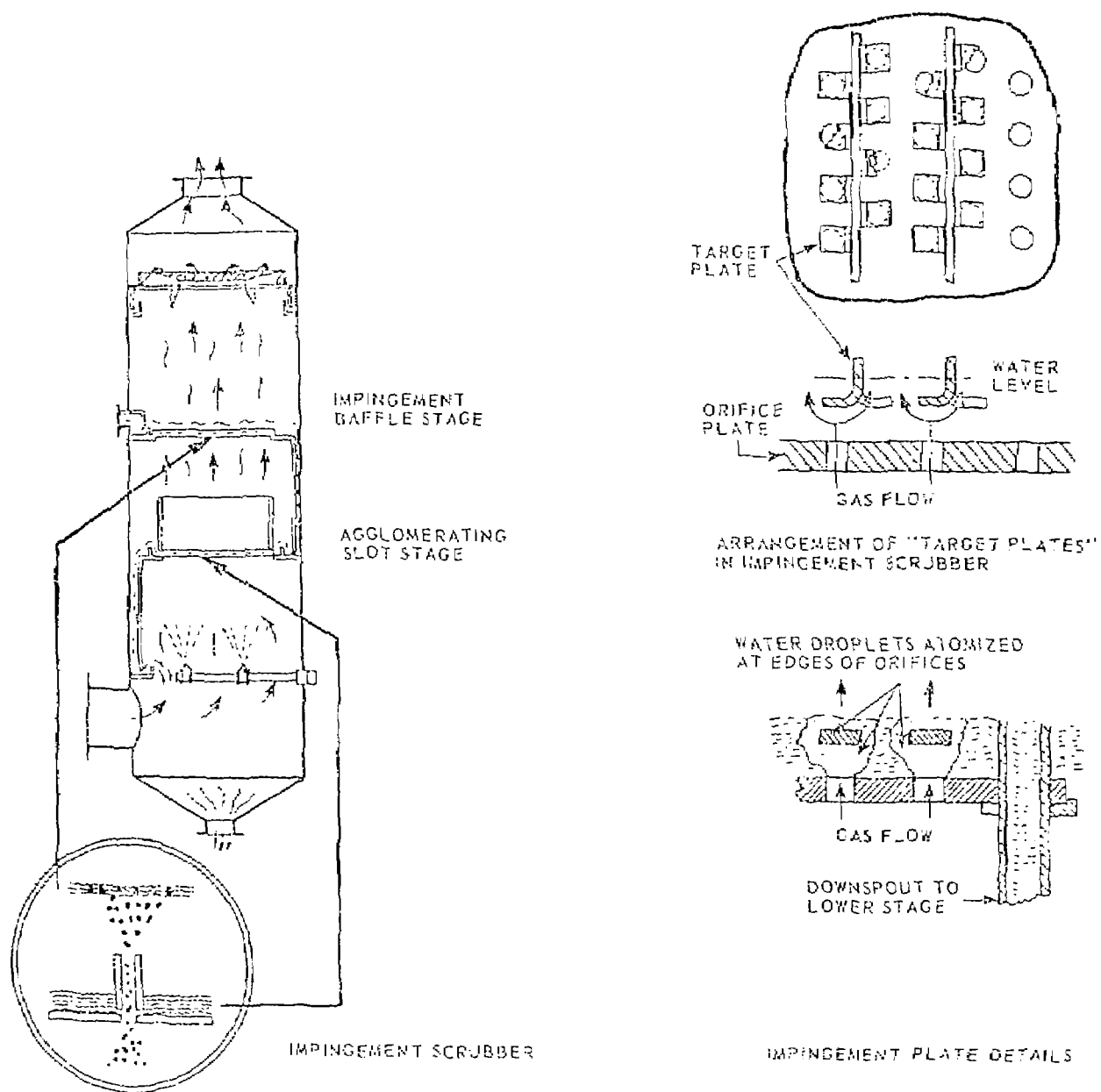


Figure 12. Impingement plate scrubber³¹

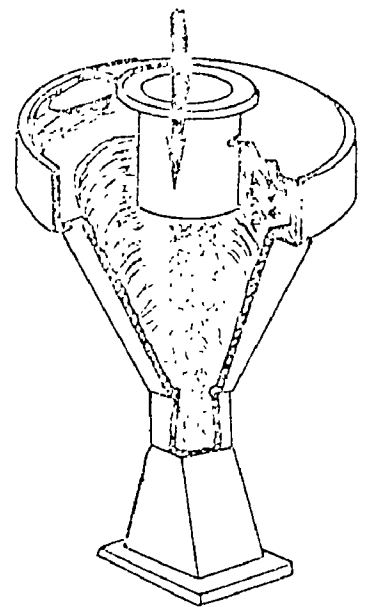
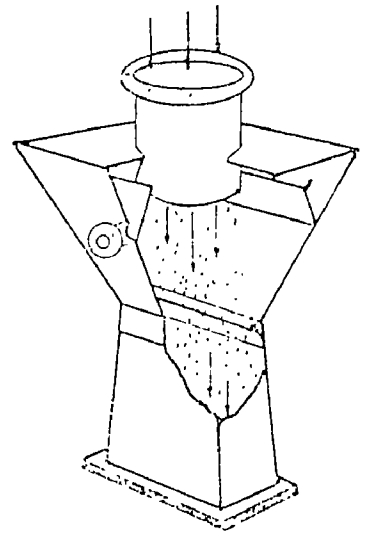
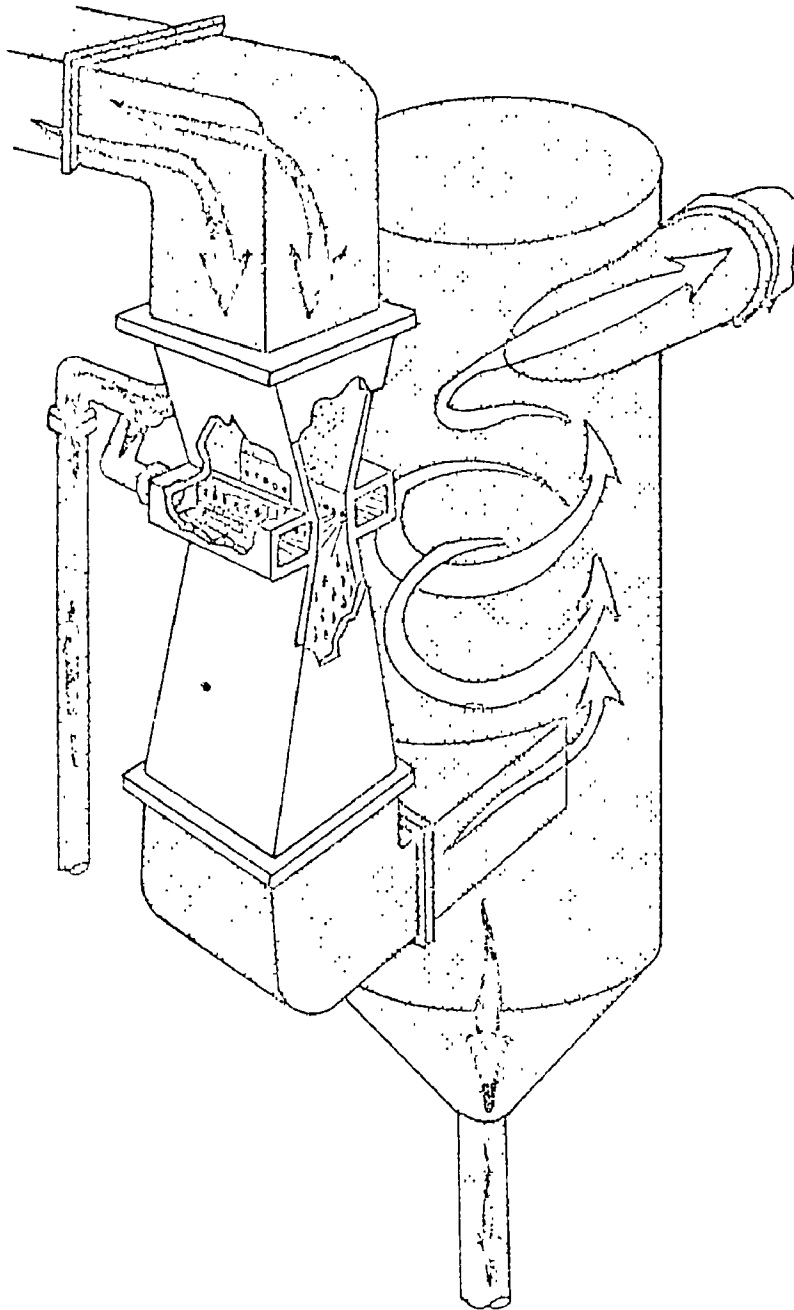


Figure 13. Venturi scrubber³¹

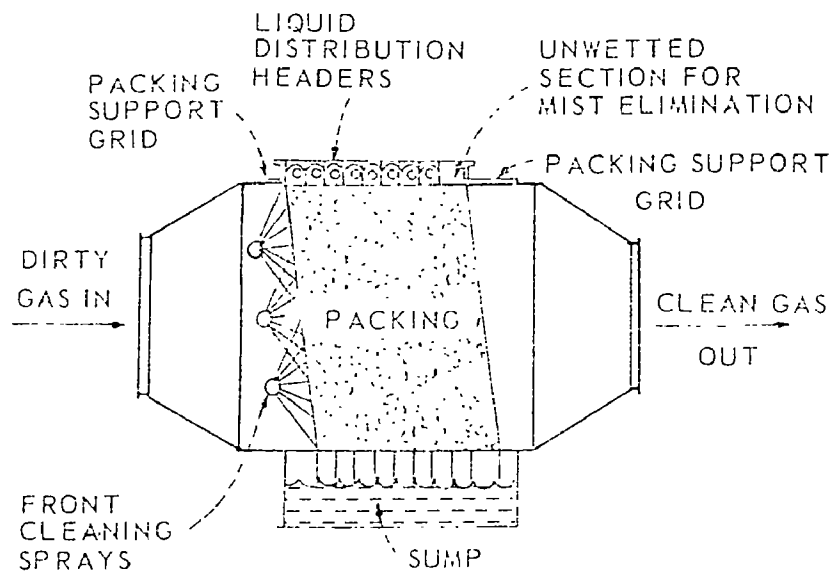
venturi scrubber is the conditioning of the particles by condensation. If the gas in the reduced pressure region in the throat is saturated or supersaturated, the Joule-Thompson effect will cause condensation. This helps the particle to grow, and the wetness of the particle surface helps agglomeration and separation.³¹

f. Packed Bed Scrubbers - Packed bed scrubbers (Figure 14) are similar to the packed bed absorbers discussed previously. The irrigating liquid serves to wet, dissolve, and/or wash the entrained particulate matter from the bed. In general, smaller-diameter tower packing gives a higher particle target efficiency than larger-size packing for a given gas velocity.³¹

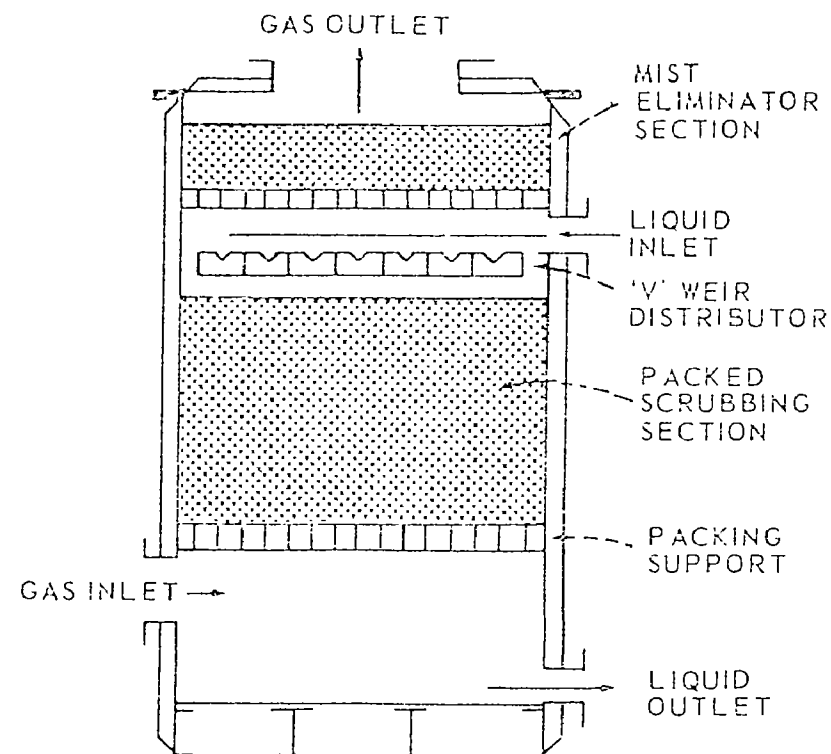
g. Self-Induced Spray Scrubbers - The self-induced spray scrubber uses a spray curtain for particle collection. The spray curtain is induced by gas flow through a partially submerged orifice or streamlined baffle. Baffles or swirl chambers are used to minimize mist carryover.

The chief advantage of the self-induced spray scrubber is its ability to handle high dust concentrations and concentrated slurries.³¹

h. Mechanically Induced Spray Scrubbers - Mechanically induced spray scrubbers use high velocity sprays generated at right angles to the direction of gas flow by a partially submerged rotor. Scrubbing is achieved by impaction of both high radial droplet velocity and vertical gas velocity. Advantages are the relatively low liquid requirements, small space requirements, high scrubbing efficiency, and high dust load capacity. The rotor, however, is susceptible to erosion from large particles and abrasive dusts.³¹



CROSS-FLOW SCRUBBER



COUNTERCURRENT-FLOW SCRUBBER

Figure 14. Packed bed scrubbers³¹

i. Disintegrator Scrubber - A disintegrator scrubber consists of a barred rotor with a barred stator. Water is injected axially through the rotor shaft and is separated into fine droplets by the high relative velocity of rotor and stator bars. Advantages of this scrubber are high efficiency for submicron particles and low space requirements. The primary disadvantage is its large power requirement.³¹

j. Centrifugal Fan Wet Scrubber - This type of scrubber (Figure 15) consists of a multiple-blade centrifugal blower. Its advantages are low space requirements, moderate power requirements, low water consumption, and a relatively high scrubbing efficiency.³¹

k. Inline Wet Scrubber - In the axial-fan-powered gas scrubber, a water spray and baffle screen wet the particles, and centrifugal fan action eliminates the wetted particles through concentric louvers. Advantages are low space requirements and low installation costs.³¹

l. Irrigated Wet Filters - Irrigated wet filters consist of an upper chamber, containing wet filters and spray nozzles for cleaning the gas, and a lower chamber for storing scrubbing liquid. Liquid is recirculated and sprayed into the surface of the filters on the upstream side of the bed. Two or more filter stages are used in series.³¹

2. Fabric Filtration

Fabric filters use a filter medium to separate particulate matter from a gas stream. Two types of fabric filters are

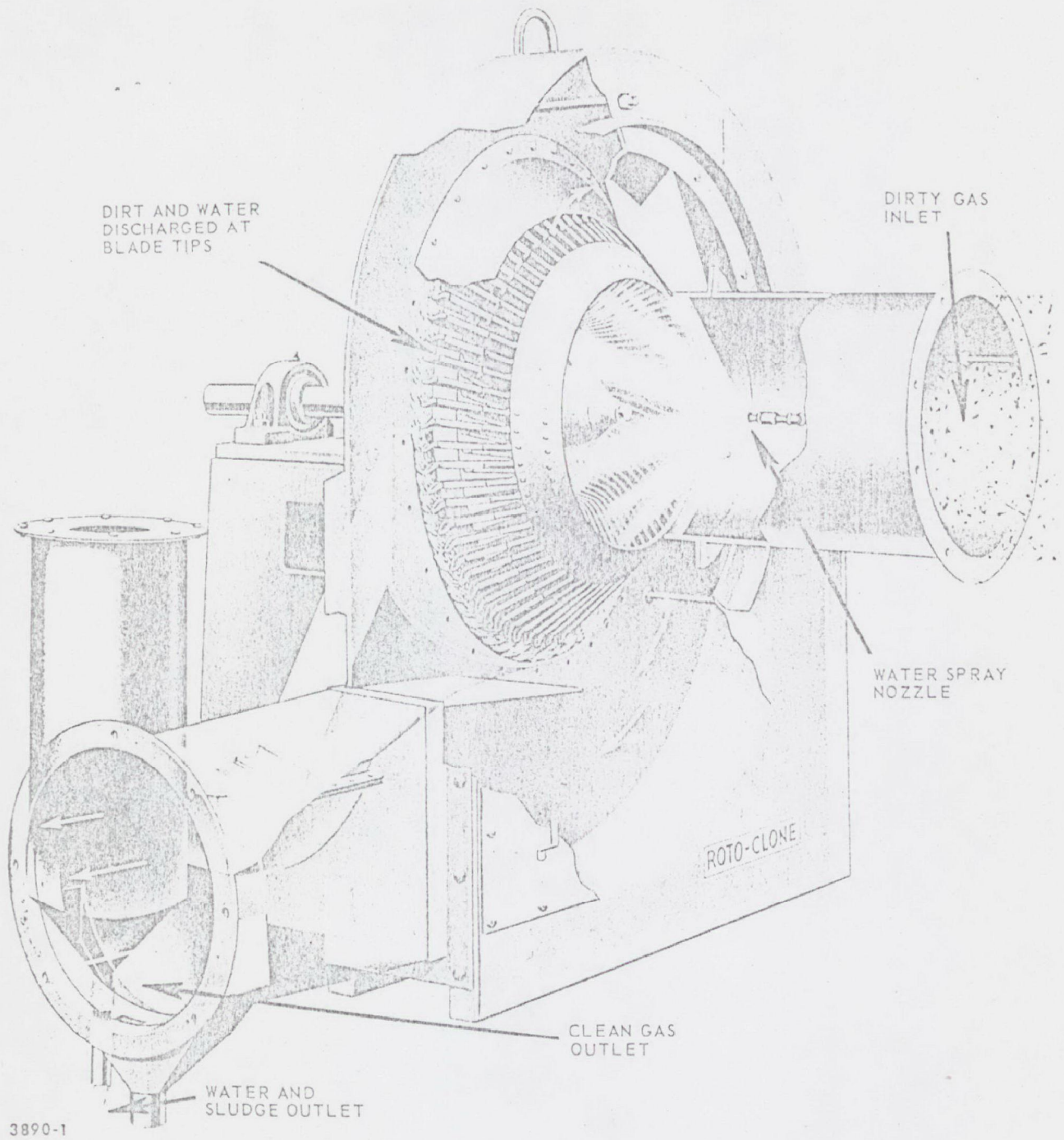


Figure 15. Centrifugal fan wet scrubber³¹

in use--high energy cleaned collectors and low energy cleaned collectors.³²

a. High Energy Collectors - High energy collectors use pulse jets to clean the filter medium, a felt fabric which is kept as clean as possible.³² The principle of the pulse jet is based on the use of an air ejector for dislodging dust from the bags. The ejector produces a short pulse of compressed air in the direction opposite to that of the gas being filtered. The jet must accomplish three things.³³

- Stop the normal filtering flow.
- Transmit a burst of air to the filtration medium, giving it a vibratory shock.
- Create enough pressure in the bag to ensure a reversal of flow from the clean side to the dirty side of the bag.

b. Low Energy Collectors - Low energy collectors use shaking or reverse air flow methods of cleaning. The filter base is a woven cloth that acts as a site on which the true filter medium, or dust cake can build up.³²

3. Mist Eliminators

Mists are liquid aerosols (collections of extremely small liquid particles suspended in an air stream). Incineration, one of three methods for controlling mists, has already been discussed. Another technique is scrubbing, but unless

³²Frey, R. E. 'Types of Fabric Filter Installations. Journal of the Air Pollution Control Association. 24:1148-1149. December 1974.

³³Bakke, E. Optimizing Filter Parameters. Journal of the Air Pollution Control Association. 24:1150-1154, December 1974.

high energy scrubbers are used, extremely fine mist will not be collected. The third method of controlling mists is with mist eliminators, of which there are four types.³⁴

a. Wet-Fiber Mist Eliminator - Wet fiber mist eliminators depend upon two mechanisms, Brownian diffusion and inertial impaction, to separate mist and dust particles from air streams. Brownian diffusion dominates when filter beds have large specific surface areas, gas velocities range from 1.5 to 9.0 m/min, and the mist consists largely of sub-micron sized particles. A characteristic of such equipment is that collection efficiency increases with decreasing gas velocity because of increased filter bed retention time. Brownian motion is an important factor in particle capture by direct interception.³¹

Inertial impaction dominates in collection of particles above 3 μ m in size at gas velocities in excess of 9 m/sec in coarse filter beds. Inertial impaction efficiency increases with increasing gas velocity.³¹

Wetted filters are available in two designs, low velocity (1.5 to 9 m/min) and high velocity (9 to 27 m/min). The low velocity design consists of a packed bed of fibers between two concentric screens. Mist particles collect on the surface of the fibers, coalesce to form a liquid that wets the fibers, and are moved horizontally and downward by gravity and the drag of the gases. The liquid flows down the inner screen to the bottom of the element to a collection

³⁴Farkas, M. D. Mist Abatement from Plastics Processing Operations. Plastics and Ecology, Society of Plastics Engineers, Inc. Cherry Hill. October 27-28, 1970. 98 p.

reservoir. Collection efficiencies are greater than 99% for particles smaller than 3 μm in diameter.³¹

The high velocity filter consists of a packed fiber bed between two parallel screens. Liquid flow patterns are similar to those of the low velocity filter and removal efficiencies range from 85% to 90% for 1 μm to 3 μm particles.³¹

b. Impingement Baffle Mist Eliminator - Baffle mist eliminators are used to control large diameter solid and liquid particles. Mist removal efficiencies of 95% may be achieved for 40 μm spray droplets up to a maximum gas velocity of 7.6 m/sec. Higher gas velocities result in reentrainment of the liquid droplets.³¹

c. Vane-Type Mist Eliminators - Vane-type mist eliminators have an operating range of 3 to 15 m/sec with collection efficiencies as high as 99% for 11 μm particles. The principal advantage of the vane-type mist eliminator over the baffle type is the wider range of operation at comparable removal efficiencies.³¹

d. Packed Bed Mist Eliminators - Packed beds can also be used as mist eliminators. Removal efficiencies range up to 65% at gas velocities of 2 to 3 m/sec. Mist reentrainment occurs at higher gas velocities.³¹

SECTION VI

GROWTH AND NATURE OF THE INDUSTRY

A. PRESENT TECHNOLOGY

The five basic steps involved in rubber processing are: compounding, mixing, forming, building, and vulcanization.

Compounding is the process of determining the proper ingredients and proportions to be used in the rubber recipe in order to obtain the required properties of the end product. The main objectives of the mixing operation are to obtain a uniform blend of the ingredients and to achieve consistent properties from batch to batch. Mixing is presently carried out as a batch process using either a two roll mixer or an internal (Banbury) mixer. Batch size varies according to mixing equipment capacity, which is typically from 68 kg to 136 kg for a 2.13 m mill and 454 kg or more for the largest internal mixers.

Forming operations usually consist of calendering or extrusion. Calendering involves forming the rubber compound into thin sheets, coating it on a fabric, or wiping it into a fabric by means of a series of rollers. Thin sheets of rubber are built up to make the final thickness desired, e.g., eight to 10 sheets may be used to make a final sheet

1.6 mm thick. Extrusion is accomplished by a power driven screw in a stationary cylinder which forces the heated rubber compound through a die to give the desired shape. Other forming operations used in rubber processing include casting, blow molding, and injection molding.

Building operations vary widely according to the product being manufactured. For example, in tire manufacture, the extruded cord plies are applied to the assembly drum one at a time to build up a two, four, six or eight ply tire.

Vulcanization, which imparts elastic characteristics to rubber, can be carried out using molds heated to 138°C for 10 min to 90 min as in tire manufacturing. Alternatively, rubber products may be cured in an autoclave with steam or water depending on the required temperature and pressure. Heated air, either at atmospheric or elevated pressure, can also be used to vulcanize products that are adversely affected by moisture. Various combinations of these cures are also used in order to achieve the desired properties in the product.

2. EMERGING TECHNOLOGY

During the 1950's and the 1960's, the rubber industry experienced a slow rate of technological advancement. However, recent years have witnessed an accelerated pace, and many new innovations are now beginning to alter the industry. For example, many plants now employ tanks and silos for bulk storage and handling of raw materials such as fillers or reinforcers. The use of large preblending systems to provide more uniform quality of raw materials is being explored. In this vein, the Farrel Company is reportedly developing technology for blending chopped or crumb rubber to even

out batch-to-batch variations.³⁵ In addition, some large production facilities now employ fully automated, computer controlled charger-mixer systems.

An improvement in the curing process is the use of cure rate integrators that employ a special sensor to accurately monitor the temperature. These devices have reportedly reduced curing times by 8%.³⁵ Another example of the trend toward increasing automation is in use in radial tire plants. The last 2 minutes of the 5-minute tire assembly operation are now said to be automated.³⁵

An important advance in blending operations, that of continuous mixing, is being actively developed. The combination of an internal mixer with some type of screw mixing will permit increased mixing capacity and reduced mixing times. At present, however, this technology is considered to be several years away.³⁵ The increasing demand for exterior automotive components made of dent-proof rubber and the steeply rising cost of energy are expected to further accelerate the development of new manufacturing processes in the rubber industry.

The new manufacturing techniques should hasten the further development of new forms of rubber and their acceptance and use by fabricators. The new forms of rubber include powdered rubber for continuous mixing, thermoplastic types which allow the vulcanization stage to be eliminated, and liquid polymers (especially polyurethanes) for use in casting and injection molding processes. One source estimates that

³⁵Survey Results on Machinery, Equipment. Rubber World. July 1974. p. 57.

within the next 5 years, liquid and powdered rubbers will account for 20% of the total rubber market in the United States.³⁶

C. MARKETING STRENGTHS AND WEAKNESSES

1. Tires

The future growth of the rubber industry is closely related to the automotive industry, since about two-thirds of all new rubber produced goes into automotive tires. Of this amount, about 85% on a unit basis (60% on a weight basis) goes into passenger car tires. Hence, the demand for rubber will be greatly affected by the total passenger vehicle miles driven and by tire design, which affects tread life. Average passenger car mileage for the past 10 years has increased steadily from about 15 Mm to 16 Mm annually. However, this figure is expected to remain nearly constant or even decline somewhat during the next several years due to increased fuel costs.

Tire tread life is expected to continue to increase due to the shifts to belted bias and radial tires and to smaller lighter weight cars. From 1968 to 1970, new car manufacturers switched almost completely from bias ply to belted bias tires, which offer about 25% better mileage. The switchover in the replacement tire market is proceeding at a much slower rate and is expected to stop at 35% to 40%, because the owner of

³⁶Status Report on Elastomeric Materials. Rubber World. February 1974. 39 p.

an older car is less inclined to buy expensive, long-wearing tires.³⁷

Another factor that may adversely affect the tire market is the trend to only four tires per car. Development work toward this objective is under way at all companies.³⁸ In addition to safety and convenience, the incentives to "eliminate the spare" include reduced car weight, more trunk space, and reduced new-car cost.

The above considerations lead to a projected increase in consumption of rubber for automotive tires from 1.95 Tg in 1974 to 2.142 Tg in 1980. The tire industry's percentage of total rubber consumption is expected to decrease from 64% in 1974 to 59% in 1980.^{37,38}

2. Molded and Extruded Products

The strengths and weaknesses of the molded and extruded rubber products markets vary with the variety of products falling in this category. Automotive products (especially those such as bumpers, seals, electrical wiring, etc., which are not normally replaced during the car's lifetime) exhibit a major weakness. These products are suffering most heavily from the effects of the recession in the automobile industry. However, the long-term outlook in this area is much better. The new emphasis on weight reduction of

³⁷Richardson, H. M. Forecasting in the Rubber Industry. In: Hydrocarbons: The Dilemma in Forecasting, (papers presented at the joint meeting of the Chemical Marketing Research Association and the Commercial Development Association, New York. May 1974.) p. 77.

³⁸Rubber Products: 1974-1975. Rubber World. January 1975. p. 27.

automobiles to improve gasoline mileage should result in the use of many more rubber and plastic parts.

Another area which could show substantial gains is the replacement of PVC products by rubber products. Over the past 8 years, vinyl resin products have replaced rubber in such products as wire and cable, garden hose, footwear, weather stripping, sealants, toys and auto mats. However, a trend back to rubber is developing due to rising costs of vinyl resins and the lower processing costs associated with thermoplastic elastomers.³⁹ This trend could be accelerated because of the health problems recently associated with vinyl chloride monomer.

Rubber parts used by the oil industry in wells, platforms, refineries, and transportation of oil also have a good outlook for the immediate and longterm future due to the renewed emphasis on drilling in the U.S. as well as other areas of the world.

The Rubber Manufacturers Association's 1975 prediction for the molded, extruded and lathe cut sectors of the rubber business, shown in Figure 16, indicates a significant increase in dollar volume in each of the three areas. Although this prediction was made in November 1974 before the sharp drop in the economy, the general strength in this area should still remain when economic recovery begins to take effect. Another indication of the strength of this segment

³⁹Dworkin, D. Changing Markets and Technology for Specialty Elastomers. Rubber World. February 1975. p. 43.

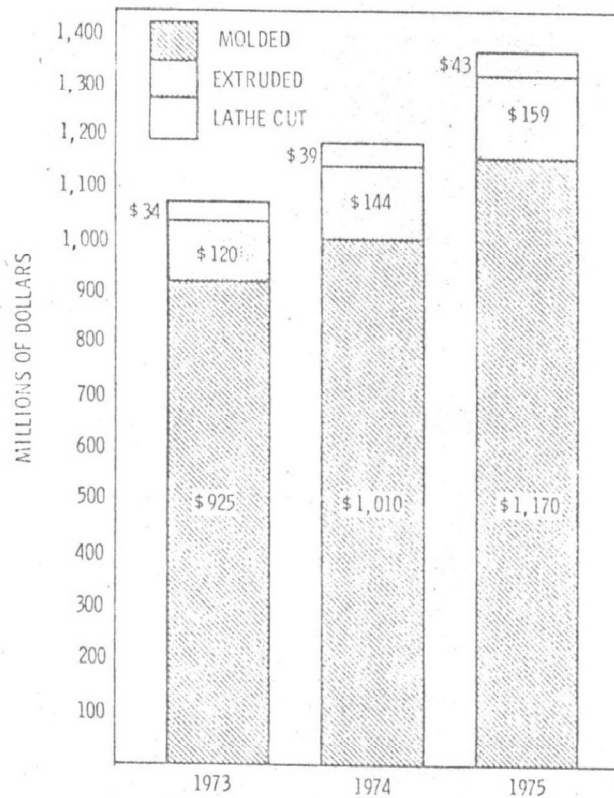


Figure 16. Domestic market estimates and forecasts
molded, extruded, lathe cut products

of the industry is the RMA data on new rubber consumption shown in Table 39. Although total consumption for 1974 shows a decline from 1973, the decrease is confined to the tire and tire products area. The non-tire products show an increase of about 4 Gg.

Table 39. NEW RUBBER CONSUMPTION³⁸

Year	(Tg)		
	Tires	Non-Tires	Total
1965	1.306	0.749	2.055
1970	1.578	0.899	2.477
1971	1.771	0.912	2.683
1972	1.919	1.010	2.929
1973	1.990	1.096	3.086
1974	1.950 ^a	1.100 ^a	3.050 ^a

^aEstimated by the Rubber Manufacturers Association.

The long-term strength in the molded and extruded products sector can also be inferred from the data in Reference 39 on specialty elastomers. These data suggest strong growth for all but a few specialty materials over the next 4 years. Since the use of specialty rubbers is heavy in the molded and extruded fields, the increases should be reflected in these areas.

3. Hose and Belting

The major strengths of the hose and belting sector of the rubber industry are in equipment for the oil industry and in automotive replacement parts. The latter field should prove particularly strong if, as expected, many people continue to defer the purchase of a new car due to high prices. On the other hand, new automobile parts represent a major weakness in this sector due to the recession in the automotive industry.

The ultimate short-term strength of this segment of the industry may well depend upon the effect of government deficits on interest rates. Many plants should be scheduled for expansion and new plants should be built if industry is to be prepared for the next round of high level business. However, high interest rates could cause postponements in construction with a resultant drop in demand for rubber hose and belting.

The long-term strength of the hose and belting sector is indicated by the RMA estimates of the market potential for these products over the next 5 years as shown in Figure 17.

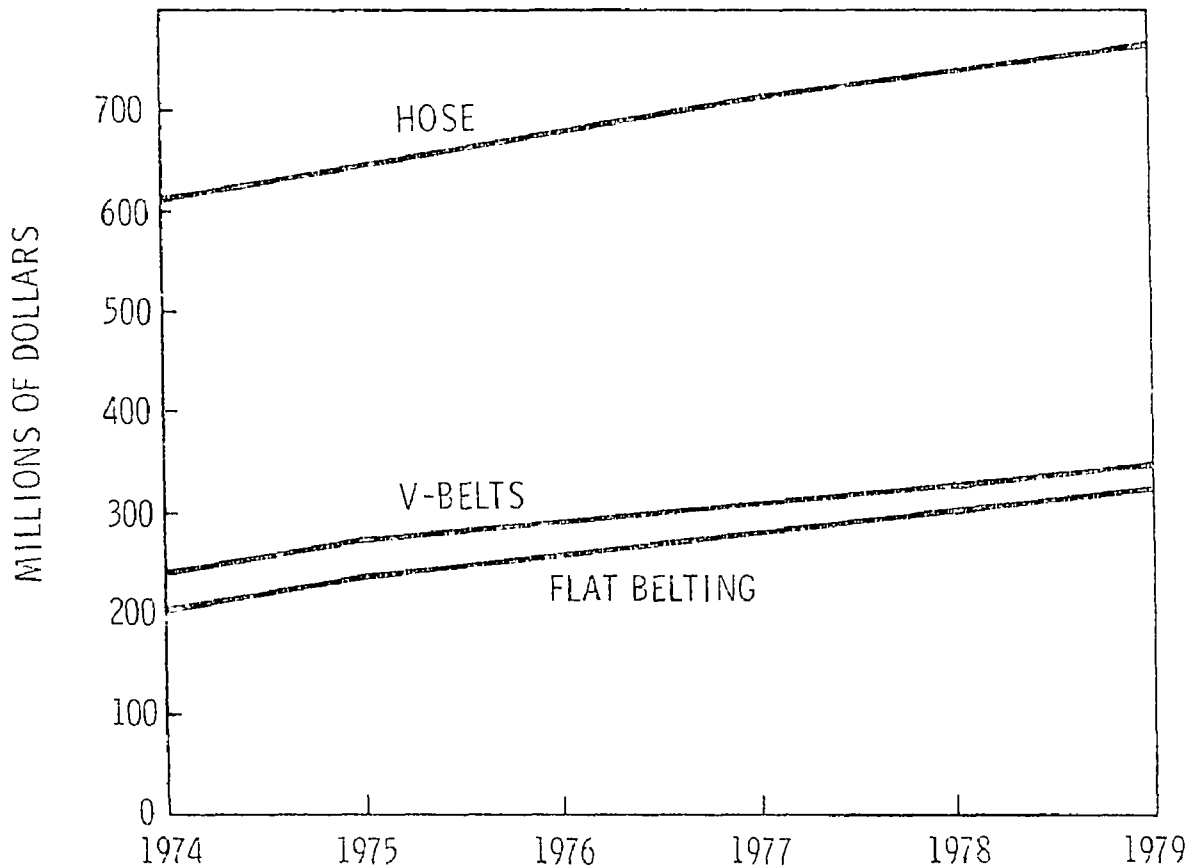


Figure 17. Market potential for rubber hose and belting³⁸

4. Natural Rubber

The long-term outlook for natural rubber is extremely good due to the problems of high prices and short supplies of raw materials for synthetic rubber created by the steep rise in petroleum prices. One source⁴⁰ estimates that the world market for natural rubber may double by 1980.

Major weaknesses over the short term are associated with the slumps in the automotive and housing industries. Two-thirds of all natural rubber is used for tires, while 40% of the latex produced is used by the carpet industry for carpet backing. The carpet business is down 30% to 40%, and many carpet mills are reportedly in danger of folding.³⁸ Another short-term problem facing the natural rubber industry is the shortage of fertilizer, which could limit the ability to increase production.

5. Total New Rubber Consumption

From 1960 to 1973, total new rubber consumption in the United States increased at an average annual rate of 5.4%.⁴¹ In 1974, consumption decreased approximately 1% from 1973. Through 1980, consumption is expected to increase at a more moderate rate, 2.4% to 3.8%,^{37,42} primarily due to the effects of energy conservation programs and the socio-economic trends in the transportation industry detailed above. This rate of growth will result in total new rubber

⁴⁰Rubber Age. June 1974. p. 18.

⁴¹Rubber Demand Faces Lower Growth Rate. Chemical and Engineering News. May 20, 1974. p. 12.

⁴²Rubber Consumption to Increase. Rubber World. May 1975. p. 83.

consumption of 3.52 Tg to 3.82 Tg in 1980, compared to an estimated 3.05 Tg in 1974. Table 40 gives a breakdown of estimated new rubber consumption for 1980 based on an average annual growth rate of 3% from 1974 through 1980. The recent history of new rubber consumption is depicted graphically in Figure 13.

Table 40. RUBBER CONSUMPTION FORECAST FOR 1980³⁷
(Tg)

	Tires	Non-Tire	Total
Styrene-butadiene rubber	0.846	0.353	1.199
Polybutadiene rubber	0.324	0.036	0.360
Isoprenic rubber	0.832	0.310	1.192
EPDM rubber	0.045	0.250	0.295
Butyl or chlorobutyl rubber	0.045	0.100	0.145
Nitrile rubber	-	0.086	0.086
All other elastomers	-	0.354	0.354
	<u>2.142</u>	<u>1.489</u>	<u>3.631</u>

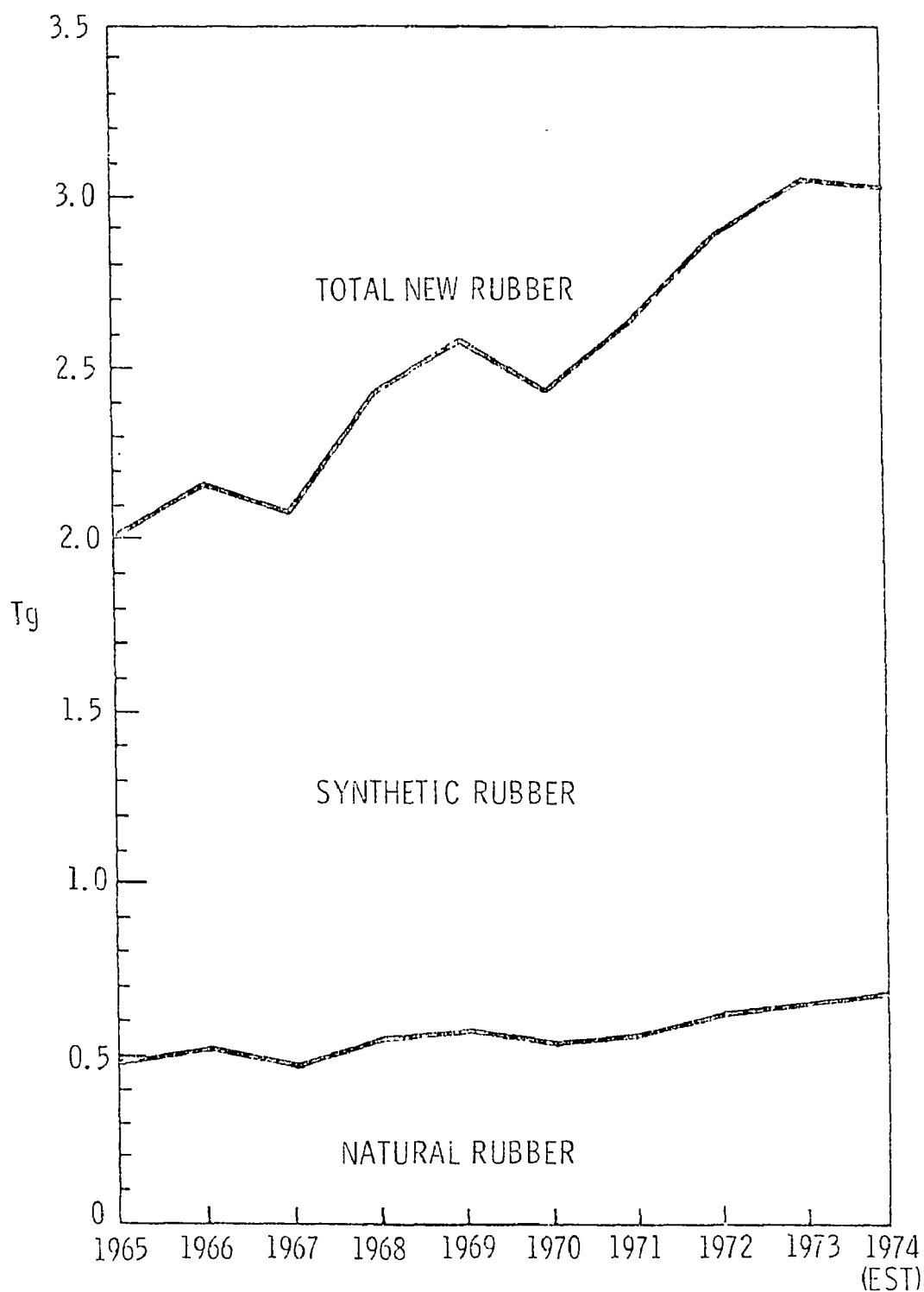


Figure 18. Total new rubber consumption, synthetic vs natural source

SECTION VII

APPENDIX

RATIONALE FOR A SAMPLING PLAN

Literature-derived emission factors were used in the preliminary assessment of rubber processing in order to calculate the state and national mass emissions, the maximum ground level concentration, and, thus, the severity factor and affected population for each pollutant shown. Additional information on emission factors from compounding and curing operations is needed to assess the environmental impact from these sources.

As described in Section IV.A.1., emissions from compounding consist of particulates and hydrocarbons. Compounding generates a cloud of 5% to 50% opacity (per EPA Method No. 9) which is removed from the building via an exhaust hood. The literature however, does not contain emission factors for either particulate or hydrocarbon emissions from compounding operations (as evident in Tables 31 and 32). Field sampling is thus required to obtain this information.

Similarly, Section IV.A.2. describes curing operations. Again, the literature does not contain emission factors for the compounds emitted and field sampling is necessary to obtain this information.

SECTION VIII

CONVERSION FACTORS^{1,3}

<u>To convert from</u>	<u>to</u>	<u>Multiply by</u>
degrees	radian	1.745×10^{-2}
foot	meter (m)	3.048×10^{-1}
foot ³	meter ³ (m ³)	2.832×10^{-2}
degree Fahrenheit	degree Celsius	$t^{\circ}\text{C} = (t^{\circ}\text{F} - 32)/1.8$
inch of water (60°F)	pascal (Pa)	2.488×10^2
pound (mass)	kilogram (kg)	4.536×10^{-1}
ton	megagram (Mg)	9.072×10^{-1}

PREFIXES

<u>Prefix</u>	<u>Symbol</u>	<u>Multiplication Factor</u>	<u>Example</u>
tera	T	10^{12}	1 Tg = 1×10^{12} g
giga	G	10^9	1 Gg = 1×10^9 g
mega	M	10^6	1 Mg = 1×10^6 g
kilo	k	10^3	1 km = 1×10^3 m
milli	m	10^{-3}	1 mm = 1×10^{-3} m
micro	μ	10^{-6}	1 μ m = 1×10^{-6} m
nano	n	10^{-9}	1 nm = 1×10^{-9} m

^{1,3}Metric Practice Guide, E 380-74. American Society for Testing and Materials. Philadelphia, November, 1974.
34 p.

SECTION IX

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