#### DRAFT

# DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS OF PERFORMANCE

## RUBBER PROCESSING INDUSTRY



PREPARED BY ROY F. WESTON, INC. FOR UNITED STATES ENVIRONMENTAL PROTECTION AGENCY UNDER CONTRACT NUMBER 68-01-1510

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#### NOTICE

The attached document is a DRAFT CONTRACTOR'S REPORT. It includes technical information and recommendations submitted by the Contractor to the United States Environmental Protection Agency ("EPA") regarding the subject industry. It is being distributed for review and comment only. The report is not an official EPA publication and it has not been reviewed by the Agency.

The report, including the recommendations, will be undergoing extensive review by EPA, Federal and State agencies, public interest organizations and other interested groups and persons during the coming weeks. The report and in particular the contractor's recommended effluent limitations guidelines and standards of performance is subject to change in any and all respects.

The regulations to be published by EPA under Sections 304(b) and 306 of the Federal Water Pollution Control Act, as amended, will be based to a large extent on the report and the comments received on it. However, pursuant to Sections 304(b) and 306 of the Act, EPA will also consider additional pertinent technical and economic information which is developed in the course of review of this report by the public and within EPA. EPA is currently performing an economic impact analysis regarding the subject industry, which will be taken into account as part of the review of the report. Upon completion of the review process, and prior to final promulgation of regulations, an EPA report will be issued setting forth EPA's conclusions concerning the subject industry, effluent limitations guidelines and standards of performance applicable to such industry. Judgments necessary to promulgation of regulations under Sections 304(b) and 306 of the Act, of course, remain the responsibility of EPA. Subject to these limitations, EPA is making this draft contractor's report available in order to encourage the widest possible participation of interested persons in the decision making process at the earliest possible time.

The report shall have standing in any EPA proceeding or court proceeding only to the extent that it represents the views of the Contractor who studied the subject industry and prepared the information and recommendations. It cannot be cited, referenced, or represented in any respect in any such proceedings as a statement of EPA's views regarding the subject industry.

U.S. Environmental Protection Agency Office of Air and Water Programs Effluent Guidelines Division Washington, D.C. 20460

#### **ABSTRACT**

This document presents the findings of an extensive study of the rubber processing industry by Roy F. Weston, Inc. for the Environmental Protection Agency, for the purpose of developing effluent limitation guidelines, Federal standards of performance, and pretreatment standards for the industry, to implement Sections 304, 306, and 307 of the Federal Water Pollution Control Act, as amended (33 USC 1251, 1314, and 1316; 86 Stat 816).

Effluent limitation guidelines contained herein set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best available technology economically achievable, which must be achieved by existing point sources by July 1, 1977 and July 1, 1983, respectively. The Standards of Performance for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives.

The development of data and recommendations in the document relate to the overall rubber processing industry, which is divided into two major groups, tire and inner tube and synthetic rubber, and further into five sub-categories, on the basis of the characteristics of the manufacturing processes involved. Separate effluent limitations were developed for each category on the basis of the level of raw waste load as well as on the degree of treatment achievable by suggested model systems. These systems include both biological and physical/chemical treatment, and for the synthetic rubber sub-categories treatment of the secondary effluent by carbon adsorption.

Supportive data and the rationale for development of the proposed effluent limitation guidelines and standards of performance are contained in this report.

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#### SECTION I

#### CONCLUSIONS

Two major and distinct categories exist within the rubber processing industry: 1) the tire and inner tube industry; 2) the synthetic rubber industry.

For the purpose of establishing limitations, the tire and inner tube industry has been sub-categorized according to the age of the production facility. Waste loads and costs of control technologies substantiate this. Factors such as the manufacturing process, final product, raw materials, plant size, geographic location, air pollution equipment, and the nature and treatability of wastewaters do not justify further sub-categorization of this industry group.

Process wastewaters for both sub-categories of the tire and inner tube industry include discharges of solutions used in the manufacturing process, washdown of processing areas, run-off from storage areas, and spills and leakage of cooling water, steam, processing solutions, organic solvents and lubricating oils. Primary pollutants in these wastewaters are oil and grease and suspended solids.

In the tire and inner tube industry, the emphasis of present environmental quality control and treatment technologies is placed on the control of particulate emission and the reduction of pollutants in non-process wastewaters. Control and treatment of many process wastewaters has been given secondary priority. As a result, no adequate overall control and treatmen technology is employed by plants within the industry. A treatment system, practicable and available to the industry, has therefore been proposed for both sub-categories. It encompasses a combination of the various technologies employed by the different segments of the industry to control one or more constituents in the process wastewaters.

Proposed effluent limitations and standards for the best practicable control technology currently available (Level I) are:

Suspended Solids 0.064 kg/1000 kg raw material 0.11 and Grease 0.008 kg/1000 kg raw material

No additional reduction is proposed for Level II limitations and standards or for new sources coming on stream after the guidelines are put into effect.

For the purpose of establishing effluent limitations guidelines and standards of performance, the synthetic rubber industry has been sub-categorized, on the basis of processing techniques, product type, and wastewater characterizations, into three separate sub-categories:

- 1. Emulsion crumb
- 2. Solution crumb
- 3. Latex

All three sub-categories generate wastewaters which contain the same constituents. However, the concentration and loading of these constituents, termed "raw waste load", vary between the sub-cateogories. The significant wastewater constituents are COD, BOD, suspended solids, and oil and grease. Latex production wastewaters, although lower in flow per unit of production than the other two categories, have the highest raw waste loads.

The wastewater parameters selected to be the subject of the effluent limitations are COD, BOD, suspended solids, and oil and grease. These parameters are present in the wastewater as a result of organic contamination. Heavy metals or toxic materials were not found in significant quantities in synthetic rubber wastewaters.

Existing control and treatment technology, as practiced by the industry, emphasizes end-of-pipe treatment rather than in-plant reductions. This is because in-plant modifications which might lead to improved wastewater management appear to adversely affect processing techniques or quality of the final product.

Current treatment technology for both emulsion crumb and latex plants involves primary clarification with chemical coagulation of latex solids, followed by biological treatment. As an alternative to chemical coagulation, air flotation clarification of primary and secondary solids is successfully practiced. Biological treatment systems include activated sludge plants and aerated lagoon and stabilization pond systems. Level I control and treatment technology for emulsion crumb and latex plants has been defined as equivalent to chemical coagulation and biological treatment.

Current treatment technology for solution crumb requires conventional primary clarification of rubber solid fines followed by biological treatment. Existing biological treatment systems employ aerated lagoon and stabilization pond systems or activated sludge plants. Level I control and treatment technology for solution crumb production facilities has been defined as equivalent to primary clarification and biological treatment.

Level II technology for the three sub-categories has been defined as equivalent to dual-media filtration followed by activated carbon treatment of the effluent from the biological treatment system to achieve acceptable COD removal. The applicability of this technology for Level II is based on very limited data. The performance capabilities of the proposed Level II treatment systems must be confirmed by further testing and evaluation before approval of this document.

Level III control and treatment has been defined as identical to Level II; that is, equivalent to activated carbon adsorption treatment of the secondary effluent.

The proposed effluent limitations and standards of performance for plants within the three synthetic rubber sub-categories can be summarized as follows, expressed as kilograms of pollutant per 1,000 kilograms of production:

Level 1

	Emulsion Crumb Plants	Solution Crumb Plants	<u>Latex</u> <u>Plants</u>
	kg/1,000 kg	kg/1,000 kg	kg/1,000 kg
COD	8.00	3.94	6.85
BOD	0.40	0.40	0.34
Suspended solids	0.65	0.65	0.55
Oil and Grease	0.16	0.16	0.14

#### Level II and Level III

	Emulsion Crumb Plants	Solution Crumb Plants	<u>Latex</u> <u>Plants</u>
	kg/1,000 kg	kg/1,000 kg	kg/1,000 kg
COD	2.08	2.08	1.78
BOD	0.08	0.08	0 <b>.0</b> 7
Suspended Solids	0.16	0.16	0.14
Oil and Grease	0.08	0.08	0.07

#### SECTION II

#### **RECOMMENDATIONS**

Implicit in the recommended guidelines for the tire and inner tube industry is the fact that process wastes can be isolated from non-process wastes such as utility discharges and uncontaminated storm runoff. Segregation of process sewers is therefore the first recommended step in the accomplishment of the reductions in oil and suspended solid loading necessary to meet the guidelines. Treatment of process wastewaters in a combined process/non-process system is ineffective due to dilution by the relatively large volume of non-process wastewaters.

It is further suggested that uncontaminated waters, such as storm runoff, be segregated from outdoor areas where the potential exists for contamination by oil or solids. This would include roofing and curbing of storage areas and the collection and treatment of runoff which cannot be isolated from such areas.

The training of operators and maintenance personnel is important in any control technology. Negligent dumping of various processing solutions and lubricants into unsegregated drains within the plant must be eliminated or at least severely diminished. Washdown of potentially contaminated areas must be eliminated whenever possible. The number and location of in-plant drains should be kept at a minimum, to reduce the possibility of process wastewater contamination to as few sources as possible.

Wet air-pollution equipment should be kept to a minimum. Discharges from wet equipment already in service should be recycled when possible. The use of dry-type pollution equipment is consistent with recovery efficiencies and prevention of wastewater control problems.

In-plant modifications which will lead to reductions in wastewater flow, increased quantity of water used for recycle or reuse, and improvement in raw wastewater quality should be implemented providing that these modifications have minimum impact on processing techniques or product quality.

End-of-pipe treatment technologies equivalent to secondary treatment should be applied to the wastewaters from all synthetic rubber subcategories to achieve Level I standards. For emulsion crumb and latex plants, chemical coagulation and clarification should be provided prior to secondary treatment.

To achieve Level II standards, end-of-pipe treatment technologies equivalent to activated carbon adsorption of secondary treatment effluent is required on all wastewaters originating in synthetic rubber plants.

Confirmatory tests are necessary to insure that activated carbon adsorption is applicable to secondary effluent wastewaters from synthetic rubber plants. These tests should be performed and evaluated prior to approval by EPA of this document and its findings.

The evaluation of carbon adsorption techniques on synthetic rubber plant wastewaters should include investigation into the character of the refractory or non-biodegradable portion of the organics in the raw waste load. These investigations should be aimed at minimizing their presence in the wastewater as well as changes in their chemical or molecular structure to make them amenable to biological oxidation or alternative treatment or removal methods.

Level III control and treatment standards, to be applied to new sources, are identical to Level II for all synthetic rubber sub-categories; that is, equivalent to activated carbon treatment of secondary treatment effluent.

The treatment, control theory, and effluent guideline recommendations for non-process wastewaters, such as boiler blowdowns, cooling tower blowdowns, and water treatment plant wastes, in the rubber processing industry should be covered by the Steam - Electric Power Generation and Water Treatment effluent guideline documents or by a separate EPA study.

#### SECTION III

#### INTRODUCTION

### Purpose and Authority

Section 301(b) of the Act requires the achievement, by not later than July 1, 1977, of effluent limitations for point sources (other than publicly-owned treatment works) which are based on the application of the "best practicable control technology currently available" as defined by the Administrator pursuant to Section 304(b) of the Act. This best practicable control technology will be referred to as Level I Control and Treatment Technology.

Section 301(b) also requires the achievement, by not later than July 1, 1983, of effluent limitations for point sources (other than publicly-owned treatment works) which are based on the application of the "best available technology economically achievable" which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) to the Act. The best available technology economically achievable as stated above will be called Level II Control and Treatment Technology.

Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants that would reflect the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the "best available demonstrated control technology, processes, operating methods, or other alternatives", including, where practicable, a standard permitting no discharge of pollutants. The best available control technology for new sources as discussed above is to be termed Level III Control and Treatment Technology.

Section 304(b) of the Act requires the Administrator to publish, within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth:

- 1. The degree of effluent reduction attainable through the application of the best practicable control technology currently available.
- The degree of effluent reduction attainable through the application of the best control measures and practices achievable (including treatment techniques, process and procedure innovations, operation methods, and other alternatives).

The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the tire and inner tube and the synthetic rubber subcategories of the Rubber Processing Industry.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b) (1) (A) of the Act, to propose regulations establishing Federal standards of performances for new sources within such categories. The Administrator published, in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the tire and inner tube and synthetic rubber subcategories of the rubber processing industry which were included in the list published on January 16, 1973.

The guidelines in this document identify (in terms of chemical, physical, and biological characteristics of pollutants) the level of pollutant reduction attainable through the application of the best practicable control technology currently available (Level I), and the best available technology economically achievable (Level II). The guidelines also specify factors which must be considered in identifying the technology levels and in determining the control measures and practices which are to be applicable within given industrial categories or classes.

In addition to technical factors, the Act requires that a number of other factors be considered, such as the costs or cost-benefit study and the non-water quality environmental impacts (including energy requirements) resulting from the application of such technologies.

## Summary of Methods Used for Development of the Effluent Limitations Guidelines and Standards of Performance

The effluent limitations guidelines and standards of performance proposed herein were developed in a stepwise manner.

The development of appropriate industry categories and subcategories and the establishment of effluent guidelines and treatment standards require a sound understanding and knowledge of the rubber industry, the processes involved, water use, recycle and reuse patterns, characteristics of wastewater, the respective raw waste loadings, and the capabilities of existing control and treatment methods.

Initial categorizations and subcategorizations were based on raw materails used, product produced, manufacturing process employed, and other factors such as plant age. Published literature was consulted to verify the raw waste characteristics and treatabilities in order to support the initial industry categorizations and subcategorizations.

The raw waste characteristics for each tentative subcategory were then fully identified. Factors considered in this analysis were: the supply and volume of water used in the process employed; the sources of waste and wastewaters in the plant; and the constituents, including thermal, of all wastewaters together with those contaminants which are toxic or result in taste, odor, and color in water or aquatic organisms. The constituents of wastewaters which should be subject to effluent limitations guidelines and standards of performance were identified.

The full range of control and treatment technologies existing within each subcategory was identified. This involved an identification of each distinct control and treatment technology (including both in-plant and end-of-pipe technologies) which are existent or capable of being designed for each subcategory. It also included an identification in terms of the amount of constituents (including thermal), the chemical, physical, and biological characteristics of pollutants, and the effluent level resulting from the application of each of the treatment and control technologies. The problems, limitations/reliability of each treatment and control technology, and the required implementation time were also identified. In addition, the non-water quality environmental impact, such as the effects of the application of such technologies upon other pollution problems (including air, solid waste, noise, and radiation) was also identified. The energy requirements of each of the control and treatment technologies were identified as well as the cost of the application of such technologies.

The information, as outlined above, was then evaluated in order to determine what levels of technology constituted the "best practicable control technology currently available" (Level I), the "best available technology economically achievable" (Level II), and the "best available demonstrated control technology, processes, operating methods, or other alternatives for new sources" (Level III). In identifying such technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects of the application of various types of control technique process changes, the non-water quality environmental impact (including energy requirements), and other factors.

Raw wastewater characteristics and treatability data, as well as information pertinent to treatment reliability and cost evaluations, were obtained from several sources, including: EPA research information, published literature, Corps of Engineers Permit to Discharge Applications, industry historical data, and expert industry consultation. On-site visits and interviews were made to exemplary tire, inner tube, and synthetic rubber production plants throughout the United States to confirm and supplement the above data. All references used in the development and preparation of the guidelines for effluent limitations and standards of performance, as implied by Levels 1, 11, and 111 Control and Treatment Technologies, are included in Supplement B to this document.

## General Description of the Industry

The categories of the rubber processing industry covered by this document are the tire and inner tube (SIC 3011) and the synthetic rubber (SIC 2822). The manufacture of tires and inner tubes utilizes completely different processing techniques than the production of synthetic rubber. In a tire or inner tube plant, stock rubber production follows a very definite formulation or recipe, and is a batching operation.

The mixed stock production is used to produce the four main ingredients of a tire: tire beads, tire treads, treated fabric, and cord fabric. These four components enter the tire building plant, where a significant amount of hand and machine lay-up is required to produce the green tires.

The synthetic rubber (or vulcanizable elastomer) industry is characterized essentially by the chemical process and unit operations necessary to convert the particular monomer or starting-block material into a stabilized, granulated, extruded, or baled material suitable for more conventional rubber processing. The processes are characterized by separation of unreacted monomer, recovery, purification and recycle of the monomer, and processing of the converted elastomer. These reactions are normally carried out batch-wise or batch/continuous.

In view of the fact that these two industry classifications, tire and inner tube manufacture and synthetic rubber production, differ considerably it is appropriate, from this point on, to describe and evaluate their water uses and wastewater generations separately.

### Tire and Inner Tube Industry

### Tire Manufacture

There are many events that have had a significant effect on the tire and inner tube industry. The first is the discovery, by Charles Goodyear in 1839, that rubber could be cured or vulcanized with sulfur. Thus, Goodyear was able to overcome the tacky, plastic properties of rubber, thereby creating a product of commercial applicability (1).

The year 1906 saw the development of the first organic accelerators. Accelerators are substances which affect the rate of vulcanization. With the entry of such substances, better products could be produced in a shorter period of time (1,2).

The next major event to affect the tire industry was the advent of the Second World War. With the drastic reduction in the supply of natural rubber, new sources had to be developed. The first substitute was reclaimed rubber which, by 1943, had completely replaced natural rubber as the basic tire material. It was not until the mid 1940's that synthetic rubber, made available due to a major governmental effort, became

the major substitute for natural rubber. By 1945, approximately 98 percent of the natural rubber had been replaced by this synthetic substitute (3). The years following the war saw the return, to a great extent, of natural rubber. However, with the technological boost given the synthetic rubber industry, it would soon again become the larger portion of the tire.

The next major event occurred in the mid 1950's and concerned the introduction of tubeless tires as original equipment on new cars. The 1950's ushered in the first tubeless tire, and major changes were made in tire design. Butyl rubber became a major constituent of automobile tires. At the same time, it sent the inner tube industry into a rapid decline. The total number of inner tube units produced declined from over 49 million in 1954 to under 25 million in 1955 (4).

The tire industry has had three eras of rapid expansion to coincide with these events. The post World War I era (1916-1929) brought the first such development. As the automobile and truck industry expanded, so did the tire industry. Large capacity tire plants were built in Ohio, California, and New England. The depression reversed this trend however, and it was not until World War II created an increased demand for tires that the tire industry again began to expand. New plants were erected in Ohio, New England, and the South. The third building expansion started in the early 1960's and is still proceeding, again occurring simultaneously with the expansion of the economy.

With the current expansion, tire companies are now located throughout the United States. Whereas the older plants of the first two expansions are located in the urban areas of Ohio, California, and New England, the newer plants are being located in rural areas with no particular emphasis placed on georgraphy.

Today's tire manufacturer produces many types of tires designed for a multitute of uses. General product categories include passenger, truck and bus, farm tractor and implement, and aircraft. Table III-1 presents a breakdown of these products for the last five years.

The key to the performance of all tires is the selection of the raw rubber and compounding materials and the proportion of these materials in any particular part of the tire. Basically, the tire consists of five parts, namely: the tread, the sidewall, the cord, the bead, and the inner liner. Each part has different service requirements; therefore, each requires a different proportion of the raw materials. For example, longevity and good traction are requirements of the tread, whereas a high degree of flexibility is the requirement for sidewalls. Basic tire ingredients include synthetic rubber, natural rubber, various fillers, extenders and reinforcers, curing and accelerator agents, antioxidants, and pigments.

A wide variety of synthetic rubbers are used inlouding SBR, polybutadiene, butyl, polyisoprene, and EPDM. Of the three categories of compounding

Table III-1

U.S. Tire and Inner Tube Production (Including Retreading)
for 1967-1971

			Tires (in million units)				
<u>Year</u>	Passenger Cars	Trucks and Buses	Farm Tractor and Implement	<u> Aircraft</u>	Miscellaneous 1	Inner Tubes <sup>2</sup> million units	Retreading Rubber <sup>2</sup> million pounds
1967	100.006	21.165	5.554	0.772	16.445	60.479	563.307
1968	128.967	25.533	5.741	1.040	17.870	65.840	610.108
1969	134.540	27.211	4.058	0.892	18.421	60.875	598.417
1970	123.356	25.680	3.568	0.822	6.866	51.534	622.413
1971	138.151	28.461	4.099	0.731	9.409	55.067	608.476

Source: "Rubber Industry Facts", Statistical Department, Rubber Manufacturers Association, New York.

 $<sup>\</sup>overset{1}{2}$  includes motorcycle, industrial, garden tractor, and bicycle tires. Includes all tire classifications.

materials used, the fillers, extenders and reinforcers are the most important. These are used:

- To dilute the raw crumb rubber in order to produce a greater weight or volume.
- 2. To increase the strength, hardness, and abrasion resistance to the final product.

Of this group, carbon black and oil are the most common. A typical rubber compound might be described as follows (1):

100 parts rubber

50 parts fillers, extenders, and reinforcers

3.5 parts curing and accelerator agents

8.0 parts antioxidants and pigments

The typical tire manufacturing process consists of the following:

- 1. Preparation or compounding of the raw materials.
- 2. Transformation of these compounded materials into the five tire components.
- 3. The building, molding, and curing of the final product.

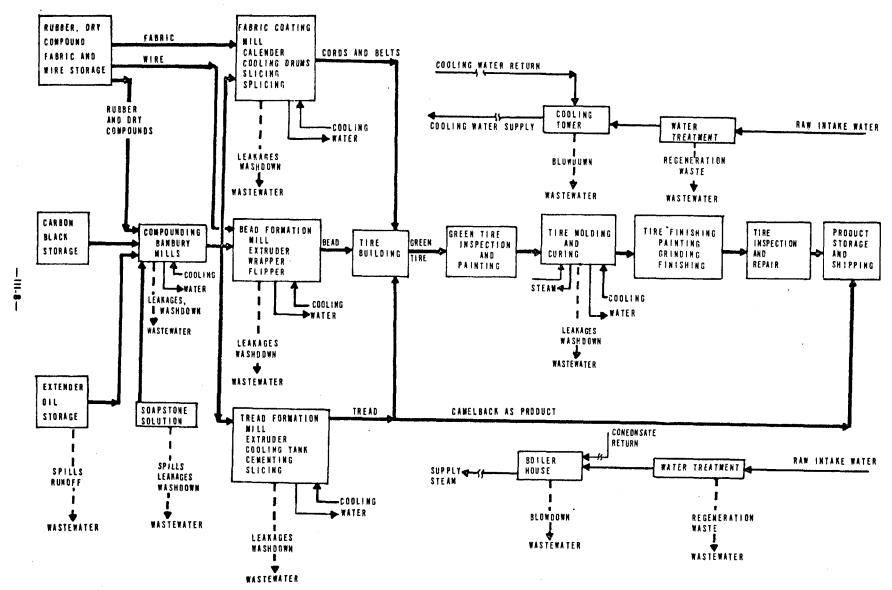
A flow diagram for the typical plant is shown in Figure III-1.

The basic machinery units used in the compounding operation are the Banbury mixer and the roller mill. A Banbury mixer is a batch-type internal mixing device and is the hub of this compounding operation. The Banbury is used for two operations. In the first, the fillers, extenders and reinforcing agents, and the pigments and antioxidant agents are added and mixed into the raw rubber stock. The resulting mixture is known as non-productive or non-reactive rubber stock. Because no curing agents have been added, this material will have a long shelf life, thus allowing large quantities of a particular recipe to be made and stored for later use. In the second operation, the curing and accelerator agents, in additon to a small quantity of the original list of elements, are added. This mixture, known as productive or reactive rubber stock, now meets the particular compounding requirements of its final destination. Since it contains the curing agents, this mixture has a short shelf life and will be used almost immediately.

Carbon black and oil are usually added automatically in the compounding operation. The other compounds (including the raw rubber) are manually weighed and fed to the Banbury. The reasons for the automatic handling equipment are:

- 1. The large quantities of these materials consumed.
- 2. To ease the maintenance and housekeeping problems created by both the oil and carbon black.

FIGURE III-1
FLOW DIAGRAM FOR TYPICAL TIRE AND CAMELBACK PRODUCTION FACILITY



Carbon black is a finely divided amorphous material that has the consistency of dust. Once left unconfined, it creates a massive air pollution problem. The compounding area is equipped with air pollution equipment to control this problem. Normal procedure is to use a bag house.

After mixing, the compound is sheeted out in a roller mill, extruded into sheets, or pelletized. The process depends on the type of batch (reactive or non-reactive) and the manufacturer. Pelletizing of a non-reactive batch enables the weighing and mixing of the reactive stock to be done automatically. The reactive compounded rubber is always sheeted out.

The sheeted material is tacky and must be coated with a soapstone solution. This solution is a slurry which, when allowed to dry on the sheeted materials, prevents them from sticking together during storage.

Because it is a slurry the soapstone solution is usually recirculated. Releasing the material into a wastewater stream would create a difficult solids problem. Spills in the soapstone area are common and do create a maintenance and wastewater problem.

If a manufacturer wishes to exclude soapstone in his final effluent, he must provide a method for coping with these spills. Current techniques include the blocking of all drains in the area, diking of the area, and the use of steel grates on the floors. The diking and sealing of drains prevents the slurry from entering the drainage system. The use of steel grates helps decrease the risk of workers slipping on spilled soapstone.

Maintenance and housekeeping problems in this area are further complicated by the leakages of oil and water from the oil seals in the mills, and oil and dust from the dust ring seals of the Banburys. Each has the potential to become a wastewater pollutant if allowed to mix with the cooling water discharges or to be washdowned and discharged without treatment.

The rubber stock once compounded and mixed must be molded or transformed into the form of one of the final parts of the tire. This consists of several parallel processes by which the sheeted rubber and other raw materials, such as cord and fabric, are made into the following basic tire components: tire beads, tire treads, tire cords, and tire belt (fabric). Tire beads are coated wires inserted in the pneumatic tire at the point where the tire meets the steel rim (on which it is mounted); they insure a proper (and possibly air tight) seal between the rim and the tire (2). The tire treads are the part of the tire that meets the road surface; their design and composition depend on the use of the tire. Tire cords are woven synthetic fabrics (rayon, nylon, polyester) impregnated with rubber; they are the body of the tire and supply it with most of its stregth. Tire belts stabilize the tires, prevent the lateral

scrubbing or wiping action that causes tread wear, and reduce heat build up, a major cause of tread wear (2).

In the formation of tire treads, the rubber stock as it is received from the compounding section is manually fed to a warm-up roller mill. Here the rubber is heated and further mixed. Heat is provided by the conversion of mechanical energy. Temperature control is provided by the use of cooling water within the rolls of the mill.

The heated stock passes from the warm-up mill to a strip-feed mill where it receives its final mixing. This mill is also cooled to control the temperature of the stock. The stock is peeled off the rollers of the mill in a thin strip which is fed continuously to an extruder. The mixing of the stock in these mills insures that the final tread will have homogeneous properties. The heating or temperature control of the stock is necessary to insure a proper extrusion with a minimum consumption of power (2).

At the extruder, two types of rubber stocks originating from two different strip mills are joined together to form the tire tread and sidewalls. The tread leaves the extruder as a continuous trip while still hot and therefore tacky. Next a cushioning layer is attached to the lower side of the tread. The tread is then cut to the proper width, cooled in a water trough, labeled, cemented, and then cut to the proper length. Trimmings are either manually or automatically transferred back to the proper strip-feed mill and reprocessed. Having been cut, the ends are cemented, and the tread is placed in a "tread book" and sent to the tire building machines.

Wastewater problems in this area arise from the spillage of the solvent base cements, from oil and water leakages from the various mills, and from accidental overflows from the cooling water system. The cooling water overflow would not normally be a problem since the rubber tread is relatively inert and therefore does not contaminate the water. However, it does serve as a washdown agent for an area contaminated with the cements and oils.

To produce tire cords and belts, rubber stock must be impregnated onto a pretreated fabric. The fabric is let off a roll, spliced onto the tail of the previous roll (either adhesively or by a high-speed sewing machine), and fed under controlled tension (via a festooner) to a latex dip tank. After dipping and while still under tension, the fabric is fed past vacuum suction lines or rotating beater bars to remove the excess dip before the fabric rises through a drying and baking oven.

After pretreatment, and still under tension, the fabric is passed through a calendering machine where rubber is impregnated into the fabric. The rubber fabric is next cooled by large water or refrigerant cooling drums; after cooling, the tension can be released. This treated fabric is still

not ready for the tire building operation. To achieve the proper bias it must be cut to the proper angle and length, and then spliced together again. The angle and length will vary depending on the size of the tire for which it is used and whether it is a cord or belt. Once spliced together, the fabric is rolled in cloth and sent to tire building.

The rubber used to impregnate the fabric proceeds through an operation similar to that of the tread process. It passes through both a warm-up mill and a strip-feed mill prior to impregnation onto the fabric. Wastewater problems in this area arise due to the latex dripping operation and to problems with oil and water leaks and spillages which are similar to those of the tread process.

Many tire manufacturers are transferring their latex dip operations from individual plants to one large central facility. In most cases, the reasons behind such a decision are as follows:

- 1. A minimal dipping operation requires a large capital expenditure.
- 2. The fabric dipping and coating operation is one of the fastest operations in the plant and, as such, is readily capable of over-supplying the plant with fabric.
- 3. Dipped fabric is not that more expensive to ship then undipped fabric.
- 4. The maintenance and housekeeping requirements of the dip operation are limited to one facility.

In the processing of rubber stock to tire beads, the rubber is extended onto a series of copper-plated steel wires, then cemented, wrapped, and cut. The rubber stock is pretreated, as before, in a warm-up mill and strip-feed mill. Excess rubber is trimmed from the bead before it leaves the extruder and is fed back to the strip feed mills. To apply cement the coated wire is passed through a trough or set of brushes. The cement is necessary to insure the proper adhesive of the bead when it is wrapped.

Wastewater problems can arise due to the use of the mills or from the spillage or overflow of the cement. They will be similar in nature to those found in this tread formation process.

The inner lining of the two is formed by calendering or extruding the rubber stock in a manner similar to either the formation of cord fabric or tread rubber. It is this inner liner that enables a tire to be tubeless since it is light and relatively air impervious.

The tire is built up as a cylinder on a collapsible, round rotating drum. First the inner liner is applied to the drum. Then layers of cord are

applied, one layer tying the beads together in one direction and another layer in the other direction. The beads are stiched to the tire by folding over the ends of the cord fabric. Next the tire belt fabric is laid onto the cord. Finally the tire tread is placed over the cords and fabric and wrapped around the beads. The cylinder is removed. These green tires (uncured tires) are now ready for final processing.

Washdown of solvents from this area can create a wastewater problem; however, this is normally dry and therefore very pollution free. Before molding and curing, the green tire must be sprayed with release agents. These agents aid in the release of air from the tire during molding and of the tire from the mold after curing. Both water- and solvent-based spray are used. Excess spray is released to the atmosphere. Most plants now place the tires in a hood before spraying in order to meet federal air quality standards.

The potential for wastewater streams exist due to the possibility of solvent spills within this area. If wet scrubbers are used to scrub the excess spray from the air, another wastewater stream will exist.

The tire is molded and cured in an automatic press. Here an inflatable rubber bladder bag is blown up inside the tire, causing the tire to take its characteristic doughnut shape. The mold is simultaneously closed over the shaped tire. Heat is applied by steam via the mold and bladder bag. Excess rubber and trapped air escape through weepholes. After a timed, temperature-controlled cure, the press is cooled, the bladder is deflated via a vacuum, and the tire is removed. The tire is next inflated with air and left to cool in the atmosphere. This last inflation insures product quality and uniformity by allowing the tire to "set up" or achieve the final limits of its cure under controlled conditions.

Because of the large number of presses in the typical plant, there is always the potential for a mold to leak or for a bladder to break. This water is released and scavenges some of the large amounts of lubricating oil used in this area. This oily water creates a water contamination problem if it is discharged.

After the molding and curing operations, the tire proceeds to the grinding operation where the excess rubber which escaped through the weepholes is ground off. If the tire is designated to be a whitewall, additional grinding is performed to remove a black protective strip. More expensive tires receive further grinding of the tread in order to balance the tire.

The weepholes which are ground off are relatively large particles of rubber which fall to the floor and are swept up. Their final destination is a landfill. The grindings from the white sidewall operation are relatively small and will stay airborne for long periods of time. The industry generally uses a particulate collection device such as cyclone

or wet scrubber to control these emissions. The discharge from a wet scrubber will have a high solids content and will therefore be a wastewater problem. The balancing operation suffers the same problems as the white sidewall grinding operation.

After the grinding operations, the whitewall portion of a tire receives a protective coat of paint. The paint is generally water based. This operation usually occurs in a hooded area. Again, any wet air pollution equipment or runoff due to over spraying of the paint will create pollution problems. After inspection and possibly some final repairs, the tire is ready to be shipped.

Table III-2 presents a review of the potential sources of wastewater streams as discussed above.

The discussion thus far has described a typical tire plant, and applies most readily to the production of the passenger tire. There are several variations. The first of these is due to the production of truck and industrial tires. Truck tires tend to have a greater amount of natural rubber in their treads. Natural rubber, as received in the plant, is much harder to handle than synthetic rubber. Additional roller mills are needed to break up and soften the rubber before it enters the Banbury mixer. There are also major differences in the building and molding of the tires as the larger sizes are approached. The building of a "giant off-the-road tire" requires the services of two men each for a half a day, whereas the passenger tire can be built in less than 5 minutes. Larger tires are cured in giant molds which are not automatically operated. Cranes or hoists are required to open and close this mold. Curing can take up to 24 hours. Hot water, instead of steam, is used in the curing operation. The process variations associated with truck and industrial tire production do not have a significant effect on the quantity and quality of the wastewaters generated when compared to those from automobile tire production.

Another variation in the typical tire production is the manufacture of camelback. Camelback is tread used for tire retreading (2). It is produced in the same manner as tread used for new tires. (See flow diagram, Figure III-1.)

Camelback production operations are usually part of a tire production facility feeding off the same machinery. Wastewater problems will be similar to those already discussed.

Radial tire production offers another variation to the overall process. Radial tires, like truck tires, contain more natural rubber, thus requiring more machinery in the compounding area. Whereas bias-ply tires are built in the form of a hollow cylinder, radial tires are built in the doughnut shape of the final product. Like truck tires, radial tires are cured using hot water instead of steam. Again wastewater problems will be very similar to those of the typical passenger tire manufacture.

Table III-2

Summary of Potential Process-Associated Wastewater
Sources from the Tire and Inner Tube Industry

Plant Area	Source	Nature and Origin of Wastewater Contaminants
Oil Storage	Run off	0:1
Compounding	Washdown, spills, leaks, discharges from wet air pollution equipment	Solids from soapstone dip tank Oil from seals in roller mills Oil and solids from Banbury seals Solids from air pollution equipment discharge
Bead, Tread, Tube Formation	Washdown, spills, leaks	Oil and solvent-based cements from the cementing operation Oil from seals in roller mills
Cord and Belt Formation	Washdown, spills, leaks	Organics and solids from dipping operation Oil from seals, in roller mills, calenders, etc.
Green Tire Painting	Washdown, spills,air pollution equipment	Organics and solids from spray painting operation Soluble organics and solids from air pollution equipment discharge
Molding and Curing	Washdown, leaks	Oil from hydraulic system Oil from presses
Tire Finishing	Washdown, spills, air pollution equipment	Solids and soluble organics from painting operation Solids from air pollution equipment discharge

### Inner Tube Manufacture

Inner tube manufacture is very similar to tire manufacture in that the process consists of the following steps:

- 1. Preparation or compounding of the raw materials.
- 2. The extension of these compounded materials to form a tube.
- 3. The building, molding, and curing to form the final product.

A flow diagram for the typical process is shown in Figure 111-2.

The basic machinery used in the compounding operation is identical with that used in the tire manufacture, namely, Banbury mixers and roller mills. Both non-reactive and reactive stocks are used. Differences arise since inner tubes are manufactured primarily from butyl rubbers. In addition, a soap rather than a soapstone solution is sometimes used to coat the non-reactive stock. Wastewater problems arising from this section are identical to those of the typical tire compounding area, i.e., leakages and dripping of oily and particulate material.

The process by which the tube is formed is similar to the extrusion of the tread. The compounded rubber is fed to an extruder via a warm-up mill and strip-feed mill. Here the rubber is extruded into a continuous cylinder, after which it is cooled and labeled. To keep the inside of the tube walls from sticking to each other, a dry soapstone powder is sprayed inside the tube as it is formed in the extruder. After cooling, the water is blown out of the tube and the same powder is sprayed on the outside of the tube. Excess powder must be collected in each dry or wet collection device. If a wet collection device is used, the discharge will be heavily laden with solids. Other wastewater problems are similar to those found in the tread formation process of tire manufacture.

Once extruded, the tube must be cut to length and the ends spliced together. A valve must also be attached. There is no potential wastewater problem arising from this area of operation.

Once formed, the tube must be molded and cured. Again, this operation is very similar to that of the tire manufacture. Wastewater problems include only water leakage and spills.

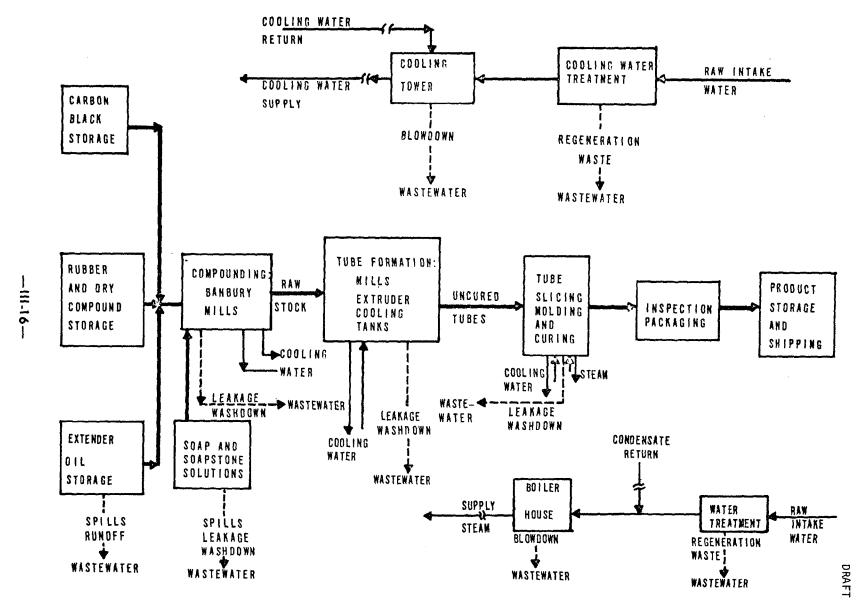
After curing, the tube is inspected for defects, packaged and sent to warehousing and shipping. Table III-2 summarizes the potential sources of wastewater streams as discussed above.

## Synthetic Rubber Industry

#### General

The synthetic rubber industry is responsible for the sythesis of vulcanizable elastomers by polymerization or co-polymerization processes. For

FIGURE 111-2
FLOW DIAGRAM FOR A TYPICAL INNER TUBE PRODUCTION FACILITY



the purpose of this classification, an elastomer is a rubber-like material capable of vulcanization.

The U.S. Synthetic Rubber Industry was fostered by the commencement of World War II when it was realized that supplies of natural rubber could be shut off by the enemy. The rubber first chosen for production was called GR-S (Government Rubber-Styrene) and would now be grouped under SBR (styrene-butadiene rubber). Since the war the price of natural rubber has been subject to great fluctuations, whereas the price stability of synthetic rubbers has undoubtedly contributed to their acceptance by the consumer. Since the introduction of GR-S, many new synthetic rubbers have been synthesized and produced on a commercial scale.

The demand for the various types of synthetic rubber is greatly affected by the needs of the tire manufacturers. Not only are tire sales important, but process and product changes within the tire industry also influence the relative demands for the various rubbers. For example, radial tires at present contain considerably more natural rubber than conventional tires. At this moment, this has little effect on the consumption of synthetic rubber because radial tires constitute a small percentage of total tire production, but it does illustrate the kind of factor which can influence synthetic rubber consumption. The U.S. production of the principal synthetic rubbers for the last several years is presented in Table III-3 together with the growth projections for the period between now and 1980. It can be seen that production of SBR-type rubber overshadows other synthetic rubber. Although the greatest growth rates over the next several years will be associated with polyisoprene and ethylene-propylene terpolymer (EPT) productions, overall the relative levels of synthetic rubber production will not be appreciably different from what they are today because the present base productions of polyisoprene and EPT are considerably lower than that of SBR, the principal synthetic rubber (5). This supports the assumption that there will be no radical changes in the industry, its products, and even its production processes in the foreseeable future.

The synthetic rubbers as listed under SIC 2822 include both the so-called tire rubbers and the specialty rubbers. The tire rubbers are typically high production volume commodities, and, as their name suggests, they are used predominantly by the tire industry. Rubber used in the tire industry is supplied in a solid form termed crumb rubber. Several different families of tire rubber are made in order to provide all the essential and varying properties required in a modern vehicle tire.

Not all tire rubber production is used in tire manufacture however. Much is used to manufacture rubber hose, belting, electrical wire and cable, footwear, mechanical rubber goods, and many other rubber-based products. Due to their superior oil and heat resistance, both nitrile and neoprene type rubbers are used more for hose, seals, gaskets, and 0-rings than for tire manufacture. However, because their annual production

Table III-3

U.S. Synthetic Rubber Production by Type (1,000 Long Tons) for 1967 to 1971 and the Projected Growth Rate to 1980

<u>Years</u>	S-Type	<u>Butyl</u>	Nitrile	Polybutadiene	Polyisoprene	Ethylene Propylene	Misc. 1	Total
1967	1,244	114	62 ·	201		05	186	1,912
1968	1,389	113	71	217		40	201	2,131
1969	1,403	130	69	263	109	75	201	2,250
1970	1,331	118	67	280	120	63	218	2,197
1971	1,417	106	65	254	117	60	222	2,241
Projected Growth Rate (%)	3.4	2.7	5.2	7.0	16.0 to 1975 8.0 to 1980	16.0 to 1975 10.0 to 1980		

Sources: Production data from "Rubber Industry Facts", Statistical Dept., Rubber Manufacturers Association.

Growth rate production furnished by Chem System, Inc., New York.

<sup>1</sup> Includes Polychloroprene (Neoprene) rubber

volume is comparable with four of the other five major synthetic rubbers used in tire manufacture, they will be considered here as tire rubbers. The tire rubbers are grouped into seven families based on their monomeric ingredients as shown in Table III-4. The annual U.S. production, polymerization process, principal end-use and other family members are also presented.

By contrast, the speciality rubbers are low production volume commodities with more diverse compositions and end uses. The largest production volume family of the speciality rubbers are the butadiene rubbers. Butadiene rubbers are generally sold in latex form. The production is similar to the production of all synthetic rubber latexes (2). Epichlorohydrin is solution polymerized with various co-polymers to produce the family of epichlorohydrin rubbers. The process is similar to that for solution tire rubbers. Epichlorohydrin rubbers are used for seals, gaskets, and 0-rings, etc. (6). The acrylic rubbers are produced by an emulsion polymerization process similar to the emulsion processes used for drive-train and axle seals, hose, tubing, and molded parts. Polyisobutylene is produced by a solution polymerization process similar to that for butyl rubber (1). It is used primarily as a blend in caulking compounds, adhesives, and plastics.

Three of the so-called specialty rubber families (silicone rubbers, urethane rubbers, and fluorocarbon derivative rubbers) are being studied as part of the plastics industry and, as such, are not covered in this document. The chlorinated and chlorosulfonated polyethylene rubbers are manufactured by processes similar to those employed for the polyethylene type plastics and are not covered in this document (2). The polysulfide rubbers are produced by a condensation process which is different from the general emulsion and solution polymerizations (2). In addition, the wastewaters generated by polysulfide production are highly contaminated and deemed more difficult to treat than the wastewaters produced by conventional emulsion or solution polymerization processes. It is therefore recommended that a separate study be made of the polysulfide rubber sector of the synthetic rubber industry.

The various methods of production of the synthetic rubber have much in common. The monomers are not particularly difficult to handle at reasonable pressures, and suitable inhibitors have been developed to impart storage stability. Dissipation of the heat of polymerization is frequently the controlling consideration. Adjustment of reaction rate to distribute the heat generation over a reasonable period of time, the use of refrigeration cooling, and operation in dilute media such as emulsions or solutions are necessary for the adequate control of polymerization reactions.

Control of molecular weight and of molecular configuration has become a very important quality consideration. The ability to control molecular weight has led to the development of oil-extended rubber. It has been found that rubber of unusually high molecular weight and normally too

TABLE 111-4

Families of Synthetic Rubbers Included in SIC 2822, Polymerization Processes, and Annual U.S. Production (1972)

Principal Synthetic Rubber	Annual U.S. Production (1,000 Metric Tons/year)	Polymerization Process	Principal End-use	Other Family Members
	(1) source (subject)			
Tire Rubbers yrene-Butadiene rubbers (SBR)	1,678 139	Emulsion Solution	General tire use Tire treads	
lybutadiene rubbers (PBR)	368	Solution	Tire treads	
lyisoprene rubbers	139 •	Solution	Tire treads	
Sylisobutylene-Isoprene rubbers (Butyl)	163	Solution	Inner tubes	
hylene-Propylene Co-polymer rubbers (EPR)	169	Solution	General tire use, non-tire goods	EPDM
rylonitrile-Butadiene rubbers (Nitrile) <sup>1</sup>	159	Emulsion	Hose, seals, gaskets, - O-rings	
lychloroprene rubber (Neoprene)	177	Emulsion	Non-tire use, general tire	Neoprene, Nitrile-Chloro-
Tire Rubber Sub-Total:	2,992		use	prene rubber, Styrene Chloroprene rubber
Specialty Rubbers				
tadiene rubbers	64	Emulsion	Adhesives, dipped goods, paints	Pyridine-Butadiene rubber
ichtorphydrin rubber	9	Solution	Seals, gaskets and O-rings	Cyclo rubber
r <sub>e</sub> lic rubbers	2	Emulsion	Seals, hosing, tubing	Acrylate type rubber, Acrylate-Butadiene rubber
lyisobutylene rubbers	4	Solution	Caulking, adhesives, plastics	
Ticone rubbers <sup>2</sup>	10	Condensation	Seals, gaskets, electri- cal tape	·
lyurethane rubbers <sup>2</sup>	14	Condensation	Solid tires, rollers, foams, fibers	Adiprene, Estane, Iso- cynate type rubber
Jorocarbon derivative rubbers 2	1	Emulsion .	Seals, gaskets, O-ring, high temperature service	Viton, Fluoro rubber
lorosulfonated Polyethylenes <sup>3</sup>	. 15	Post-polymeriza- tion chlorination	Wire and cable, shoes, linings, paints	Chiorinated rubber, Hypalon
lysulfide rubbers	10	Condensation	Sealing, glazing, hose	Thiol
Specialty Rubber Sub-Total	129			
Synthetic Rubber Total .	3,121			

Although Nitrile and Neoprene-type rubbers are not normally termed tire rubbers, they are relatively large production volume rubbers and, for convenience, can be included with the major tire rubbers.

Silicone, Polyurethane and Fluorocarbon derivative rubbers are considered part of the Plastics and Synthetics Industry and are not covered by this

Chlorosulfonated and chlorinated polyethylenes should be considered part of the Plastics and Synthetics Industry. They are not covered by this

Polysulfide rubbers are produced by a condensation-type reaction which is not directly comparable to either emulsion or solution polymerization. Per unit of rubber production, generated wastewaters are of considerably poorer quality and more troublesome to treat than those of either emulsion or solution processes. Polysulfide rubber production is not covered by this document. It is recommended that a separate study be made of the polysulfide rubber industry.

Source: "The Rubber Industry Statistical Report" - C.F. Ruebensaal, International Institute of Synthetic Rubber Producers, Inc.

tough to process through factory equipment can be made workable by the addition of up to 50 parts of petroleum-base oils per 100 parts of rubber. These extending oils make the rubber easier to process without sacrifice in physical properties. Another improvement has been the preparation of black masterbatches, the name given to mixtures of carbon black and rubber without the curing ingredients. This process is of great importance to small manufacturers and tire retreaders who lack facilities for mixing in carbon black or who wish to avoid atmospheric pollution with the fine black.

## Synthetic Rubber Production

## Emulsion Crumb Production

Of the several methods of polymerization employed to produce synthetic rubber, the two most commonly used processing techniques are polymerization in homogeneous solution and polymerization in emulsion. Solution polymerization may be considered to include bulk polymerization where excess monomer serves as a solvent. Emulsion polymerization may be considered as the bulk polymerization of droplets of monomers suspended in water. Emulsion polymerization is performed with sufficient emulsifier to maintain a stable emulsion. Solution polymerizations generally proceed by ionic mechanisms. However, polymerization initiators which operate by ionic mechanisms are usually too reactive to be stable in water; therefore, emulsion polymerization systems are initiated by agents which produce free radicals (2).

Emulsion polymerization is the traditional process for the production of synthetic rubber. Since World War II (and for the foreseeable future), the bulk of synthetic rubber has been produced via emulsion polymerization. The use of emulsion polymerization systems is common because both high conversion rates and high molecular weights are possible. In addition, other advantages are: a high rate of transfer of the heat of polymerization through the aqueous phase, ready removal of unreacted monomers, and high fluidity even at high concentrations of polymer. The majority of styrene-butadiene rubber (SBR), the principal synthetic rubber, is produced by emulsion polymerization. The emulsion polymerization process is used to produce either rubber latex or rubber crumb. Crumb is solid and is usually formed into 75 pound bales.

Figure III-3 shows a generalized materials flow diagram for the continuous production of crumb SBR by the emulsion polymerization process. This schematic is essentially typical of all emulsion processes. In the typical production facility, operation is 24 hours per day, 365 days per year. Each plant consists of several production lines where different process recipes can be applied and various types of SBR can be produced, including non-extended, oil extended, and carbon black masterbatch varieties.

COAGULATING COAGULATING SULFURIC BRINE ACID WASTEWATER HEAVY LIGHT SCREEMS CL.
SCREEMS CL.
WWW.MYCHO CL.
CELTRATER RETURN
FILERATE MONDMER WASTEWATER MONOMER SEPARATION SEPARATION COOLING COOLING RAW INTAKE WATER WASTEWATER TOWER TREATMENT WATER RECYCLE RECYCLE COOLING WASTEWATER BLOWCOWN WATER UNINHIBITED MONOMER SHORT SUPPLY WASTEWATER STOP ANTIOXIDANT CRUMB RINSING PRODUCT MOHOMER COAGULATION STEM LATEX NOW ON ER POLYMER-VACUUM STORAGE INH ( B) TOR **CRYING** BALING STORAGE STORAGE STRIPPING DISTILLATION AH D I ZATION REMOVAL SCREENING DEWATERING SHIPPING AMD REACTORS WASH INNIBITED MONOMER EQUIPMENT CLEANUP SPENT LIVE STEAM EQUIPMENT **EQUIPMENT** EQUIPMENT CLEANUP CAUSTIC CLEANUP B LIVE CLEANUP F WASTEWATER - STEAM EQUIPMENT 🕹 CLEANUP STEAM SOAP WASTEWATER WASTEWATER WASTEWATER WAS TEWATER WASTEWATER TREATED PROCESS WATER SDAP EXTENDER DIL SOLUTION CARBON BLACK SURRY TREATED TREATED PROCESS PROCESS WATER WATER CONDENSATE ACTIVATOR RETURN PACTIVATOR CATALYST CATALYST MODIFIER MODIFIER SELUTIONS SUPPLY EXTENDER OIL STREAM BOILER MAKEUP HOUSE BOILER FEED WATER WATER RAW INTAKE WATER TREATMENT WATER CARBON BLACK CAR BON UNITS SLURRY **BLACK** BLOWDOWN REGENERATION SPILLS WASTE WASTEWATER WAS TEWATER

WASTEWATER

FIGURE III-3
GENERAL WATER FLOW DIAGRAM FOR AN EMULSION POLYMERIZED CRUMB RUBBER PRODUCTION FACILITY

Styrene and butadiene (referred to as monomers) are either piped to the plant from adjacent suppliers, or shipped in by tank car or tank truck. The monomers are stored in a tank farm which is diked to retain major monomers spills and leakages and, in the case of fire, to control the spread of flaming liquid. The fresh monomers are piped to the plant from the tank farm and, if necessary, passed through a caustic soda scrubber before mixing with recycle monomers. Some monomers, such as butadiene, have inhibitors added to prevent premature polymerization during shipment and storage. These must be removed before the monomer can be polymerized. The inhibitor is removed in the caustic scrubber by the circulation of a caustic soda solution, approximately 20 percent. The caustic soda solution is discarded periodically or can be subjected to continual make-up and blowdown.

Soap solution, catalyst, activator, and modifier are added to the monomer mixture prior to entering the polymerization reactors. The soap solution is used to produce an emulsion of the monomers in an aqueous medium. The principal ingredients of this solution are generally a rosin acid soap and a fatty acid soap. Thy catalyst is a free radical initiator and can be a hydroperoxide or a peroxysulfate. The catalyst initiates and promotes the polymerization reaction. The activator assists in generating the free radicals more rapidly and at lower temperatures than by thermal decomposition of the catalyst alone. The modifier is an additive which adjusts the chain length and molecular weight distribution of the rubber product during polymerization. It is necessary that all the above solutions be made with high quality water. Usually city or well water is deionized for the preparation of the solutions.

The polymerization proceeds stepwise through a train of reactors. The reactor system is capable of producing either "cold" (40-45°F, 0-15 psig) or "hot" (122°F, 40-60 psig) rubber. The "cold" SBR polymers, produced at the lower temperature and stopped at 60 percent conversion, have improved properties when compared to "hot" SBR's. The "hot" process is the older of the two. For "cold" polymerization, the monomer-additive emulsion is cooled prior to entering the reactors, generally by using an ammonia refrigerant cooling medium. Depending on the polymerization temperature, the medium could be chilled brine or chilled water. In addition, each reactor has its own set of cooling coils, usually containing ammonia refrigerant, and is agitated by a mixer. The residence time in each reactor is approximately one hour. Any reactor in the train can be by-passed. The reactor system contributes significantly to the high degree of flexibility of the overall plant in producing different grades of rubber. The overall polymerization reaction is ordinarily carried to no greater than 60 percent conversion of monomer to rubber since the rate of reaction falls off beyond this point and product quantity begins to deteriorate. The product rubber is formed in the emulsion phase of the reaction mixture. The reaction mixture is a milky white emulsion called latex.

Short stop solution is added to the latex leaving the reactors to stop the polymerization at the desired conversion. Two common short stop ingredient are sodium dimethyl dithiocarbamate and hydroquinone. The "stopped" latex is held in blowdown tanks prior to the stripping operation. The blowdown tanks act as flow regulating holding tanks.

Recovery of the unreacted monomers and their purification is an essential step in economic synthetic rubber production. Butadiene, which has a lower boiling point than styrene, is first vacuum stripped from the latex. stripping operation is generally carried out in a vacuum flash tank at about 80-90°F. The butadiene vapors are compressed and condensed before entering a receiver. A very small quantity of water collects in the receiver and is discharged periodically. The condensed butadiene is recycled to the feed area and mixed with fresh monomer prior to the polymerization step. Styrene recovery from the latex usually takes place in perforated plate stripping columns. These operate with steam injection at approximately 140°F. The steam-styrene vapor mixture is condensed and sent to a receiver where the styrene and water are decanted. top styrene layer is recycled to the monomer feed stage; the bottom layer of the receiver, which is styrene-laden water, is discharged. vacuum and steam strippers foul periodically with rubber solids. These must be removed by hand, followed with both steam or water jets. This cleaning operation puts the stripper out of commission and produces large quantities of wastewater.

An antioxidant to protect the rubber from attack by oxygen and ozone is added to the stripped latex in a blend tank. The latex is now stabilized and, as a result, different batches, recipes, or dilutions can be mixed. These mixing operations take place in the blend tanks. The latex is pumped from the blend tank to the coagulation step where dilute (pH 4-4.5) sulfuric acid and sodium chloride solution are added. The acid brine mixture is called the coagulation liquor and causes the rubber to precipitate from the latex. Theoretically, precipitation will occur with a coagulation liquor consisting of any combination of electrolyte and dilute acid. However, the quality and intended end use of the rubber limit the choice of coagulants. For example, some types of "hot" SBR which are used as insulation covering on electrical wire are coagulated with an acid-polyamine solution in order to produce a rubber with low electrical conductivity.

As mentioned earlier, rubber can be extended to improve its properties by using oils and carbon black. Carbon black and oil can be added to the latex during the coagulation step to produce a more intimate mixture than can be obtained by the subsequent addition of these materials to the crumb rubber as is the case with conventional rubber compounding. Wastewaters generated subsequent to the masterbatch operation (addition of carbon black) are usually black due to colloidal carbon black particles. The oil is added as an aqueous emulsion, and carbon black is blended

into the latex as an aqueous slurry (approximately 5 percent by weight). There are various types of extending oils; some are staining and others non-staining. Non-stained rubber is required for some non-tire uses. If a non-stained rubber is to be produced, not only must the extender oil be non-staining, but also lighter-colored soaps, short stops, and antioxidants must be used.

The coagulated crumb is separated from the coagulation liquor on a shaker screen. The coagulation liquor is recycled after make-up with fresh acid and brine and blowdown of part of the diluted liquor. The screened crumb is resuspended and washed with water in a reslurry tank. This operation serves to remove extraneous compounds from the rubber, particularly residual coagulation liquor. The crumb rubber slurry is then dewatered, generally using a vacuum filter, and the filtrate wash water is recycled to the reslurry tank for reuse with fresh water make-up and as an overflow. The overflow is necessary to blowdown accummulating rubber solids and contaminants. The coagulation liquor blowdown and crumb slurry water overflows are usually passed through separators. These facilities, called crumb pits, are generally outside the processing building and trap the floatable crumb rubber. The clarified underflow is discharged.

The rinsed and filtered rubber crumb is finally dried with hot air in a continuous belt or screen dryer. After drying, the rubber is weighed and pressed in bales and stored prior to shipment. Normally rubber bales weigh 75 pounds and are wrapped in polyethylene film. The balers are operated hydraulically with oil or water as the hydraulic fluid. Due to the jarring baling action and the high hydraulic pressures, fluid leaks are frequent and, in the case of oil-driven balers, the leaked oil should be prevented from entering the plant drain system.

In addition to the processing operations described above, other operations are carried out regularly, though not necessarily continuously, which generate considerable quantities of wastewater. These include equipment cleanout and area washdown operations. Principal equipment cleanouts include the polymerization reactors, blowdown tanks, butadiene flash tanks, styrene stripping columns, and latex blend tanks. In most cases, high volumes of wastewater are produced that are laden with uncoagulated latex solids and are characterized by a milky white appearance. When the flash tanks and stripping columns are cleaned, the wastewaters contain rubber solids, due to premature coagulation of the latex, in addition to uncoagulated latex. Area wash downs are frequent, and the wash waters pick up primarily latex, rubber solids, and oil. The carbon black slurrying area is generally contaminated with carbon powder. Area washdowns and storm run off typically pick up the carbon, resulting in a fine carbon suspension.

It is opportune at this point to review the potential wastewater sources in a typical emulsion plant. Table III-5 summarizes the principal wastewaters and the nature or appearance of their constituents.

Table 111-5

Summary of Potential Process-Associated Wastewater Sources from Crumb Rubber Production via Emulsion Polymerization Processing

Processing Unit	Source	Nature of Wastewater Contaminants
Caustic Soda Scrubber	Spent caustic solution	High pH, alkalinity, and color. Extremely low average flow rate.
Monomer Recovery	Decant water layer	Dissolved and separable organics.
Coagulation	Coagulation liquor overflow	Acidity, dissolved organics, suspended and high dissolved solids, and color.
Crumb Dewatering	Crumb rinse water overflow	Dissolved organics, and suspended and dissolved solids.
Monomer Strippers	Stripper cleanout rinse water	Dissolved organics, and high suspended and dissolved solids. High quantities of uncoagulated latex.
Tanks and Reactors	Cleanout rinse water	Dissolved organics, and suspended and dissolved solids. High quantities of uncoagulated latex.
All Plant Areas	Area washdowns	Dissolved and separable organics, and suspended and dissolved solids.

### Solution Crumb Production

As pointed out earlier, solution polymerization is a newer, less traditional, process for the commercial production of crumb rubber in the U.S. Solution polymerization systems permit the use of stereospecific catalysts of the Ziegler-Natta or alkyl-lithium types which have made it possible to polymerize monomers, such as isoprene or butadiene, in a suitable organic solvent so as to obtain the cis structure (up to 98 percent) characteristic of the natural rubber molecule and with a high degree of regularity. Rubbers with the cis structure are desired since they are usually rubbery, whereas the trans-configuration is more rigid and similar to plastics. Cis-polybutadiene, for example, has higher abrasion resistance than the usual SBR type and is being used mainly to extend and partially replace both SBR and natural rubber in tires. Reports indicate that tread wear is improved by up to 35 percent in a 50-50 blend of polybutadiene and SBR.

A relative newcomer on the rubber scene is based on the cheap monomers, ethylene and propylene. Although not stereo-regular, these polymers can be produced in solution plants and can use similar catalysts. The polymer chain, based on ethylene and propylene, does not contain sufficient unsaturation for conventional curing. The incorporation of a third monomer, usually a diene (thus EPDM - ethylene propylene diene monomer), adds unsaturation and facilitates conventional curing.

The production of synthetic rubbers by solution polymerization processes is a stepwise operation, and, in many aspects, is very similar to production by emulsion polymerization. There are distinct differences in the two technologies however. For solution polymerization, the monomers must be extremely pure and the solvent (hexane, for example) should be completely anhydrous. In contrast to emulsion polymerization, where the monomer conversion is taken to approximately 60 percent, solution polymerization systems are polymerized to conversion levels which are typically in excess of 90 percent. The polymerization reaction is also more rapid, usually complete in one to two hours.

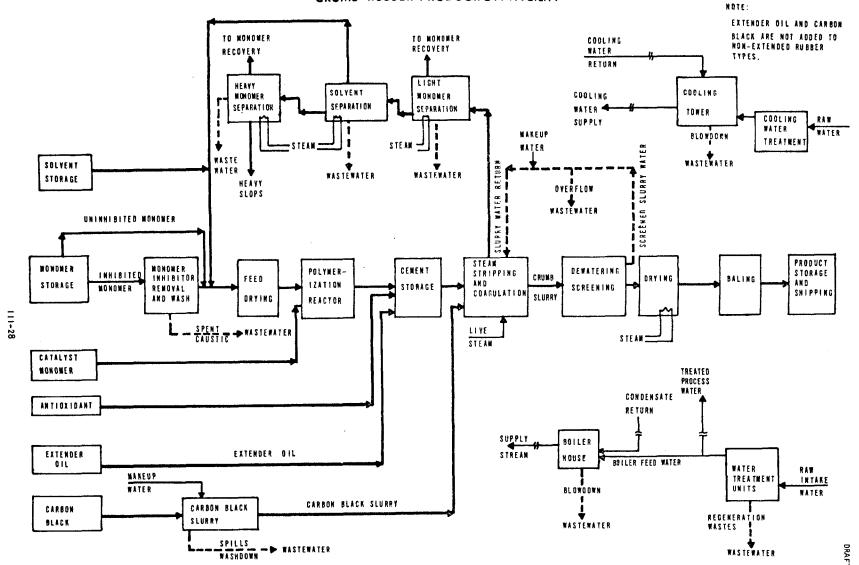
Figure III-4 is a generalized materials flow diagram for the production of crumb SBR by a solution polymerization process. The processing steps shown are essentially typical of all solution polymerization processes. As in the case with emulsion plants, solution plants comprise several processing lines where different types of rubber for distinct end uses can be produced (including non-extended, oil-extended, and carbon black master batch varieties). Plant operation is typically 24 hours per day, 365 days per year.

The fresh monomers are pumped to the plant from the tank farm. Inhibited monomers are passed through a caustic soda scrubber to remove the inhibitor. The monomers are then sent to fractionator drying towers where extraneous water is removed. Fresh and recycled solvent (for example,

FIGURE 111-4

GENERAL WATER FLOW DIAGRAM FOR A SOLUTION POLYMERIZED

CRUMB RUBBER PRODUCTION FACILITY



hexane) is also passed through a drying column to remove water and extraneous light and heavy components. The light- and heavy-components build up in the system as unwanted by-products or unrecovered monomer during the polymerization step and must be removed. The purified solvent and monomers are then blended. The mixture is generally termed the "mixed feed". The mixed fixed can be further dried to remove final traces of water using a desiccant column.

The dried mixed feed is now ready for the polymerization step and catalysts can be added to the solution (solvent plus monomers). The catalyst systems used vary. Typically they are titanium halide plus aluminum alkyl combinations or butyllithium compounds. The catalysts can be added to the mixed feed just prior to the polymerization stage or to the lead polymerization reactor.

The blend of solution and catalysts is polymerized in a series of reactors. The reaction is highly exothermic and heat is removed continuously by either an ammonia refrigerant or by chilled brine or glycol solutions. The reactors are similar in both design and operation to those used in emulsion polymerization. The mixture leaves the reactor train as a rubber cement, i.e., polymeric rubber solids dissolved in solvent.

A short stop solution is added to the cement after the desired conversion is reached. The stabilized cement is pumped to cement storage tanks prior to subsequent processing. At this point other ingredients, such as antioxidants, can be added. If the rubber is to be oil extended, oil can be added to the cement. The oil is usually blended with the cement at some point between the storage tanks and the steam stripping operation.

The rubber cement is pumped from the storage tank to the coagulator where the rubber is precipitated into crumb form with hot water under violent agitation. Wetting agents (surfactants) can be added to promote the control of crumb size and to prevent reagglomeration. In addition to coagulation, much of the solvent and unreacted monomer are stripped overhead. For carbon black masterbatch rubbers, the carbon black slurry is added to the coagulator in much the same manner as for emulsion crumb rubber.

The resultant crumb slurry passes to a series of strippers where steam stripping drives off the remaining monomers and solvent. The strippers are generally a flash tank or agitated kettle strippers. The steam, solvent, and monomer vapors are condensed and sent to a decant system. The bottom decant layer, saturated in monomers and solvent, is discharged. The organic layer is sent to a multi-stage fractionator (described earlier). Light fractions are removed in the first column and generally consist of unreacted light monomer (for example, butadiene). This is normally reclaimed at the monomer supply plant. The second column produces purified solvent, a heavy monomer-water fraction, and extraneous heavy components.

The heavy monomer (for example, styrene) is condensed, decanted, and recycled. The bottom water layer is discharged. The purified solvent is dried and reused. The heavy monomer is a waste stream which can either be decanted before disposal or can be incinerated as a slop oil.

The stripped crumb slurry is separated and further washed with water on vibrating screens. The slurry rinse water is recycled in part to the coagulation stage with water or steam makeup. The remaining portion of the slurry rinse water overflows and is discharged. This water contains floating crumb rubber fines and is generally passed through a crumb pit before discharge. The crumb fines are trapped in the pit. The screened rubber is passed through an extruder-dryer for further dewatering and drying. Dewatering and drying can also be carried out with a rotary filter and hot air oven dryer. The dried rubber is pressed into 75-pound bales and is usually wrapped in polyethylene for shipment. Balers, identical to those employed in emulsion processing, are used in solution-polymerized rubber production. Oil leaks are a potential problem.

In addition to the processing operations described above, area wash-downs occur. These are frequent and produce large volumes of wastewater which can be contaminated with dissolved organics, floating organics, oils, and suspended solids. Since the majority of the processing steps are operated on a strict water-free basis, there is little need for equipment cleanout operations with water. The processing units which are kept free of water are cleaned out with solvent when necessary. This cleaning solvent is stored separately and is used solely for the cleanout operation. Process pumps, handling in particular the dried mixed feed prior to and during the polymerization stage, use a non-aqueous fluid (usually an oil) as a seal in lieu of water to prevent contamination of the process streams with water. Leaking fluid is a potential source of oil which can be picked up by area washdown waters. The carbon black slurrying area is a source of wastewaters laden with carbon fines.

The main wastewater sources in a typical solution polymerization plant are summarized in Table III-6.

#### Latex Production

In addition to solid crumb rubber, emulsion polymerization is also used to produce latex rubber. Latex production follows the same processing steps as emulsion crumb production with the exception of latex coagulation and crumb rinsing, drying, and baling. Only about 5 to 10 percent of SBR is used as latex, but approximately 30 percent of the nitrile rubbers (NBR) enter the market as latex. Commercially available SBR latexes contain about 45- to 55-percent solids, although some can be as high as 68 percent. Most NBR latexes are in the 45- to 55-percent solids class. The polymerizations are taken essentially to completion (about 98 to 99 percent conversion) as opposed to emulsion crumb rubber production where conversion per polymerization pass is approximately 60 percent.

Table III-6

Summary of Potential Process-Associated Wastewater Sources from Crumb Rubber Production via Solution Polymerization Processing

Processing Unit	Source	Nature of Wastewater Contaminants
Caustic Soda Scrubber	Spent caustic solution	High pH, alkalinity, and color. Extremely low average flow rate
Solvent Purification	Fractionator bottoms	Dissolved and separable organics.
Monomer Recovery	Decant water layer	Dissolved and separable organics.
Crumb Dewatering	Crumb rinse water overflow	Dissolved organics, and suspended and dissolved solids.
All Plant Areas	Area washdowns	Dissolved and separable organics, and suspended and dissolved solids.

As a result, the recovery of unused monomer is not economical. Process economics are directed towards maximum conversion on a once-through basis.

Figure III-5 is a generalized materials flow diagram for the production of latex SBR by emulsion polymerization. The steps shown are typical of all latex production processes. Although latex plants are generally operated 24 hours per day and 365 days per year, the production runs for each recipe or type of latex are shorter than in emulsion or solution crumb rubber plants because latex consumption is on a smaller scale and latex consumers are usually outside companies with varying product needs. By contrast, the majority of crumb rubber is made for tire manufacture, is consumed by major tire companies, and is produced by their own synthetic rubber producing divisions. This has the effect of limiting the number of types of product and recipe, rationalizing production schedules, and, in the final analysis, leading to long production runs. Latexes are used to manufacture dipped goods, paper coatings, paints, carpet backing, and many other commodities.

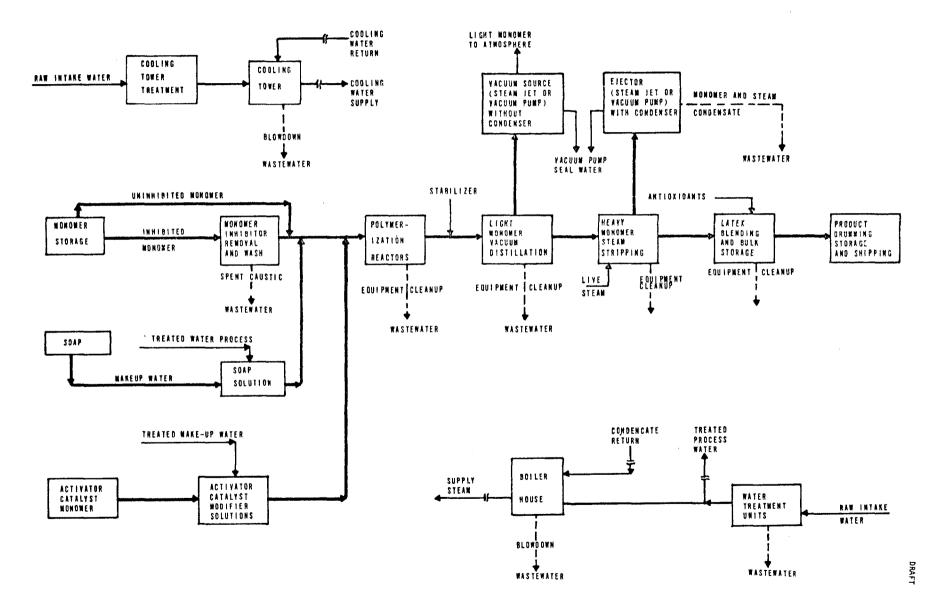
The monomers are piped from the tank farm to the processing plant. Monomer inhibitors are scrubbed out by using caustic soda solution. Soap solution, catalysts, and modifiers are added to the monomer to produce a feed emulsion prior to feeding to the reactors. The water used in the preparation of the above solutions is generally deionized city or well water. The number of reactors in the reactor train is usually smaller than that used for emulsion crumb production. The temperature is generally kept at approximately 40 to 45°F and, therefore, most latexes are made by the "cold" process. When the polymerization is complete, the latex is sent to a blowdown tank for intermediate storage or holding. Stabilizers are usually added to the latex at this point to stop the polymerization and to stabilize the latex.

The latex passes from the blowdown tanks to a vacuum stripper where the unreacted butadiene is removed. The butadiene is vented to the atmosphere. The vacuum is pulled with either a vacuum pump or steam jet. The excess styrene is stripped from the latex in a steam stripper. The steam and styrene are condensed and sent to a receiver. The bottom water layer is decanted off and discharged. The styrene layer is not recycled and requires disposal.

The stripped latex is passed through a series of screen filters to remove unwanted large rubber solids. The latex is finally stored in blending tanks where various additives (for example, antioxidants) are mixed with the latex. The latex is shipped from the blending tanks by tank car or tank truck, or is drummed ready for dispatch.

Since short production runs are common to the industry, the major wastewaters generated in a synthetic latex plant stem from equipment cleanout operations. When production is switched from one type of rubber to another, reactors, blowdown tanks, strippers, and filters require cleaning

FIGURE 111-5
GENERAL WATER FLOW DIAGRAM FOR AN EMULSION LATEX RUBBER PRODUCTION FACILITY



for the new product. In addition, tank cars and tank trucks owned or leased by the plant require cleaning after each trip. Area washdowns are frequent inside the processing buildings and at the vehicle loading-unloading areas. All the above wastewaters will contain oils, dissolved organics, and high concentrations of latex solids.

Table III-7 summarizes the origins and nature of the principal wastewater sources generated in a typical synthetic latex plant.

### Summary

The growth of the tire and inner tube industry has been closely linked to the growth of the automobile industry. Current production is over 210 million tires per year with one quarter of this production destined for original equipment on new vehicles. The production of both tires and inner tubes consist of the compounding, extruding, calendering, and molding of solid raw materials. There is considerable heat generated by these processes and it must be dissipated and controlled to insure the quality of the final product. Water used in the process, other than for utilities, consists of makeup water for soapstone solution and latex dip solutions.

The production capacity and output of the synthetic rubber industry are expanding steadily and are linked very closely to consumption by the tire industry. The relative production levels for the various types of synthetic rubber will not change significantly over the next several years to affect the operations or wastewater impact of the industry as a whole. Two distinct processing technologies (emulsion and solution) exist. Process variations within each of these two technologies are only minor. Two different types of rubber product are manufactured: crumb and latex rubbers. The so-called specialty rubbers are manufactured by processes similar to those used to produce the so-called tire rubbers and are in similar product forms, i.e., solid and latex rubbers.

Table III-7

Summary of Potential Process-Associated Wastewater Sources from Latex Production via Emulsion Polymerization Processing

Processing Unit	Source	Nature of Wastewater Contaminants
Caustic Soda Scrubber	Spent caustic solution	High pH, alkalinity, and color. Extremely low average flow rate.
Excess Monomer Stripping	Decant water layer	Dissolved and separable organics.
Tanks, Reactors, and Strip⊶ pers	Cleanout rinse water	Dissolved organics, suspended and dissolved solids. High quantities of uncoagulated latex.
Tank Cars and Tank Trucks	Cleanout rinse water	Dissolved organics, suspended and dissolved solids. High quantities of uncoagulated latex.
All Plant Areas	Area washdowns	Dissolved and separable organics, and sus- pended and dissolved solids.

#### SECTION IV

#### INDUSTRY CATEGORIZATION

#### Introduction

Industry categories and subcategories were established so as to define those sectors of the rubber industry where separate effluent limitations and standards should apply. In the final analysis, the underlying distinctions between the various categories and subcategories have been based on the wastewater generated, its quantity, characteristics, and applicability of control and treatment. The factors considered in determining whether such categorizations are justified were the following:

- 1. Manufacturing Process.
- 2. Product.
- 3. Raw Materials.
- 4. Plant Size.
- 5. Plant Age.
- 6. Plant Location.
- 7. Air Pollution Control Equipment.
- 8. Nature of Wastes Generated.
- 9. Treatability of Wastewaters.

As indicated in Section III, there are inherent differences between the tire and inner tube sector, and the synthetic rubber sector of the rubber industry; therefore, the two have been separated to produce the two principal industry categorizations.

# Tire and Inner Tube Industry

# Manufacturing Process

The process steps by which tires are made are similar throughout the industry. Although there are variations due to equipment manufacturer and automation, these differences do not lead to significant variations in the volume or constituents of process waters.

#### Product

Examination of existing plants indicates that the end product is not a reasonable basis for categorization. Manufacturing steps for all tire production are similar; inner tube manufacture, although different in some respects, generates the same type of process wastewater streams as does the tire production. The characteristics of the waste stream and the potential treatment technologies are not significantly different.

Radial tire manufacture is different in the building, molding, and curing operations; however, these differences do not significantly

impact on wastewater quantity or quality. In addition, radial tires are generally produced in the same plants as bias tires.

#### Raw Materials

Since the basic raw materials for the entire industry are rubber, carbon black and oil, categorization based on raw material usage is not reasonable. The quantities and form of the different raw materials received varies, but these do not significantly affect the control or treatment technologies applicable to the industry. The handling of raw materials, particularly the carbon black, also varies within the industry. However, this again does not affect the process wastewaters or their treatability.

#### Plant Size

A listing of most plants currently operating and their production rates is given in Table IV-1. The distribution of these is presented in Figure IV-1. From inspection of existing and plant visit data, it was learned that plant size has no significant effect on the quality or treatability of wastewaters. Process effluent quantities varied significantly but was not directly related to plant size. The only significance of size is the cost of treatment of wastewater streams, which, of course, is related to other factors.

#### Plant Age

The age of plants currently in operation will fall into three basic categories depending on the expansion period in which the plant was built. The oldest plant in operation is an inner tube facility built in 1888.

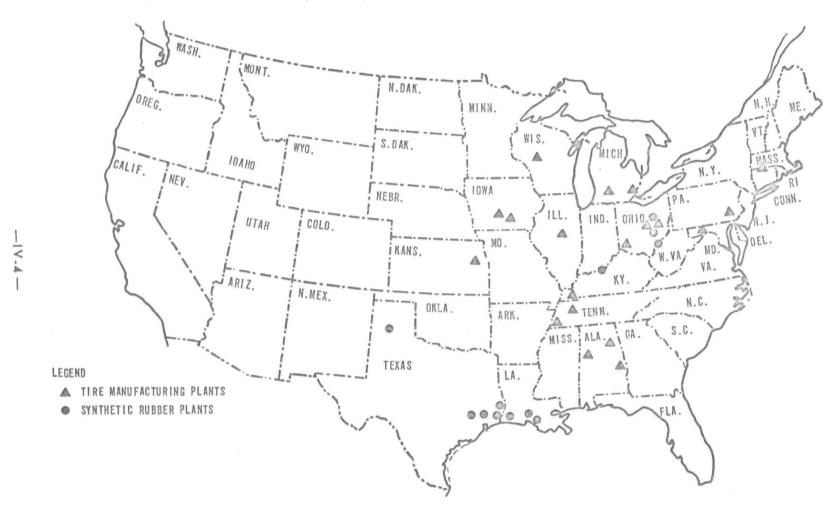
As constructed, production facilities built during the first two expansion periods tend to be multi-storied, with process lines located on many floors and confined to small areas. In addition, plants from the first expansion period most probably have undergone modifications in order to update their machine processing technology (for example, the installation of internal mixers). Most likely this would further congest the processing area. Much of the equipment in these older plants is old and of designs that have since been updated to reduce maintenance and operational costs. Process, non-process, and domestic wastewater sewers exist as a combined sewer, thus making process contaminants difficult to locate or treat once they reach the drainage system. Engineering diagrams of sewers within the plant are dated and possibly non-existent. Drains that do exist were located for ease of washdown of contaminants, thus making their position inappropriate by current thinking and standards.

The newer plants of the last expansion period have the benefit of modern

Company	Location	<u>Units/day</u>	Company	Locat ion	Units/day
Armstrong	DesMoines, la.	20,000	Goodrich	Akron, Ohio	6,000
	Hanford, Cal.	10,500		Ft. Wayne, Ind.	18,000
	Natchez, Miss.	14,600		Los Angeles, Cal.	11,500
	W. Haven, Conn.	13,500		Oaks, Pa.	19,000
				Tuscaloosa, Ala.	21,000
Carlisle	Carlisle, Pa.				
•			Goodyear	Akron, Ohio	38,000
Cooper	Findlay, Ohio	13,000		Conshohocken, Pa.	13,000
	Texarkana, Tex.	11,500		Cumberland, Md.	20,500
				Danville, Va.	4,100
Corduroy	Grand Rapids, Mich.	***		Freeport, Ill.	14,000
_				Gadsden, Ala.	44,000
Denman	Warren, Ohio			Jackson, Mich.	30,000
<b>5</b> 1.	5 5 5 1 11 11			Los Angeles, Cal.	
Dunlop	Buffalo, N.Y.			Topeka, Kans.	30,000
<b>F</b> !		07.000		Tyler, Tex.	15,000
Firestone	Akron, Ohio	27,000		Union City, Tenn.	30,000
	Albany, Ga.	17,000	Mana 61 - 1 .1	M 51 11 001-	11, 000
	Barberton, Ohio	8,500	Mansfield	Mansfield, Ohio	14,000
	Bloomington, Ill. Dayton, Ohio	50 20 <b>,</b> 700		Tupelo, Miss.	12,500
	Decatur, III.	22,000	Macroney	Indiana Da	2 500
	DesMoines, la.	22,000	McCreary	Indiana, Pa.	3,500
	Los Angeles, Cal.	15,500	Mohawk	Akron, Ohio	6,000
	Memphis, Tenn.	28,000	HOHOWK	Salem, W. Va.	4,700
	Pottstown, Pa.	30,000		W. Helena, Ark.	10,000
	Salinas, Cal.	15,500		w. Horena, Alk.	.0,000
		.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	Schenuit	Baltimore, Md.	
Gates	Denver, Colo.	18,200			
	Nashville, Tenn.	10,000	Uniroyal	Chicopee Falls, Mass.	29,000
			•	Detroit, Mich.	39,745
General	Akron, Ohio	9,050		Eau Claire, Wis.	30,000
	Bryan, Ohio	30		Los Angeles, Cal.	16,500
	Charlotte, N.C.	12,000		Opelika, Ala.	13,500
	Mayfield, Ky.	23,000			
	Waco, Tex.	16,000			

Source: "Rubber Reuse and Solid Waste Management," U.S. Environmental Protection Agency, 1971.

LOCATION OF TIRE MANUFACTURING PLANTS, PRODUCTION GREATER THAN 20,000 UNITS/DAY, AND SYNTHETIC RUBBER PRODUCTION PLANTS, PRODUCTION GREATER THAN 60,000 LONG TONS/YEAR, WITHIN THE U. S. 1972.



design criteria and updated thinking in both the sanitary and maintenance engineering fields. Buildings are single-story and contain more area per process line. Equipment and area locations have been designed for a cleaner, more maintenance-free operation. Sewers are no longer combined, thus making process sewer wastewaters easier to locate and treat. Drains are not located in areas where contaminants can gain easy entrance.

By the above reasoning, the process wastewater streams from older plants should be larger in volume and should contain higher loadings of both oily and solid materials. Control and treatment should be more difficult. Examination of plant wastewater streams from all these areas bears this out.

The years between 1950 and 1960 are the transition period between the second and third expansion period. Plants constructed in the early 1950's were built during the Korean War and will most likely have the same problems as those built in the World War II era. Few (if any) plants were built after the Korean War until 1959, when the current expansion began. The year 1959, therefore, is the demarcation point between old and new facilities.

#### Plant Location

From inspection and wastewater sampling of plants located in three geographical areas of the country and from analysis of existing data. plant location will have no effect on the quality or quantity of the process wastewater streams. These geographical areas included the South, the Far West, and the Northern Midwest. Geographical location has a significant effect on the supply of water; therefore, management of non-process streams such as cooling water and steam varied from region to region. Recirculation of cooling water is very common in the Far West (where water supplies are short), whereas it is less common in other sections of the country. Reduction of non-process wastewaters by recycle increases the treatability of process wastewaters when combined with non-process wastewaters in an end-of-pipe treatment facility. Treatability of process wastewater streams, however, is more effectively carried out before combination with non-process streams. In addition, geography does not limit the use of recirculated water to the Far West. Plants in other parts of the country are also using recycle, though not necessarily for the same reasons.

Plants visited also represented both rural and urban areas. Plants located in urban areas tended to occupy and own less land, thus increasing treatment cost where available open land is a consideration. However, both the location and the characteristics and quantity of the water to be treated are better related to the age of the plant. Urban plants are older facilities, whereas rural plants tend to be newer. Therefore,

location is not a reasonable basis for categorization.

### Air Pollution Control Equipment

The type of air pollution equipment employed by a facility can have a great effect on the characteristics and treatability of the process wastewater streams. The use of dry equipment or the recycling of discharges from wet equipment was observed in all areas of the plant which are currently served by such devices. Therefore, since company policy (rather than the situation to be controlled) dictates the type of equipment used, air pollution equipment does not form a suitable basis for categorization.

#### Nature of Wastes Generated

From evaluation of all available data, the type of wastes generated by all facilities in the tire and inner tube industry are similar. The addition or subtraction of the latex dipping of fabric from the process line can affect the characteristics of the process wastewaters. However, as supported by existing data, this discharge is not large and can be easily contained. Therefore, it does not necessarily affect the treatability of process wastewaters and does not form a basis for categorization.

# Treatability of Wastewaters

The treatment technologies employed by companies throughout the industry are similar. Wastewater constituents are also very similar: mainly oil and solids. Treatability is more a factor of age than of the specific pollutant and, therefore, does not form a basis for categorization.

#### Summary

Only the age of the production facility forms a rational basis for categorization. As indicated, tire manufacturing facilities built in earlier periods, although using similar manufacturing techniques, have greater wastewater problems than do new plants built in recent times. On this basis, there should be two separate categories: old plants, and newer plants. Plants built prior to 1959 are considered old; those built during and after 1959 are considered new. Inner tube facilities, although producing a different product, incur the same difficulties as do the older plants and should be included in the "old" category.

Camelback operation, a small segment of the industry, should also be included in the "old" or "new" categorization of tire plants depending on the tire facility of which it is a part. If located by itself, the camelback should meet standards according to the date of its construction. Compounding operations, another small segment of the industry, should fall into the category of the plants with which they coexist. If

located by itself in a separate location, the compounding facility should meet standards of "old" or "new" tire plants depending on its original date of operation.

As a consequence, only two categories are indicated for SIC code 3011, namely "old" and "new" tire facilities. The demarcation date between the categories is the year 1959.

# Synthetic Rubber Industry

# Manufacturing Process

As described in Section III of this document, there are two basic processing techniques in common use in the industry to produce synthetic rubber: emulsion polymerization processing and solution polymerization processing.

Emulsion polymerization as a commercial process dates back to World War II. No significant changes have been made in the basic process since the first emulsion polymerization plants were built. Emulsion polymerization processing is used, however, to make both emulsion crumb and latex rubber. From both operational and wastewater points of view, crumb and latex production techniques should be considered separately.

Solution polymerization production facilities are different from emulsion plants from both process and wastewater points of view and have been considered as a separate sub-category. Differences among solution rubber production plants are minor. All solution plants consist of feed preparation, polymerization, solvent and monomer recovery, coagulation, and rubber finishing operations. The operations that have the greatest wastewater impact in solution plants are those operations which are most similar plant to plant.

It was therefore concluded that there are essentially three manufacturing process variations which merit separate subcategories: emulsion polymerization to crumb rubber; solution polymerization to crumb rubber; and emulsion polymerization to latex.

#### Product

There are two principal product sub-categories in the synthetic rubber industry, crumb and latex product.

Within the crumb sub-category there are several product variations which involved the type of rubber (styrene-butadiene, or polybutadiene, etc.) and whether the rubber is extended or not. The two principal products made by emulsion polymerization are SBR and nitrile rubber. The process operations for the two rubbers are identical, and the same or similar equipment is used. Several types of rubber are produced by solution polymerization processes; in many cases similar solvents and monomers are used, equivalent processing operations are carried out, and identical processing

equipment is used.

The processing variations involved in the manufacture of either oilextended or carbon-black-extended rubber are minor. In addition, the oil and carbon black are very effectively tied up with the rubber, thus reducing the potential for wastewater impact.

The effects that the various types of latex rubber (for example, SBR and NBR) have on the production operations and wastewaters are minor. The same equipment and processes are used for all types.

As pointed out in Section III, the specialty rubbers are essentially similar to the tire rubbers from a processing point of view, and no separate categorization is deemed necessary.

It has been concluded that only two principal product subcategories are required to adequately define the synthetic rubber industry. They are crumb and latex rubber.

# Raw Materials

The monomeric raw materials used to produce the various types of synthetic have similar properties. They are usually unsaturated hydrocarbons with extremely low solubility in water. Chloroprene, a chlorinated hydrocarbon used to make neoprene rubber, is also insoluble in water. In addition to low solubility, most of the monomers used have high volatility and, consequently, a monomer floating on wastewater soon evaporates. Most solvents used also have low solubility and high volatility and do not remain in a wastewater. The catalysts, modifiers, antioxidants, etc. used in polymerizations are generally similar and are used in such low concentrations that their effect on wastewater is minimal. Their presence is generally undetectable in the wastewaters.

In conclusion, there is no need for a subcategorization based on the raw materials used.

### Plant Size

Most emulsion and solution crumb rubber plants consist of several parallel and integral processing lines. Each of these lines tends to be of similar size. The wastewaters generated by a plant, therefore, are normally directly proportional to the production capacity.

Small production facilities (for example, latex plants), will bear a somewhat higher treatment cost than larger plants. However, these plants are generally part of a larger synthetic rubber or organic chemical complex, and the treatment cost can be shared. In any case, latex plants are considered as a separate sub-category.

For these reasons, sub-categorization according to plant size is not necessary.

### Plant Age

Many emulsion plants (crumb and latex rubber) were built during or shortly after World War II. Few have been built since. In addition, technology has not changed appreciably since that time.

Solution plants are generally newer, but all have been built in the last 13 years. The technology has not changed radically during that time period.

It has been concluded that plant age is not a significant factor for separate subcategorization.

### Plant Location

Most of the larger synthetic rubber plants are located in one geographic region. (Refer to Figure IV-1.) This fact is closely connected to the availability of the monomeric raw materials. The location of the plants does not influence the processing operation. However, geographic location can influence the performance of aerated lagoons and stabilization ponds. Comparable secondary wastewater treatment alternatives, such as activated sludge, do exist, but the performance is not dependent on geographic location. It is not necessary to subcategorize the synthetic rubber industry by plant location.

# Air Pollution Control Equipment

Generally, air pollution control devices are not required by the industry. Odor problems do exist at some plants, but these are controlled by devices which are either dry or which do not impact on the wastewaters of the plant.

Air pollution control is not a subject for subcategorization of the synthetic rubber industry.

#### Nature of Wastes Generated

The differences in the characteristics of wastewaters generated by production of non-extended, oil-extended, and carbon-black-extended emulsion crumb rubber were not discernible. Similarly, the wastewater characteristics produced by non-extended, oil-extended, and carbon-black-extended solution crumb plants were essentially identical; however, wastewaters from emulsion crumb, solution crumb, and latex rubber production facilities were significantly different to warrant subcategorization.

These facts indicate that separate subcategories are required only for emulsion crumb, solution crumb, and latex rubber production.

# Treatability of Wastewaters

Since the wastewaters generated by emulsion crumb and latex production require chemical coagulation prior to primary clarification whereas the wastewaters produced by solution crumb plants do not, there is a difference in the treatability of synthetic rubber wastes. In addition, the COD and BOD loading from latex plants is considerably higher than from emulsion and solution crumb plants, and requires more extensive treatment.

It was concluded that, based on the treatability of the wastewaters, three subcategories were required: emulsion crumb, solution crumb, and latex rubber production.

#### Summary

For the purpose of establishing effluent limitations guidelines and standards, the synthetic rubber industry should be separated into three subcategories which are based on distinct processing and product differences. These subcategories are:

- 1. Emulsion crumb rubber.
- 2. Solution crumb rubber.
- Latex rubber.

### SECTION V

#### WASTE CHARACTERIZATION

# Tire and Inner Tube Industry

A general process flow diagram for a typical tire production facility is presented in Figure III-1. Figure III-2 presents a typical inner tube production process diagram.

The primary water usage in a tire and inner tube facility is for non-contact cooling and heating. Discharges from service utilities supplying cooling water and steam are the major source of contaminants in the final effluent. Characteristics of these wastewaters are COD, BOD, suspended solids, and dissolved solids.

Table V-1 presents the raw waste loading for the combined process and non-process wastewaters of the plants visited. Flow variations are due mainly to the use of once-through cooling water in certain plants as opposed to recirculating cooling water. Plants A and B are new plants using totally recirculated cooling water. Plants E and G are old facilities also using recirculated water. A comparison of these four plants indicates that no significant variations in flow exist due to age of the plant.

Plant F typifies a plant using once-through water as its primary source of process cooling. COD and BOD loadings vary to a great degree by the type and amount of chemicals used in the treatment of boiler and cooling tower makeup waters. Larger loadings for older plants indicate an increased amount of process wastewater pollutants in the effluent. Loadings measured in Plant A are high due to the practice of discharging washdowns of soapstone and latex dip areas noticed during the sampling period. This plant uses holding lagoons. Because all wastes are contained within the plant's boundaries, Plant A discharges contaminants which other exemplary plants (using different technologies) can not accomplish. These contaminants lead to a correspondingly higher loading.

Suspended solid loadings evolve primarily due to water treatment blowdowns, wastes, and boiler blowdowns. In addition, the suspended solid loadings in process wastewater can increase due to spills, leakage, and soapstone discharge. Loadings for old plants tend to be higher than those for new plants. This is due in part to the use of older water treatment techniques and the larger volumes of process wastewater containing solids discharged by older facilities.

The quantity of dissolved solids discharged is related to the amount of recirculated non-process water and the water supply source. Plants using well water typically have higher dissolved solid loadings, than those using municipal or river water sources.

TABLE V - 1

Raw Waste Loads of Untreated Effluent From Tire and Inner Tube Facilities

<u>P1</u>	ant	Cate- gory	FLOW liters/1,000 kg of raw material	COD liters/1,000 kg of raw material	BOD liters/1,000 kg of raw material	SS liters/1,000 kg of raw material	TDS liters/1,000 kg of raw material	OIL liters/1,000 kg of raw material
	A	Hew	6344.0	1.890	0.067	0.960	4.800	0.249
	В	New	3430.0	.184	0.002	0.047	0.159	0.075
	c <sup>1</sup>	ilew	8251.0	-	-	1.155	-	0.794
	D	New	10883.0	0.142	0.012	0.092	0.879	0.009
	Ε	01d	5453.0	0.100	0.001	0.440	0.001	0.0272
	F	01d	123480.0	3.398	0.296	1.358	0.001	0.650
V-2	G	01d	3220.0	0.645	0.093	3.429	0.000	0.267
	н	01d	72427.0	0.001	0.036	0.676	0.000	0.167
	1	01d	10610.0	0.615	0.148	2.812	1.810	0.172

<sup>1</sup> Estimated, raw material consumption not known.

<sup>2</sup> Includes treatment by in-plant sumps.

Table V-1 also shows that the plant's final end product has no significant effect upon the raw waste loading in the final effluent. Data from Plant H, which produces primarily truck and industrial tires, is not substantially very different from Plants E, F, or G, which, while producing a combination of products, produce mainly passenger tires. Loadings from Plant I are similar to the others, even though this plant's primary product is the manufacture of inner tubes.

To substantiate the data and conclusions on total final effluent, Corps of Engineers water discharge permit applications were obtained for a large segment of the tire and inner tube industry. Comparison of Corp. permits for plants considered old and new revealed that the above findings and conclusions are substantially correct. Table V-2 lists the main characteristics and the loadings corresponding to a typical old and typical new tire production facility.

Raw waste loads in the process wastewaters leaving the production facility are presented in Table V-3. Flows rates are estimates only, mainly due to the intermittent nature of the waste discharges. Although there appears to be no significant difference in the measured flow rates as shown by data, the composition of the flows originating from old and new plants differs greatly. New Plant A uses large amounts of washdown water which comprises the bulk of their process wastewaters. New Plant B process wastewaters consist largely of discharges from an extensive wet air pollution train. The discharges from this equipment are the primary constituent of the process wastewaters. The process wastewater flow rates leaving older plants are due to other factors such as spills, leakage, runoff from storage areas and inherent plant practices of older facilities. Therefore the data indicate that, given the same housekeeping policies and the same degree of wet air pollution equipment and controls, the process wastewater flow rates from older plants will be higher than from newer plants.

Two important characteristics of the process wastewaters are suspended solids and oil. The suspended solids are generally higher from older plants due to greater maintenance and poorer housekeeping and control practices. The same can be said for the oil. Suspended soilids evolve from the powdered substances used in the compounding area and from the collection of particulates by wet air pollution equipment. The oil is primarily lubrication and hydraulic oils from in-plant sources, and extender and fuel oil from run-off in storage areas. Both parameters can be treated successfully. Plant B is using a sedimentation lagoon to settle solids collected in the compounding area from wet air pollution equipment. It has been demonstrated by Plants A and E that solids collected in other areas can be separated easily by convential equipment. American Petroleum Institute (API) type separators are being used to treat oily waste effluents of Plants B, D, and E.

The primary constituents of the process wastewaters are presented in Table V-4, along with their sources and characteristics.

TABLE V - 2

Average Valves of Raw Waste Loads for Tire Industry

	FLOW liters/1,000 kg of raw material	COD liters/1,000 kg of raw material	SS liters/1,000 kg of raw material	TDS liters/1,000 kg of raw material	OIL liters/1,000 kg of raw material
Old Tire Facilities (to 1958)					
Minimum	6267.0	0.088	0.001	0.349	0.003
Maximum	386478.0	7.294	5.854	105.660	3.363
Average	37000.0	0.780	1.000	12.000	0.120
New Tire Facilities (1959 to Present)		·			
Minimum	2303.0	0.083	0.032	0.387	0.011
Maximum	48070.0	2.020	1.397	12.980	0.187
Average	10500.0	0.580	0.310	5.535	0.042

Source: Corp of Engineer Permit Applications

TABLE V - 3

Raw Waste Loads of Process Wastewaters From Tire and Inner Tube Facilities

<u>P1</u>	ant	Cate- gory	FLOW <sup>1</sup> liters/l,000 kg of raw material	COD liters/1,000 kg of raw material	BOD liters/l,000 kg of raw material	SS liters/1,000 kg of raw material	TDS liters/1,000 kg of raw material	OIL liters/1,000 kg of raw material
	Α	New	290.0	1.57	0.067	0.882	5.12	. 248
	В	New	1650.0	-	0.001	0.013	0.3739	. 075
	c <sup>2</sup>	New	-	-	-	-	-	-
	D	New	-	0.193	0.010	0.064	3.210	0.008
	E	01d	110.0	0.046	0.000	0.017	0.019	0.027
۷-5	F	01d	700.0	-	-	0.57	-	0.650
Ğ	G	01d	590.0	-	-	0.001	-	0.260
	Н	01d	4300.0	2.199	0.356	0.520	19.765	0.163
	ı	01d	769.0	-	~	2.610	-	0.172

<sup>!</sup> Estimated

<sup>2</sup> No data available from Plant C

TABLE V - 4

The Sources and Characteristics of Process Wastewaters from the Tire and Inner Tube Industry

Wastewater Type	Source	Flow	Characteristics
Soapstone	Compounding Area: Washdown and System Cleanout; Runoff from Spills and Leakage	Intermittent 0 - 5,7000 Liters	Suspended Solids, BOD, COD, Oil
Latex Dip	Fabric Dipping Area: Discharge of Waste Solution; Washdown; Run-off from Spills and Leakage	Intermittent O - 200 Liters	Suspended Solids, BOD, COD
In-Plant Spills and Leakage	All Areas of Plant where Water Cooled Machinery is used; also Latex and Soapstone Dipping Areas	Intermittent 0 - 220 Liters	Oil, Suspended Solids
Oil and Solvent Stor- age and Maintenance <sup>*</sup> Area Runoff	Storm and Washdown Runoff from these areas	Intermittent	011
Air Pollution Equip- ment Discharges	Compounding Areas, Tire Finish-ing Areas	7 - 340 Liters/ minute	Suspended Solids
Part Cleaning Dis- charges	Steam Cleaning; Spillages in Solvent Cleaning Area	Intermittent	Oil, Suspended Solids

Maximum and minimum flows from plant visit data are presented here.

# Synthetic Rubber Industry

#### General

Wastewater characterization data was obtained from literature, EPA documents, and company records. Plant visits (refer to Section VII) were made to selected plants to confirm existing data and fill the data gaps. Figures III-3, III-4, and III-5 are generalized flow diagrams of emulsion crumb, solution crumb, and latex production facilities, respectively; they indicate the location of water supply and wastewater generation.

Data on total effluent flow and characteristics include utility wastewaters. It is virtually impossible to determine meaningfully total plant effluent flows and characteristics exclusive of utility wastes. It should be noted here that utility wastewaters are amenable to treatment by the existing treatment facilities in use and commonly practiced by the industry.

### Emulsion Crumb Rubber Subcategory

### Flow Analysis

Table V-5 lists the total effluent flows for plants producing various emulsion crumb rubber products based on a unit of production. This data was obtained by plant visits. Although three plants were sampled, six cases of emulsion crumb production were studied. The wastewater contributions of other facilities included solution crumb production and non-rubber commodities.

It can be seen from Table V-5 that, for similar products, separate plants appear to have different effluent flows. However, different products at the same plant seemingly produce identical wastewater flows. This is due to the following distinct facts:

- The water use practices in one plant for different emulsion crumb products are based on one technology, namely that of the company's process design and engineering.
- The inability of the sampling team to discern small differences in effluent flows for different products at the same plant.

It can also be noted that there is no significant trend in wastewater generation rate between the various types of emulsion crumb rubber product (non-extended, "hot", oil extended, and carbon black extended).

The average effluent flow rate for emulsion crumb is 16,600 liters per metric ton (1,000 kg) of production.

<u>P 1</u>	ant	Product	FLOW Liters/1,000 kg	COD kg/1,000 kg	B0D kg/1,000 kg	ss <sup>2</sup> kg/1,000 kg	01L kg/1,000 kg
	J	SBR and NBR Part Oil and Carbon Black Extended	15,000	11.98	N.A.	3.73	2.09
	К	SBR Part Oil Ex- tended	18,500	22.23	2.13	2.30	0.13
	К	SBR Oil Extended	18,500	19.76	2.13	11.31	3.54
V-8	L	SBR Oil and Carbon Black Extended	16,500	8.72	2.84	3.94	0.48
	L	SBR "Hot", Hon- Extended SBR	15,500	29.24	2.84	N.A.	1.31
	t.	SBR Hon-Extended	15,500	25.87	2.84	11.94	1.45
		Average Value		19.63	2.56	6.64	1.5

Raw waste load determined downstream of crumb pits, where the suspended solids and oil levels'are reduced. N.A. Data not available.

 $<sup>\</sup>frac{1}{2}$ includes utility wastewaters.

#### Raw Waste Loads

Table V-5 also summarized the raw waste loads for the six cases. It can be seen that the parameter with the highest concentration is COD. The BOD values are generally much lower. The high COD to BOD ratio is indicative of the high resistance of many of the constituents in the wastewaters to biological oxidation.

The raw suspended solids concentration in the emulsion crumb wastewaters were determined after separation of the rubber fines in the crumb pits. Since all emulsion crumb plants have separation pits, this raw waste load data is applicable to the industry. Much of the suspended solids contribution is due to uncoagulated latex solids. The concentration of oil does not appear to be related to the degree to which the crumb rubber is oil extended. The oil analysis cited is really "carbon tetrachloride extractables" and will also include insoluble monomers.

Another significant parameter in emulsion crumb wastewaters is total dissolved solids. This has two principal sources:

- 1. The crumb coagulation and rinse overflows.
- 2. The utility wastes (boiler and cooling tower blowdowns, and water treatment regeneration wastes).

Surfactants are another characteristic produced by the emulsifying agents. The level of surfactants in the wastewater is considerably lower than the parameters reported in Table V-4.

#### Individual Waste Streams

Table V-6 presents the major constituent loadings of the principal wastewater streams in an emulsion crumb plant. The most significant parameter is total dissolved solids which is produced by the acid and brine coagulation liquors. The coagulation liquor and crumb rinse overflows, along with the utility wastes, provide the bulk of the total dissolved solids in the plant effluent. It can be seen that the quantity of surfactants produced are much lower than the other parameters. Surfactants are not generated in appreciable quantities by waste streams not included in Table V-5. The suspended solids are much higher than in the total effluent since the crumb pits remove much of the suspended solids in the crumb rinse overflow. Removals better than 95 percent are common. Oil entrained in the rubber is also removed along with rubber crumb solids.

When comparing the sub-total parameter values of Table V-6 with the average total effluent loads of Table V-5, it can be seen that the three streams listed in Table V-6 are the major contributors to the total effluent.

The spent caustic scrub solution is an extremely low flow rate wastewater which has very high COD, alkalinity, pH, and color characteristics. It

TABLE V  $\sim$  6

Raw Waste Loads of the Principal Individual Wastewater Streams in an Emulsion Crumb Rubber Plant

	Wastewater Stream	COD kg/1,000 kg	B0D kg/1,000 kg	ss <sup>1</sup> kg/1,000 kg	TDS kg/1,000 kg	01L <sup>1</sup> kg/1,000 kg	SURFACTANTS kg/1,000 kg
	Monomer Recovery	0.66	0.14	0.08	1,26	0.11	0.0001
	Coagulation Liquor Overfl	ow 1.30	N.A.	N.A.	46.25	0.10	N.A.
V-10	Crumb Rinse Overflow <sup>2</sup>	6.39	0.46	33.44	42.33	1.46	0.0077
	Sub-Total	8.35	0.60	33.52	39.74	1.67	0.0078

Raw waste load determined prior to crumb pit, where the suspended solids and oil levels are reduced.

In one case, the crumb rinse overflow is combined with the coagulation liquor overflow and discharged as one combined stream.

N.A. Data not available.

is not, however, a significant waste stream when combined in the total effluent. It is usually bled-in at low flow rates into the effluent.

Area washdown and equipment clean-out wastewaters are highly loaded with COD and suspended solids, and, by nature, are intermittent in flow. They cannot be characterized because they are generated on an irregular basis and have greatly variable concentration loadings.

Chromium and zinc are present in low concentrations (1 mg/L) in the final effluent. They are present due to cooling water treatment, and can be eliminated by substitution of chromium-free corrosion inhibitors. Heavy metals from catalysts and other reaction ingredients are not present in measurable concentrations in emulsion plant wastewater effluents.

# Solution Crumb Rubber Subcategory

# Flow Analysis

Table V-7 presents the total effluent wastewater flows for facilities producing various solution crumb rubber products. The flow data is given in terms of liters per kilogram of production. Five plants were visited and eight types of solution crumb product were sampled. Some plants are multi-product facilities, and the contributions of the solution crumb facilities were accounted for.

Table V-7 shows that there is no discernible difference in the effluent flows between types of product. There appears to be more correlation between products at the same plant site. This is similar to the findings for emulsion crumb rubber production.

One plant (Plant M) has a considerably lower effluent flow than all the other facilities. The apparent reason for this difference is the use of a special rubber-finishing process which generates very little or no wastewater.

The average effluent flow for solution plants is similar to emulsion plants, and typically approximates 16,600 liters per metric ton of production.

#### Raw Waste Loads

Table V-7 also presents the raw waste loads for the four main parameters. It can be seen that the constituent levels are approximately one half of those present in emulsion crumb wastewaters. This supports literature and company data which indicate that the solution production processes are "cleaner" than their emulsion counterparts. The main factor behind this is the absence of coagulation liquor and uncoagulated latex. The COD to BOD ratio is high which indicates that a considerable proportion of the raw wastewater components are not readily biologically oxidizable.

TABLE V - 7

Raw Waste Loads for Solution Crumb Rubber Plants

<u>P</u>	lant	<u>Product</u>	FLOW Liters/1,000 kg	COD kg/1,000 kg	BOD kg/1,000 kg	ss <sup>1</sup> kg/1,000 kg	01L kg/1,000 kg
	K	SBR Oil Extended	10,500	4.04	0.09	0.81	M.A.
	К	SBR Carbon Black Ex- tended	17,800	20.80	0.18	2.20	N.A.
	L	PBR Oil Extended	28,500	13.40	1.55	5.72	2.43
	L	SBR Non-Extended	14,700	13.28	0.82	1.79	1.43
	М	PBR Non-Extended	3,400	0.17	0.06	0.05	0.07
V-12	n	IR Non-Extended	11,900	3.61	1.37	N.A.	0.01
2	N	PBR Part Oil Extended	11,900	3.01	1.37	5.38	2.32
	0	PBR, IR EPDM Part Oil and Carbon Black Extended	29,000	5.33	3.57	3.71	0.23
		Average Value		9.03	1.13	2.81	1.08

Raw waste load determined downstream of crumb pits, where the suspended solids and oil levels are reduced.

N.A. Data not available.

The total dissolved solids content of solution crumb wastewater is considerably lower than for emulsion crumb plants. This again is mainly due to the absence of the coagulation liquor.

Surfactant concentrations in the total plant effluent are low. Surfactants are used to de-agglomerate the crumb rubber during coagulation and rinsing.

The solvent recovery systems do not produce any significant effect on the COD or BOD content of the effluent.

One plant (Plant M) has considerably lower loadings than the others. This is probably due to the fact that rubber for non-tire use is produced at this plant. This rubber is used to manufacture impact-resistant resins, and its quality and production controls are extremely critical. In addition, special finishing equipment appears to be used.

# Individual Waste Streams

The crumb rinse overflow produced at a solution crumb plant is similar to that produced at an emulsion crumb plant, with the exception that uncoagulated latex is not present. The suspended solids, mostly crumb rubber fines, are similar to those in emulsion crumb rinse overflows; the crumb pits produce the same reductions.

The monomer and solvent recovery wastes are comparable to the monomer recovery wastes from emulsion plants. Although heavy slops are produced in some plants, these are usually disposed of by drumming or incineration. Since monomer purities must be high, recovered butadiene, for example, is returned to the monomer supply plant and has no impact on the solution crumb rubber wastewater.

Equipment clean-out wastewaters are less of an environmental problem in a solution plant because much of the processing equipment must be kept dry or water free. Area washdowns are similar in volume, but do not contain latex. These washdowns do pick-up rubber solids and oil from pumps and machinery areas.

The spent caustic scrub solution, where used, is identical to that used in emulsion crumb production. In plants where emulsion and solution crumb rubber is produced, the same caustic scrub system is used for both facilities.

Catalysts and other reaction ingredients do not produce discernible quantities of heavy metals or toxic constituents. Chromium and zinc in cooling tower blowdown are present in some plant effluents, but in very low concentrations. These can be eliminated by using chromium-free corrosion inhibitors.

# Latex Rubber Subcategory

# Flow Analysis

Table V-8 lists the total effluent flows for latex rubber plants. Only two plants are presented, but the similarity between the data values is good. Latex plants are generally part of larger complexes, and flow data for latex operations is difficult to obtain. The flow from latex plants appears to be lower than from either emulsion crumb or solution crumb facilities. The major flow contributions at latex plants originate with equipment cleaning, area washdown operations, and waters from vacuum pump seal systems.

#### Raw Waste Loads

The raw waste loads of latex plant wastewaters are considerably higher than either emulsion or solution crumb plants. Equipment cleanout and area washdowns are frequent due to smaller produce runs, and considerable quantities of uncoagulated latex are contained in these wastewaters. The high COD to BOD ratio is typical of all synthetic rubber subcategories and underlines the resistance to biological oxidation of the wastewater constituents. Oil concentration is lower than in emulsion or solution crumb facilities and is contributed by separable monomers, such as styrene, in the wastes. The suspended solids in the effluent are due mainly to uncoagulated latex. Total dissolved solid levels are lower than for emulsion plants because of the absence of the coagulation liquor stream. Surfactants are present, but in much lower concentrations than the other parameters.

#### Individual Waste Streams

Tank, reactor, and filter cleaning produces considerable quantities of wastewater. These are characterized by high COD, BOD, and suspended solids. In addition, unloading and product loading areas and general plant areas are frequently washed down. The characteristics of these wastes are similar to those produced by usual equipment cleaning in this industry. Vacuum pump seal waters contain small quantities of organics which produce moderate levels of COD from the vacuum stripping operation. The stripping condensates contain condensed monomers. Most of these monomers are decanted from the water and re-used. The water layer overflow from the decanter has high COD and BOD concentrations.

Spent caustic scrub solution is an extremely low flow waste and has similar characteristics to spent solutions produced in emulsion crumb and solution crumb plants.

Plant	Product	FLOW liters/1,000 kg	COD kg/1,000 kg	B0D kg/1,000 kg	SS kg/1,000 kg	01L kg/1,000 kg
Р	SBR and NBR	14,900	36.37	5.61	6.70	N.A.
Q	SBR	12,500	33.52	5.01	5.63	0.33
Average Va	a l u <b>e</b>		34.95	5.31	6.17	0.33

.M.A. Data not available.

#### SECTION VII

#### CONTROL AND TREATMENT TECHNOLOGY

# Survey of Selected Plants General Approach and Summary

In order to review and fully evaluate the wastewater control and treatment technologies used in the rubber processing industry, selected plants were visited to conduct operation analyses, review water and wastewater management programs, and evaluate wastewater treatment facilities. The plants were selected as being exemplary or advanced in their wastewater control and treatment technologies, based on effluent and treatment data from the technical literature, EPA documents, Corps of Engineers Permit to Discharge Applications, and individual company treatment data.

Plants producing passenger tires (both bias and radial ply), truck tires, camelback, and inner tubes were visited and studied to determine if the type of product affected the quality and quantity of wastewater streams and/or the control and treatment technology employed. Both single-product and multi-product plants were included so that the effects of combined lines on the plant wastewaters could be evaluated; likewise, plants of various sizes were studied to determine the impact of production levels. Age was a major consideration because determination of the effect, if any, of newer processing technology and machinery on the control and treatability of process waste streams was one of the principal objectives of the investigative phase of this project. Table VII-1 is a summary of the products manufactured, raw material usage, and wastewater control and treatment technologies utilized at the tire and inner tube plants visited.

In the synthetic rubber production segment of the industry, the field visits included plants employing emulsion and solution polymerization processing methods and involving all types of synthetic rubber products: "cold crumb", "hot crumb", non-extended, oil-extended, carbon-black-extended, and latex rubbers. As in the tire and inner tube segment, the effects of single- and multi-product lines, plant size, and plant age on wastewater volume and characteristics and related control and treatment technology were evaluated. A summary of the products, processes, production capacities, and wastewater control and treatment technologies of the exemplary synthetic rubber plants visited is presented in Table VII-2.

Table VII-1 Wastewater Control and Treatment Technologies at Exemplary Tire and Inner Tube Plants

Primary Effluent

Secondary Effluent

	Plant	<u>Product</u>	Raw Material Usage (Kg/day)	Control Measures	Treatment	Treatment
V11-2	A	Passenger Tires, Implement Tires, Front Tractor Tires	120,000	Recirculation of Soapstone, Absence of Drains in Dirty Areas	Sedimentation and Holding Lagoon	No Discharge due to Spray Irrigation and Evaporation of Wastewaters
	<b>B</b> ·	Passenger Tires, Industrial Tires	310,000	Recirculation of Soapstone, Baffled Oil Separator for Oil Storage Area, Absence of Drains in Dirty Areas	Sedimentation and Lagoons	None
	C	Passenger Tires	349,000	Recirculation of Soapstone	Primary Settling Basins	None
	D	Passenger Tires, Truck Tires, Tractor Tires, Camelback	840,000	Recirculation of Soapstone, Oil Separator, Local Oil Sumps	Gravity Separator for Boiler Blowdown, Some Water Treatment Wastes and Wash- down of Soapstone Area	Discharge of Some Water Treat- ment Wastes to Municipal Treat- ment Facility
	E	Passenger Tires, Truck Tires	210,000	Blockage of Drains, Local Oil Sumps and Gravity Separators, Curbing of Soapstone Area, Re- circulation of Soapstone	None	Discharging of Process Waste to Municipal Treatment Facility
	F	Passenger Tires, Truck Tires, Inner Tubes, Camelback	681,000	Recirculation of Soapstone, Oil Sump for Oil Storage Area	Primary Settling Basin and Clarifying Basin	None
	G	Passenger Tires, Truck Tires	246,000	Recirculation of Soapstone, Oil Sump and Curbs for Oil Storage Area	None	None
	н	Truck Tires, Industrial Tires	244,000	Recirculation of Soapstone	Sedimentation Basins for Boiler Blowdown, Cooling Tower and Water Treatment Wastes	Discharge of Treated Wastes to Municipal Treatment Facility
	ı	Inner Tubes	75,000	Containment of Soap and Soapstone Solutions	None	None

Table VII-2
Wastewater Control and Treatment Technologies at Exemplary Synthetic Rubber Plants

Plant	Product 1	Process	Production Capacity (metric ton/year)	Control Measures	Primary Effluent Treatment	Secondary Effluent Treatment
J	Crumb SBR Crumb NBR	Emulsion	390,000 10,000	Crumb Pits, Carbon Slurry Pit	Chemical Coagulation and Clarification	Aeration, Settling and Stabilization Lagoons
К	Crumb SBR	Solution Emulsion	130,000 200,000	Crumb Pits, Carbon Slurry Pit	Air Flotation Primary Clarification	Aerated Lagoon and Air Flotation Secondary Clarification
ι	Crumb SBR Crumb, hot SBR Crumb PBR Crumb SBR	Emulsion Emulsion Solution Solution	120,000 3,700 52,000 10,000	Crumb Pits	Chemical Coagulation and Settling Ponds	Aeration Lagoon and Stabilization Ponds
M	Crumb PBR	Solution	85,000	Crumb Pit, Dry De- solventizing Process, Spent Caustle Pit with Slow Bleed Dis- charge	Oil Separator	None
N	Crumb IR Crumb PBR	Solution Solution	65,000 110,000	Crumb Pits	Equalization Basin	Activated Sludge
0	Crumb PBR Crumb IR Crumb EPDM	Solution Solution Solution	56,000 50,000 25,000	Crumb Pits, Carbon Slurry Pit	Settling Lagoons	Stabilization Lagoon
P	Latex SBR Latex NBR	Emulsion Emulsion	18,000 3,000	Excess Monomer Decant System	Coagulation and Settling Pit	Activated Sludge
Q	Latex SBR	Emulsion	21,000	Excess Monomer Decant System	Chemical Coagulation and Clarification	Discharge to a Municipal Sewage Treatment Plant

SBR: styrene-butadiene rubber, NBR: acrylonitrile-butadiene rubber, PBR: polybutadiene rubber, EPDM: ethylene-propylene diene rubber.

# Tire and Inner Tube Plants Plant A

This plant, built in 1961 and located in an arid rural community, produces passenger tires, small-implement tires, and front tractor tires. Production rate for passenger tires at the time of the visit was 12,000 units per day. In addition to the normal tire processing and production lines, this plant has a latex fabric-dip operation. Raw material consumption was over 120,000 kg(264,000 lbs) per day.

The actual production facility occupies approximately 40 acres of land. The plant boundaries surround another 350 acres of land currently devoted to agricultural use.

The only source of raw water supply is well water. It is used for cooling, steam generation, domestic use, and all other plant needs.

The principal process wastewaters from this plant are water and steam leakages, and wash waters from the cleaning of equipment and general work areas. Water leakage occurs at various water-cooled machinery units, including mills, Banburys, tread extruders, and tread-cooling tanks. In addition, water can escape from the hydraulic water system used in the Banbury and press areas. Water and steam occur in the process wastewater in the press area as the result of broken seals or failing bladder bags. Oil and solid matter which have collected on the floors are carried along by these various water streams into the area drainage system. The oil is lubrication oil which has dripped or leaked from oil seals on mills, pumps and like equipment, from open gears, from gear boxes, and from the hydraulic water system. Additional oil and soild materials result from leakages at the Banbury dust and oil rings.

Daily washdowns include steam and solvent cleaning of the tread books and miscellaneous machinery parts and the cleaning of the latex dip tank. Weekly cleanups, which occur on the weekends (non-production days), include washdown of the steel grates in the soapstone area.

This plant was specially laid out and engineered so as to keep spills and leakages from becoming a problem. Drains are non-existent in the soapstone area and in many of the mill areas. Removable steel grates have been provided in the soapstone dip area so that spilled soapstone solution will not create a work hazard. Housekeeping practices and schedules have been set up to keep leaks and spills of lubricating oil on the floors of the flant to a minimum. When steam and water leakages do occur, they are directed (along with all other process and non-process wastes) to a collection pond. Equipment-cleaning wastewaters are also discharged to this pond.

The principal non-process wastewaters are boiler and cooling pond blowdowns. In addition, there is a hot-water-sump overflow. The hot-water sump is used as a collection point for recycled press cooling water. Contaminants in these wastes are suspended and dissolved solids.

End-of-pipe treatment at this plant includes pH control and the lagooning of all effluents, both process and non-process. The wastewaters, after pH adjustment, are directed to the 11 million liter (3 million gallon) collection and storage pond. The residence time in this pond is approximately four days. Settling of suspended solids and the reduction of both COD and oil occur during this period of time. From here, the wastewaters are fed to a second pond. Water leaving the second retention pond can be used for any of three functions. It can be used for irrigation on the company-owned farm acreage around the production facility (its primary function), it can evaporate, or it can percolate into the sandy ground below the pond. (The water table at this plant is approximately 76 meters (250 ft.) below the surface.)

In addition to containment of all process and non-process wastewaters, all storm runoff from within and around the plant confines is directed to and contained in these lagoons.

# Plant B

This plant, located in a rural area, started operating in 1964. Plant-owned ground is now almost entirely utilized by processing and warehousing buildings, parking lots, and wastewater treatment facilities.

The facility produces passenger tires and heavy off-the-road tires. Production rates are currently running at 24,000 passenger and 2,000 off-the-road tires per day.

Water for all plant uses, including makeup for the cooling towers, boiler and various dipping solutions, is supplied by the municipality.

The principal process wastewaters from this plant are: water and steam leakages, runoff from the process oil storage area, and discharges from wet air-pollution control equipment.

Water and steam leakages occur in the press room of both the passengertire and truck-tire facilities. These streams become contaminated with oil scavenged off machinery parts and the floor. Runoff from the oil storage area is continuous due to the placement of a steam blowdown pipe nearby; oil is scavenged from the area and becomes entrained with the condensate wastewater stream. Wet scrubbers are used to control air emissions from the compounding area and from the green tire painting area. Collectively, these scrubbers represent the largest single discharge in the plant. Contaminants include COD and suspended solids, as well as some oily matter.

Maintenance and housekeeping practices at this plant are directed at keeping leakage at a minimum and well contained. Runoff from the process oil-storage areas is pretreated in a baffled oil separator chamber before flowing to the end-of-pipe treatment facilities. The separator unit effectively removes oil from the small volume of water in the influent.

Water discharged from air pollution equipment passes into the plant's endof-pipe treatment facility untreated.

The principal non-process wastewaters are boiler and cooling tower blow-downs, and water treatment wastes; these are segregated from the process wastewaters and are discharged, without subsequent treatment, into the storm drainage system.

In addition, there are blowdowns from various presses throughout the plant; these contain COD, suspended solids, and dissolved solids.

End-of-pipe treatment at this plant involves the use of two lagoons. The wet scrubbers and steam blowdowns flow into the first lagoon, which is used to separate settleable solids and separable oil. This pond has a surface area of 0.52 acres and a baffled effluent weir. Wet scrubbers, and some once-through cooling water flow to the second lagoon. This has approximately 0.74 acres of surface area and is also used to remove separable solids and oil from the influent.

#### Plant C

This production facility consists of two plants, the older of the two dating from 1945 and the newer one coming on stream within the last decade. The facility is located in an industrialized area on the fringes of an urban center. Most of the land within the plant boundaries is occupied by production buildings and by the necessary auxiliary buildings, waste treatment facilities, and parking areas. The facility produces only passenger tires (both bias ply and radial). Raw material consumption is approximately 349,000 kilograms (770,000 pounds) per day. Exact unit production rates are unknown, although the figure is known to be well above 20,000 units per day.

The principal process wastewaters are water and steam leakages, overflow from various sumps, and runoff from oil storage areas. Water leakages occur throughout the plant wherever there is water-cooled machinery, such

as mills and Banburys. Water and steam leakages occur in the press area due to leaking seals, failing bladder bags, and leakages in the hydraulic water system. The process wastewaters scavenge oil and solid materials, which flow to the nearest drain. Oil and solid material accumulate on the floor and in the various machinery basins due to dripping and leaks from the Banbury dust rings, mill and pump oil seals, open gears, and the hydraulic water system. Runoff from oil storage areas occurs during rainstorms and washdowns, and is another source of oily process wastewater.

This plant at one time had a process wastewater discharge of soapstone solution. After extensive studies showed that this solution caused excessive BOD and total solids in the wastewater, this discharge was eliminated. The current practice is to recycle this solution.

Wastewater streams resulting from the use of other solutions in the plant, such as the latex dip, have also been eliminated. These streams are dumped into a sump, which is periodically emptied into drums and sent to a landfill site.

The principal non-process wastewaters are boiler and cooling tower blow-down, once-through tread cooling water, and water treatment wastes. In all cases, dissolved solids are a problem, and suspended solids will be a problem in the water treatment waste and boiler blowdown.

Process wastewaters and all the non-process wastewaters (with the exception of boiler blowdown) are combined and then directed to a primary treatment facility. This treatment facility consists of two settling basins, operating in parallel. Each provides 24 hours retention for the waste streams. Settleable solids are removed periodically (approximately every two years), and floating oil is removed by a belt filter. Boiler blowdown and sanitary wastes are treated in a package extended aeration sanitary wastewater treatment plant. All treated wastewaters are discharged to the river.

## <u>Plant D</u>

This plant, started up in the early 1940's, is located in an urban, industrialized area. It has recently undergone extensive modifications, and, therefore, production levels are not well established. However, past data indcate that the plant is producing 22,000 passenger, truck, and tractor tires per day. The plant also produces camelback. Raw material consumption is in the neighborhood of 840,000 kilograms (1.85 million pounds) per day.

Raw water is supplied by the municipality and from company-owned deep wells. The city water is used to supply domestic and air conditioner

cooling needs. The wells supply once-through cooling water, cooling tower makeup, boiler feed water, and processing solution makeup.

The principal process wastewaters from this plant include: water leakages, steam leakages, a weekly washdown of the soapstone recirculation system, equipment and floor cleaning washdowns, and minor runoff from the oil storage area.

Water leakages arise from the oil seals and open gears on mill calendars and pumps and from the hydraulic water system used in the Banburys and presses. Steam leakages occur in the press room from broken or leaking seals and failing bladder bags. Both types of leakage are heavily laden with oil picked up from the seals and from lubricating oil drippings. The soapstone recirculation system is cleaned out once a week, and the effluent has high BOD and suspended solids loadings. The floors are cleaned with an automatic sweeper that uses a soapy water solution as a cleaning agent. Drainage from this system also has a high BOD and suspended solids loadings. Steam cleaning is used for small machinery parts, and the discharges are significantly contaminated with oil.

Water and steam leaks in the press area are pumped to an oil separator, where the floating oil is removed and disposed of by an outside contractor. Water leakages in the mill area are kept at a minimum by careful house-keeping and maintenance practices, and do not appear to be a serious problem. Runoff from oil storage areas is collected in sumps, which are pumped out on an "as required" basis.

Floor-cleaning machinery discharges and steam-cleaning discharges flow into the sanitary sewer.

The principal non-process wastewaters are boiler and cooling tower blow-downs, water treatment wastes, and once-through cooling water. In the first three cases, dissolved solids constitute a problem. Boiler blowdowns and water treatment wastes may also contain high concentrations of suspended solids, depending on the treatment process being used. COD and pH may also be problems.

There is no end-of-pipe wastewater treatment facility which covers the entire process wastewater stream. Some non-process wastewater and the weekly dump of the soapstone slurry are directed to a holding basin for removal of settleable solids before discharge.

## Plant E

This facility which was started up in 1920, is a sprawling complex occupying 25 major buildings and more than 74 acres of ground. Although it is located in a very congested urban area, the plant boundaries enclose approximately 13 acres of open ground.

The plant was originally set up to produce many rubber products, including tires, belting, and inner tubes. However, with the passage of time and because of specialization, production of all rubber products with the exception of tires has been discontinued. Current production levels are 10,400 passenger tires per day and 4,400 truck tires per day. Total raw material consumption is 210,160 kilograms (462,900 pounds) per day.

Production facilities are located in three buildings. The Banburys and mills of the compounding operation and the presses of the molding and curing operations are located in separate buildings (Banbury and Press Buildings). The mills, extruders, calendars, etc. of the tread and bead formation lines and of the fabric-coating operations are all located in a large building (Rubber Mill Building) located between the compounding and curing buildings. The buildings are interconnected so as to approximate a continuous production line. Fabric is shipped to this plant pretreated, and no additional dipping operations are performed.

The plant has two separate sources of raw water supply: well water and municipally supplied water. The well water is used primarily for cooling tower makeup, and the municipal(city) water is used as boiler makeup, after treatment. The city water is also used in making the soapstone and other solutions used in tire manufacture.

The principal process wastewaters include water and steam leakages, steam cleaning, and wet air-pollution equipment discharges. Water leakages arise from water-cooled machinery, such as mills, Banburys, tread extruders, and tread cooling tanks. In addition, water can escape from the hydraulic water system used in the Banbury and press areas. Water and steam leakages occur in the press building due to broken seals and failing bladder bags. These wastewater streams are heavily laden with oil picked up from the seals and from floor areas and basins. Machinery parts such as gears and bearings are cleaned with steam, and the resulting waste contains both oil and suspended solids. Grinding operations within the plant are equipped with wet particulate collectors. Effluents from these collectors are small in volume but contain a high concentration of heavy rubber as suspended particles. Zinc and chromium are used as corrosion inhibitors and will therefore be present in the collector discharge.

Leakages, both steam and water, are collected in two sumps, one located in the press building and the other in the rubber mill building. These sumps separate the oil, and the resulting underflow is released to a sanitary sewer. Sanitary sewers within the plant are connected to the municipal sanitary sewer system and eventually to the municipal wastewater treatment plant. Oil from the sump is removed periodically by maintenance personnel.

Steam cleaning of machinery parts is carried out in a non-congested out-door area of the plant. Curbing and concrete flooring are used to direct the wastewaters into three small basins connected in series. The area is supplied with a roof to prevent storm water from diluting the wash water and upsetting the settling operation. Storm runoff from this area is directed into the storm-water catch basins. These catch basins act as gravity separators, allowing the separable suspended solids to settle out and oil to float to the surface. The effluent from the basin discharges into the sanitary sewer. Solids and oil are removed from these basins periodically.

The effluent from the wet particulate collectors flows into a set of similar settling basins, where most of the solids are settled out. The effluent then discharges into the sanitary sewer. These basins are equipped with automatic solids-removal equipment.

All solids and oil removed from the various treatment facilities are containerized and disposed of by contract hauler to a landfill.

The principal non-process wastewaters are boiler and cooling tower blow-downs, and water treatment wastes. In all cases, dissolved solids are present in the wastewater, generally at high concentrations. Boiler blow-downs and water treatment wastes also contain high concentrations of suspended solids. The water makeup for the cooling tower which supplies cooling water to the press building is treated with a corrosion inhibitor containing chromium and zinc, and these metals are present in the blowdowns.

At this plant, there is no end-of-pipe treatment facility. All contaminated process and non-process wastewaters (with the exception of the main cooling tower) are discharged to a municipal treatment facility.

#### Plant F

This production facility, built in 1928, is located in a minor urban area, on a large (more than 2.8 billion square meters (700 acres)) plot of ground, of which the actual production facility occupies only a small proportion.

Production lines include passenger tires, truck tires, inner tubes, flaps, bladders, and camelback. The plant, as currently designed, is divided up into separate product unit buildings for each end product. Daily production rates are currently running at 40,000 passenger and truck tires, 36,000

inner tubes, 13,000 bladders and flaps, and 60,000 lbs. of camelback. Daily raw material consumption is 681,000 kilograms (1.5 million pounds). This plant utilizes river water for production and utility purposes and city water for domestic purposes.

The principal process wastewaters from this plant include: water and steam leakages and overflows, runoff from process oil-storage areas, soapstone solution spillages, and wash downs and runoff from process or storage areas.

Water leakages occur at various water-cooled machinery units, including mills, Banburys, tread extruders, and tread cooling tanks. In addition, water can escape from the hydraulic water system used in the Banbury and press areas. Water and steam leakages occur in the press area due to broken seals, failing bladder bags, and overflows from the collection pumps, Oil and solid matter which have collected on the floor are scavenged by these various water streams and are carried untreated to the drainage system. Oil on the floor spaces is lubricating oil which has dripped or leaked from oil seals on mills, pumps, and like equipment, from open gears, from gear boxes and from the hydraulic water system. Oil and solid materials result from leakages at the Banbury dust and oil rings.

Soapstone solution which has spilled and dripped on the floor is washed down periodically and enters the drainage system untreated. Typical contaminants are BOD, suspended solids, and dissolved solids.

Washdown water and storm runoff are allowed to drain through the process oil-storage area, where oil is scavenged and carried to the drainage system. Before discharge to the sewer, this stream is pretreated in a baffled sump, where oil is separated, removed by a belt filter, and disposed of at a sanitary landfill. The sump is baffled, but provides no excess capacity for oil separation during a storm runoff.

The aforementioned process wastewaters are mixed with non-process wastewaters in the drainage system. The non-process wastewaters include once-through river water, boiler blowdown, and a small overflow from the numerous small pump sumps located throughout the plant.

End-of-pipe treatment facilities consist of a two-stage detention basin. The primary facilities provide approximately 2,000 square meters for bottom and surface removal of separable materials. During dry-weather flow the surface loading is 49,000 liters/day/sq. m. (1,200 gals/day/sq. ft.), which is too high for effective treatment of wastewater of this character. It is estimated that the facilities provide little or no treatment whatso-ever during periods of significant runoff. The primary facilities are followed in series by a pond baffled down the middle to retain floatable materials. Some additional settleable materials are also contained, but no facilities are provided for removal of floatable or settleable materials except on "as required" basis.

The secondary pond provides a theoretical detention time of twelve hours during dry-weather flow. However, this is significantly reduced by short circuiting attributable to the location of the inlet and outlet connections. Surface loading on this pond is adequate for removal of separable materials during dry-weather flow as well as during storm weather runoff conditions. However, the surface of the pond is subject to wind turbulence, which may remix the separated floatable materials.

## Plant G

This production facility, built in 1928 is located in a highly congested, highly industrialized suburban area. Built and originally operated by another company, it was bought by the current operator in the 1930's and converted to tire manufacture. The facility produces passenger and truck tires. Daily production rates are currently running at 18,300 passenger tires and 1,150 truck tires. Raw material consumption is over 246,000 kilograms (541,000 pounds) per day.

The plant occupies approximately 280 million square meters (70 acres) of ground, with most of the land occupied by production and warehousing buildings. Because of the industrial development around the plant, there are no foreseeable plans for expansion at the current facility.

Well water is the only source of raw water supply to this plant, and is used for all plant water needs.

The principal process wastewaters from this plant are water and steam leakages, and washdown and runoff from the machine shop area. Water leakages occur in the press are due to broken or leaking seals and failing bladder bags. These process wastewaters scavenge oil and solid materials as they flow to the drains. Oil and solid materials accumulate on the floor and in various machinery basins due to drippings and leaks from the Banbury dust rings, mill and pump oil seals, open gears, and the hydraulic water system. In the machine shop area, steam used for cleaning of parts and runoff from painting and washdown operations is allowed to enter the storm drain; these wastewaters may be contaminated with both oil and solid material.

Runoff from the oil-storage is not a problem in this plant, because the drain in this area has been surrounded by a curb which prevents normal spills from entering the sewer system. In addition, there is a straw filter covering the drain inlet. Oil that spills in this area is pumped into a special storage tank which is periodically emptied; this waste oil is sent to a landfill site.

Both process and non-process wastewaters flow to a common sewer, where they are discharged to the municipal storm sewer. Before leaving the plant, all wastewaters must flow through a shredded plastic filter which retains floatable oil. This filter is replaced periodically. The oil trapped behind the filter is also removed periodically.

## Plant H

This facility, built in 1945, is located in highly congested and highly industrialized area. Essentially all of the plant-owned land is utilized for production and warehousing facilities, utility systems, and wastewater treatment facilities. Expansion of the current plant would necessitate the leasing of land from adjacent landowners.

The facility produces truck tires, industrial and farm tires, giant offthe-road tires, and various other minor products including bladders and rubber gaskets for the curing presses.

Current production levels for the major products are 6,850 truck tires and 2,430 industrial, farm and giant off-the-road tires per day.

Sources of raw water include surface water from a nearby river and municipally supplied water. Surface water is used as the primary source of once-through cooling water and for makeup to the cooling tower and other recirculating water systems. City water is used as for boiler feed water and also as a backup for the surface water in recirculating water systems.

The principal process wastewaters are from water and steam leakages from presses and mills. These leakages occur at the oil seals of mills, at the hydraulic water system, and at the curing presses. The leakages scavenge oil and soilds spilled in press and mill basins due to open bearings and lubrication of machinery parts.

The principal non-process wastewaters are the overflows and blowdowns from various recirculating water systems, the once-through cooling water, boiler blowdown, and water treatment wastes. Contaminants in these wastewaters include suspended and dissolved solids; these wastewaters also require pH adjustment.

Whenever possible, oil that leaks or spills onto the floors or basin areas is collected. This oil either is drummed and sent to a sanitary landfill or is filtered and reused. Plant engineers are currently examining the feasibility of using this oil as a fuel admixture in the boilers. With the oil on the floor kept at a minimum, less can be scavenged by water or steam contact. There is however, no treatment at this plant for the oily wastewaters that do occur; they would be discharged with either once-through cooling water or the utility wastewaters.

There is no end-of-pipe treatment for the once-through (non-contact) cooling water; except for oil picked up due to leakages and spills this water is

uncontaminated, and discharges back to the river. Discharges from the other utility systems, such as boiler blowdown, cooling tower blowdown, and water treatment wastes are directed to an effluent basin, where settleable solids are removed. The surface loading is (600 liters/day/sq. meter), and the theoretical detention time is 24 hours. There is no provision for continuous removal of solids or oil. Discharges from the effluent basin are directed via a sanitary sewer system to a municipally operated treatment plant.

# Plant I

This plant, built in the late 19th century, is now involved in the manufacture of inner tubes, valves, flaps, and simlar items associated with automobile tire applications. Raw material consumption is approximately 75,000 kilograms (165,000 lbs.) per day. This amounts to an equivalent of over 50,000 inner tubes per day.

The production facilities occupy a multi-story building in the downtown area of a major city. There has been no expansion at this plant for the last fifty years. Because of the extremely tight land situation and because of the relatively stable tire-tube market, no expansion is planned in the foreseeable future.

All the raw water used in this facility is provided by the city.

Principal process wastewaters are water and steam leakages, and the wash-down of dusty areas within the plant. These streams become contaminated with oil and dust that is scavenged from floor and machinery areas. These wastewater streams flow into a sewer and are combined with non-process wastewaters before discharge from the plant. Non-process wastewaters include once-through cooling water, cooling tower and boiler blowdowns, and water treatment wastes. Suspended solids will be present in substantial quantities in the blowdowns and water treatment wastes.

The city sewers are combined sewers; consequently, domestic, process, and non-process wastewaters are mixed and treated in the municipal wastewater treatment facility.

The housekeeping practices in the plant are unique. Spillages of soap and soapstone solutions do occur, but the quantities are so slight that they tend to evaporate on the spot; soapstone solution is neither dumped nor recirculated. In processing areas, water is not used for washdown. Dust is such a problem (due to the use of soapstone in dry form) that any attempt to use water for washdown merely complicates the problem.

There were no wastewater treatment facilities operating at the plant at the time of the visit. The upgrading of air quality within the plant has completely occupied the attention of the engineering staff, thus relegating concern for water effluent quality to a secondary position.

# Synthetic Rubber Plants Plant J

Emulsion styrene-butadiene (SBR) and acrylonitrile-butadiene (NBR) synthetic rubbers are produced at this plant. The annual production capacity is 390,000 metric tons of SBR and approximately 10,000 metric tons of NBR. The plant is located in an industrial area with land available for expansion.

Both SBR and NBR are produced by emulsion polymerization processes. The monomers are shipped into the complex from adjacent plants. The SBR crumb is produced in non-extended, oil-extended, and carbon-black-extended forms, while the NBR is produced in non-extended form only. The crumb rubber is used principally as tire rubber. There are sixteen coagulation and finishing lines in the plant.

The plant's intake water comes from two sources. River water is used for cooling tower makeup, crumb rubber washing-slurrying, and area washdown. Plant well water is softened and then used for solution preparation. The plant does not have its own steam generating plant and purchases steam from an adjacent facility.

The main process wastewaters are generated at monomer recovery, crumb coagulation, and rubber washing operations. Decant water from the monomer decant system is recycled in part to the crumb slurrying operation. The remainder, containing styrene and acrylonitrile, is discharged to the process sewer system and has a significant COD. The coagulation liquor overflow is a brine-sulfuric acid mixture, with a low pH, high total dissolved solids, and moderate COD. The crumb slurry overflow contains COD, crumb rubber particles as suspended solids, and oil (when oil-extended forms are produced). The crumb-laden slurry overflow and the overflow of coagulation liquor pass through crumb settling pits where the crumb separates and is removed periodically by a scoop. The cleaning of the crumb pits results in a temporary upset as the settled crumb is disturbed and re-suspended. This results in poor effluent quality from the pits for a short period.

The cleanup wastes from the latex vacuum and steam stripping units are another process wastewater source. This wastewater is characteristically high in COD and suspended solids, and contains uncoagulated latex. The units are cleaned periodically and large volumes of water are used in this operation. The resulting wastewaters are passed through settling sumps, where rubber solids settle out.

Clean-out wastewaters from reactors and holding tanks are also produced on an intermittent basis. These wastewaters, containing COD and suspended solids, both as rubber solids and as uncoagulated latex, are also passed through settling pits. Spent caustic soda scrub solution used to remove inhibitor from butadiene prior to its polymerization, is bled into the plant effluent; this waste stream has high COD, pH, alkalinity and color, and contains some phenols. Its flow rate, however, is very low.

The carbon black storage facilities, consisting of railroad unloading equipment, a storage hopper, and slurrying equipment, generates a wastewater which is laden with fine carbon black particles. This wastewater is the result of the washdown and cleanup of carbon black spills and air-borne fallout. These wastewaters pass through two settling pits, which operate in parallel. When one pit is full of carbon black wastewater, the wastewater is allowed to settle and the second pit is filled. The settling pits achieve satisfactory clarification of the wastewater.

The utility wastewaters consist of cooling tower blowdown and water softener regeneration wastes. (There is no boiler blowdown, since the plant's steam is purchased.) One cooling tower has a very low blowdown rate, since a high proportion of the tower's makeup is steam condensate. The other cooling tower has a normal blowdown rate and generates wastewater containing chromium, zinc, and other heavy metal ions.

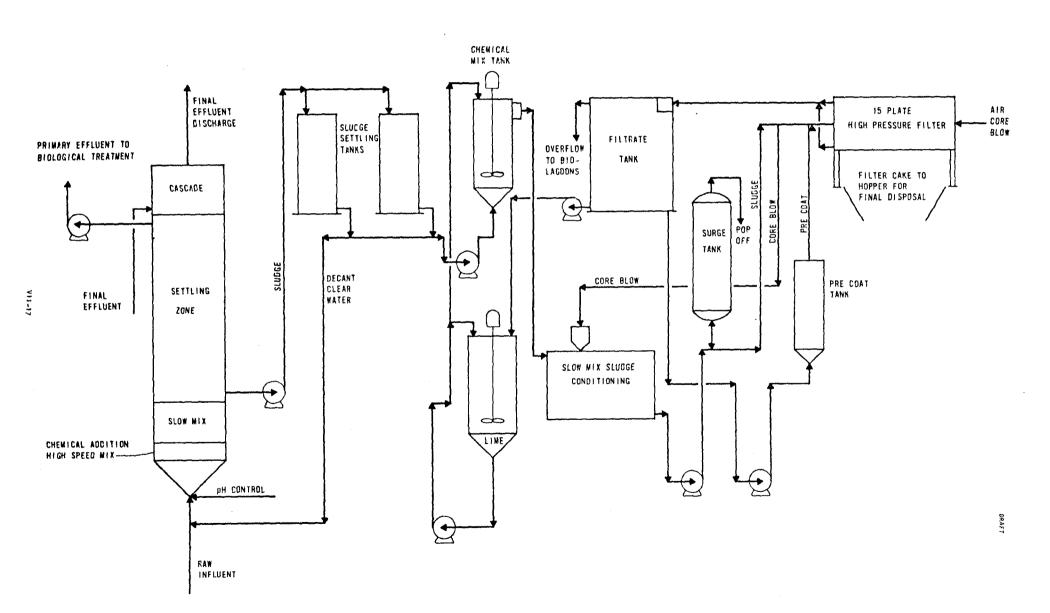
The plant's effluent treatment system consists of chemical coagulation and primary settling, followed by an aeration lagoon and a settling lagoon. The primary settling facility and the sludge handling system are shown in Figure VII-1. In the chemical coagulation process, the pH of the influent wastewater is first adjusted using sulfuric acid and caustic soda. Coagulation chemicals (alum and polyelectrolyte) are added, together with clay. The latex and fine suspended solids coagulate around the clay, which causes the coagulated solids in the primary clarifier to sink. The solids from the primary clarifier are thickened and pressure filtered, using a lime slurry and filter aid. The filter cake is hauled away by truck to a landfill. The thickener supernatant is returned to the head end of the plant, and the filtrate is discharged to the aeration lagoon. The plant effluent quality is good:

COD	325 mg/L
BOD	25 mg/L
SS	30 mg/L

The high residual COD concentration is typical of the high biological resistance of the wastewater components. The plant currently is conducting pilot studies to investigate the feasibility of using activated carbon to reduce the residual COD. The results to date indicate that a final effluent COD of 130 mg/L could be reached, but the company concluded that the costs to implement this system would be prohibitive.

FIGURE VII-1

PLANT J: CHEMICAL COAGULATION AND CLARIFICATION PLUS SLUDGE HANDLING SYSTEM FOLLOWED BY BIO-OXIDATION TREATMENT



## Plant K

The plant complex consists of emulsion and solution styrene-butadiene rubber (SBR) production facilities. The annual production capacity of emulsion SBR is 200,000 metric tons and of solution SBR is 130,000 metric tons. The complex is located in an industrial area with virtually no land available for further expansion.

The emulsion crumb rubber is produced in non-extended, oil-extended, and carbon-black-extended forms. The emulsion rubber processing plant is arranged into essentially two parallel operations; each operation consists of a solution preparation building, a polymerization area, a coagulation and finishing building, and a monomer recovery complex. The solution crumb rubber is produced also in non-extended, oil-extended and carbon-black forms. The solution rubber processing facilities are similarly divided into two parallel units; each unit consists of a polymerization area, a crumb slurrying and finishing building, and a solvent and monomer recovery complex. The solvent used is hexane.

The plant water supply is from on-site wells. The boiler feed water is subjected to hot lime softening and normal boiler feed treatment chemicals. The cooling tower makeup is treated with corrosion inhibitors, anti-sealing agents, and slimicides. The process water used in emulsion rubber production is zeolite softened. Untreated well water is used for slurrying, rinsing, and washdown.

The principal emulsion process wastewaters are the coagulation liquor overflow, the crumb rinse overflow, and the monomer recovery streams. The coagulation liquor is a sulfuric acid-brine mixture with a low pH, high total dissolved solids, and moderate COD. The crumb rinse overflow contains floatable crumb rubber as suspended solids. In addition, the slurry overflows have high total dissolved solids and moderate COD.

The coagulation liquor and crumb slurry overflow pass through settling pits, where the rubber solids separate. Under normal operation, the separator pits work well, but they are not cleaned frequently enough, and short-circuiting occurs. Furthermore, during the cleanout operation the pit is disturbed, and the once-separated rubber escapes into the effluent. Some pits contain an oil layer because baler hydraulic fluid or extender oil leaks onto the floor and is washed down into the settling pit.

The wastewaters from the monomer recovery area are characterized by high COD and suspended solids. These wastewaters originate at monomer decant systems and cleanup operations, and contain uncoagulated latex. The wastewaters from the periodic cleaning of the monomer recovery stripping columns

contain high concentrations of COD and of latex and rubber solids. These waters pass through settling sumps to separate the rubber solids and the floating oils. These pits are also cleaned out periodically.

The caustic scrub solution is discharged to the final effluent when it becomes saturated with inhibitor. This wastewater is of very low flow (less than 1 gpm), but has high COD, pH, alkalinity and color. When the latex storage and the blend tanks are cleaned, the latex-laden rinse water can be used for latex blending if its solids content is greater than 2 percent. Tankage rinse waters with rubber solids levels of less than 2 percent are discharged to the plant effluent. The major contaminant in this water is uncoagulated latex.

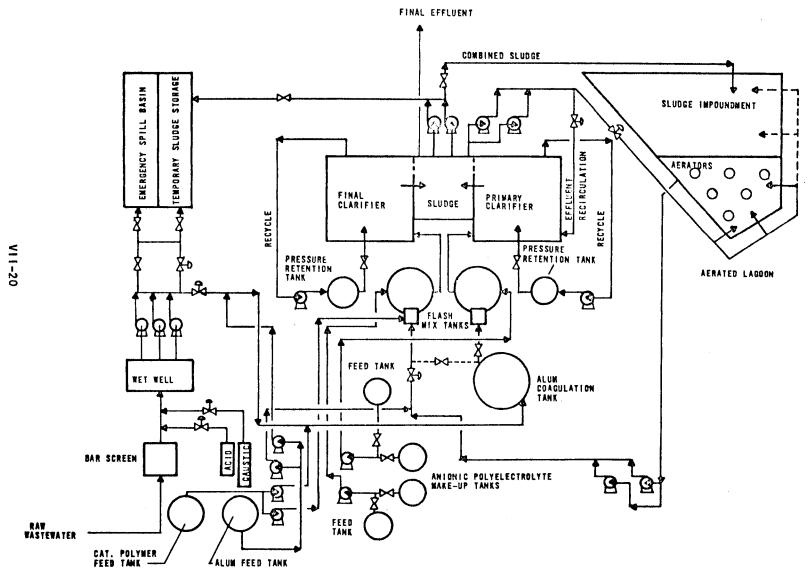
The carbon black slurrying area is equipped with a settling pit which receives spillages and washdown wastewaters. The carbon black settles out, and the wastewater overflows at a very low flow rate into the final effluent. The settling pit is cleaned out periodically with a vacuum truck.

The solution rubber process wastewaters are very similar to those of other solution rubber production facilities. The principal streams originate at the crumb slurrying operation and the solvent-monomer recovery areas. The crumb slurry overflow has moderate COD, suspended solids, and total dissolved solids. It passes through a settling sump, where suspended solids are removed. The wastewaters from the solvent and monomer recovery areas are stripped condensates and decants, and are characterized by moderate amounts of COD and floating oils.

The utility wastewaters are boiler and cooling tower blowdown and water treatment wastes. The boiler blowdown has high total dissolved solids and a high pH. The cooling tower blowdown contains high total dissolved solids and moderate levels of chromium and zinc from chemical inhibitors. The spent lime slurry from the hot lime water treatment system exhibits a high pH and suspended solids level. The lime slurry settles out in the plant drain and must be mechanically removed at periodic intervals. The waste from the zeolite softener regeneration is a concentrated brine solution with high total dissolved solids.

The wastewater treatment system consists of air flotation clarification and biological treatment (refer to Figure VII-2). The wastewater first passes through a mechanical bar screen which removes large rubber solids, and is neutralized to pH 7.0 and dosed with coagulant and flocculant aids in a rapid-mix tank. The wastewater then passes through a flocculator tank and into the primary clarifier, where a slip-stream laden with air is released near the bottom of the unit. The rising air bubbles carry the suspended solids and oil-type contaminants to the surface, where they

FIGURE VII-2
PLANT K: AIR FLOTATION AND BIO-OXIDATION WASTEWATER TREATMENT FACILITY



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are skimmed off. The clarified effluent flows into an aerated lagoon, equipped with six aerators, where it is retained for 24 hours.

Effluent from the aerated lagoon is pumped to the secondary air flotation clarifier, where biological solids are removed. Operations include rapid mix of coagulation chemicals, flocculation, and clarification. The primary and secondary sludges are pumped to an on-site sludge lagoon for dewatering and drying. Studies are being conducted to dispose of this sludge by off-site landfill or via incineration. The treatment plant produces a high-quality effluent. Pollution parameters which are still present at substantial levels after treatment are total dissolved solids and COD. The residual COD underlines the inherent biological resistivity of some of the wastewater constitutents.

## Plant L

This plant has SBR, polybutadiene, resin, and oil-additive production facilities. In addition, there is a rubber compounding facility which produces sheet rubber as a customer service. The annual production rates are:

Cold-emulsion SBR	120,000 metric tons
Hot-emulsion SBR	3,700 metric tons
Solution-type polybutadiene	52,000 metric tons
Solution SBR	10,000 metric tons

The plant is located in a rural area with land available for expansion. Emulsion rubber production stared in 1943, solution type polybutadiene in 1960, and solution type SBR in 1963.

The cold-emulsion type SBR is produced in non-extended, oil-extended, and carbon-black-extended forms. It is used primarily in tire manufacture. This type of emulsion SBR is similar to that produced at the other plants described in this section. The process for hot-emulsion SBR is a higher-temperature polymerization and is non-extended; this product is used primarily for electrical wire covering. The solution type polybutadiene is produced as non-extended and oil-extended rubbers and is used primarily in tire manufacture; toluene is the solvent. Solution SBR is non-extended and has several end uses. The butadiene used in the plant is received by pipeline from a neighboring plant, and the styrene is shipped in by tank truck.

The plant's water supply consists of well water. The plant does not have steam generating facilities but purchases steam from an adjacent plant. The well water is treated with corrosion inhibitors, slimicides, and dispersants for cooling tower makeup and is softened to provide process water for preparation of the emulsion rubber solution.

The process wastewaters from emulsion rubber production originate principally in two areas: crumb slurrying and monomer recovery operations. These wastewaters are typical of emulsion rubber production facilities. The slurry overflow is passed through a crumb pit to separate the crumb rubber fines. The monomer strippers are cleaned periodically. The vacuum stripping vessels and steam stripping columns are flooded with wash water, and the residual latex and rubber solids are discharged with the wash water. The units are finally rinsed, producing more wastewater with additional suspended solids.

Both of the solution type rubbers are produced by similar processes. The main process wastewaters are the crumb slurry overflow and the solvent-monomer recovery wastes. The slurry overflow is passed through a pit, where the crumb rubber is separated and periodically removed. As is the case with all the plants visited, the crumb pits are not cleaned regularly, and during cleaning the crumb is disturbed and escapes the pit. The wastewaters from the solvent-monomer recovery area are condensates from monomer decant systems and solvent distillation condensates. They are characteristically high in COD, BOD, and total dissolved solids.

The plant's utility wastewaters are cooling tower blowdown and zeolite softener regeneration wastes. The blowdown has high chromium and zinc concentrations, from the corrosion inhibitor. The softener regeneration waste is a strong brine solution and therefore has a high total dissolved solids concentration.

The plant's wastewater treatment facilities consist of settling ponds, followed by aerated and stabilization lagoons. The plant's final effluent is treated with alum and polyelectrolyte to obtain proper coagulation of latex solids and fine rubber crumb particles.

The wastewater flows through two parallel sets of two settling ponds each, where the settleable solids and oils separate. The wastewater then flows through two further settling ponds in series. The total detention time in the six settling ponds is four days. Troublesome oil is skimmed from the ponds. The wastewater then passes to a mechanically aerated lagoon, which provides approximately three days of detention. The aerated lagoon effluent passes through two oxidation ponds, which stabilize the wastewaters and settle the biological solids. The total detention time in the oxidation ponds is approximately thirteen days.

Although overall treatment provided by the facilities is good, the effluent quality (BOD particularly) does not meet the State requirements. It has been established by analyses that the stabilization ponds are not producing the soluble BOD removals that were expected, but the cause of

the problem has not been determined. There are indications that the effectiveness of the ponds is dependent on the water temperature (and, therefore, the time of the year) but this hypothesis has yet to be confirmed.

#### Plant M

The total plant complex consists of a butadiene plant and a polybutadiene production facility. The butadiene plant started production in 1957 and the polybutadiene facility in 1961. The polybutadiene production facility, which uses butadiene as a feed monomer, has a capacity of 85,000 metric tons per year and is adjacent to the butadiene facility. The complex is located in a rural area with good potential for expansion and land acquisition.

The polybutadiene is produced by a solution-type polymerization process using butadiene as the feed monomer and hexane as the solvent. The crumb polybutadiene rubber is used principally as a tire rubber. In addition, a high-grade variety is used as an ingredient in the manufacture of impact-resistant plastic. The rubber is not oil- or carbon-black-extended.

The polybutadiene plant has two sources for water supply, well water and river water. The well water is used primarily for boiler and cooling tower makeup, while the river water (after clarification, filtration, and softening) is used in the crumb slurrying operation and for general plant cleanup.

The principal process wastewaters originate in the solvent-monomers reclaim area and in the crumb slurrying operation. The wastewaters produced in the reclaim area originate from several operations: solvent recovery, monomer recovery, and feed drying. The major component of these wastewaters is produced by a decant system fed from the solvent and monomer stripping operation. This wastewater is relatively clean, its only contamination being due to hexane at saturation solubility. The other wastewater streams from the reclaim area have very low flow and are essentially innocuous with the exception of dissolved hexane.

Impure recovered butadiene monomer is returned to the butadiene production plant for purification. Heavy slops (oily wastes) produced in the hexane recovery operation are sent to the butadiene plant for disposal or are used as a waste fuel. The other major process wastewater, the crumb slurrying overflow, is laden with rubber crumb in the form of suspended solids. The suspended solids are significantly reduced by in-plant screening and clarification in a pit.

At least one finishing line recovers the solid rubber product directly from the rubber cement. No water rinse system is used. The "finishing

machine" takes cement and produces material ready for baling and packaging. This machine was not seen, and presumably is some type of extruder for removing solvent. It obviously has a potential for reducing the effluent flow and leading attributable to the crumb rinse overflow.

There are two other process-associated wastewaters. Spent caustic soda solution, from scrubbing of butadiene inhibitor (to prevent premature polymerization during storage and shipping), is batch discharged. This stream has extremely high COD, pH, alkalinity, and color, and contains phenols. The batch discharge is containerized in a pit and bled into the plant effluent at a very low flow rate. With such handling or pre-treatment, it poses no wastewater problem.

The other wastewater which should be mentioned results from frequent area washdowns. This picks up primarily crumb rubber and oils. The oils originate from leaks in baler hydraulic systems and leaks of pump seal oil. In solution-type polymerization, water must be eliminated from much of the process equipment. Oil is used to seal and lubricate the process pumps. The washdown wastewaters contribute the major proportions of suspended solids, soluble organics, and oils in the final effluent.

The principal non-process wastewaters are boiler and cooling tower blowdowns and water treatment wastes. The wastewater characteristics of these streams are high total dissolved solids, and moderate COD, suspended solids, and pH. The cooling tower makeup is treated with a corrosion inhibitor containing chromium and zinc. These metals appear in the cooling tower blowdowns.

The total effluent from the butadiene and polybutadiene plants passes through an oil separator and straw filter before discharge. Since the quantity and loading of the wastewaters from the butadiene plant are far greater than those from the polybutadiene plant, no meaningful treatment data could be obtained. The raw wastewater flow and loading of the polybutadiene plant were the lowest of any of the synthetic rubber plants visited.

It is planned to expand the synthetic rubber plant production facilities shortly. This expansion will approximately double the existing synthetic rubber production capacity.

#### Plant N

The plant complex consists of isoprene, polyolefin resin, polyisoprene, and polybutadiene production facilities. The complex was completed in 1962. The polyisoprene production capacity is 65,000 metric tons per year and the annual production of polybutadiene is 110,000 metric tons. The complex is located in a rural area with expansion capability and undeveloped land of its own.

The polyisoprene is produced by solution polymerization with hexane as the solvent, using isoprene from the neighboring isoprene plant as feed monomer. Several types of polyisoprene are produced in this facility. Each type requires a separate production run on common processing equipment. The crumb rubber is used mainly for tire manufacture and is not oil or carbon black extended.

There are two polybutadiene lines which employ slightly different processing techniques. There is no significant difference in the overall wastewater flows and loadings from these two processes. The polybutadiene is consumed principally in tire manufacture, and approximately 50 percent of the polybutadiene is oil extended.

The plant's water supply is river water. Process and boiler makeup water receives extensive treatment, consisting of coagulation, clarification, filtration, chlorination, and softening.

The main process wastewaters are produced in the monomer-solvent reclaim area and the crumb slurrying operation. The wastewaters generated in the reclaim area have low flow rates and, with the exception of saturation with solvent or monomers, are relatively clean.

Part of the recovered isoprene is sent in a slip stream to the isoprene production plant for purification. This procedure serves to blow down the accumulated impurities. Impure butadiene recovered from the polybutadiene plant is hauled from the plant as a waste. The crumb slurrying overflows are passed through settling pits where the crumb is trapped and periodically removed. Surfactants are added to the crumb-water mix during the coagulation operation to prevent the crumb from agglomerating into masses which are too large. These surfactants enter the crumb slurry overflow.

One type of polyisoprene produces a crumb slurry effluent which has a considerably higher dissolved organic loading than the other polyisoprenes or the polybutadiene types. This difference is inherent in the chemistry of the process and is not a general or widespread problem in the synthetic rubber industry.

Area wash-down and cleanup is a major contributor of contaminants to the final effluent. Crumb screens used inside the processing areas are hosed down to remove coagulated rubber. The resulting wastewater has high suspended solids levels and is passed through the crumb settling pits. Spent caustic solution from the inhibitor removal system is containerized and bled into the final effluent. It has the typical high, COD, pH, alkalinity, and color.

Typical utility wastewaters, principally boiler and cooling tower blowdowns and water treatment wastes, are generated at this plant. Characteristics of these wastes are high total dissolved solids, with moderate COD, suspended solids, and pH. The cooling tower makeup is treated with a low chromium corrosion inhibitor. This produces chromium levels in the cooling tower blowdown that are less than one quarter of those associated with conventional cooling tower corrosion treatments.

The wastewater treatment system consists of an equalization basin (four-day detention), a neutralization sump, with nutrient addition, followed by an activated sludge plant (refer to Figure VII-3). The waste activated sludge is first thickened and then pumped to a sludge drying basin on the plant property. The treatment plant gives very good BOD effluent levels (10 mg/L), however, the effluent COD level is considerable (250 mg/L). This is due to the biological stability of many of the wastewater components such as the monomers and solvents, which, although generally considered insoluble, do have some solubility in water.

An apparent characteristic of the plant's wastewater which can be attributed to the synthetic rubber production is foaming in the aeration basins and in the final outfall. This is apparently caused by excessive use of surfactants by the production personnel in the crumb rinse operation. Another problem is poor settling of the biological sludge in the secondary clarifier. Efforts were made to assist settling, and achieve additional COD removal, by adding activated carbon granules to the aeration basins upon which biological solids could nucleate. This did not produce satisfactory results. The current technique which is proving more successful is the addition of coagulation aids to the clarifier influent. This, however, is proving to be expensive on an annual-cost basis. A less frequent problem, but more serious, is an apparent high BOD slug loading, with associated toxicity, that unpredictably occurs in the plant influent. This problem is uncontrolled at present, but appears to originate with the production of either the polyolefin resin or one type of polyisoprene.

#### Plant 0

The plant complex consists of polybutadiene, polyisoprene and ethylene-propylene diene terpolymer (EPDM) rubber production facilities. The commissioning of all the production facilities occurred between 1967 and 1970. The annual production capacities are: polybutadiene 56,000 metric tons, polyisoprene 50,000 metric tons, and EPDM 25,000 metric tons. The plant is located in a rural area and has considerable land for expansion.

FIGURE VII-3 PLANT N: ACTIVATED SLUDGE WASTEWATER TREATMENT FACILITY NUTRIENTS - ACID NEUTRAL-**EQUALIZATION** IZATION BASIN RAW INFLUENT BASIN - ALKALI VII-27 TOWBRO CLARIFIER SUPERNATANT EFFLUENT BRINGTING FINAL STATION AERATION BASINS **EFFLUENT** RETURN SLUDGE WASTE SLUDGE TANK CHLORINATOR DRAFT SANITARY WASTE RAW SANITARY SECONDARY TREATMENT WASTEWATER

Each of the three synthetic rubber products has its own production facility and is produced in a solution polymerization process. Polybutadiene rubber is carbon black extended. The principal end-use of the crumb rubbers is in tire manufacture.

The plant's water supply is well water. Well water is treated with corrosion inhibitors and slimicides for use as cooling tower makeup, and softened for use as boiler quality water.

Principal process wastewaters originate in the crumb slurrying overflow and presumably in the solvent, monomer, and reclaim areas. Carbon black added at the coagulation-slurrying stage is essentially trapped in the crumb rubber matrix. Carbon black spills and leaks pass through a settling sump and are allowed to overflow into the final effluent. The settled carbon black is removed by vacuum truck.

Extender oil that is not entrained in the rubber crumb can contaminate the slurry overflow wastewater. It is understood that screens, with higher crumb removals than conventional equipment, have been installed in this plant. The butadiene monomer is inhibited and presumably there is an associated spent caustic scrub solution discharge. Area washdown and cleanup is on a shift-by-shift basis. Whenever possible, the material is cleaned up in such a manner to eliminate wastes from the wastewater system.

The plant's utility wastewaters are characterized by high levels of total dissolved solids and moderate pH. The cooling tower blowdown has high chromium and zinc content originating from the cooling tower corrosion inhibitors used.

The plant's wastewaters are first passed through skimming and settling basins where the rubber crumb is trapped. The waste crumb rubber is removed every two to three months by dip bucket. The effluent from these pits flows into two 12,000 sq. meter (3-acre) lagoons. The process effluent from the lagoons combines with treated sanitary, storm, and utility wastewaters before entering first a 60,000 sq. meter (15-acre) lagoon and finally a 120,000 sq. meter (30-acre) lagoon before discharge to the receiving waters. The final wastewater quality is good. COD, BOD, and suspended solids are at an approximate level of 50, 5, and 10 mg/L, respectively. This plant, however, is particularly fortunate in having considerable land for use as wastewater lagoons. It is not possible for all synthetic plants to have the same or even comparable facilities.

#### <u>Plant P</u>

This plant produces styrene-butadiene (SBR) and acrylonitrile-butadiene (NBR) latexes. In addition, the plant produces polyvinyl acetate emulsions and hot melt adhesives. The annual production rates of the latexes are: styrene-butadiene latex 18,000 metric tons, acrylo-

nitrile-butadiene latex 3,000 metric tons. The plant is located in a rural area with land available for expansion.

The butadiene latexes manufactured at the plant are made similarly utilizing equipment trains of a similar nature. The monomers are shipped into the plant by both tank car and tank truck. The latexes produced are used for carpet backing, dipped goods, and adhesives.

The plant's water comes from on-site wells. The water is treated in a dual-bed demineralizer to supply boiler quality makeup water and process water for solution preparation. The cooling tower water is treated with a corrosion inhibitor and algicide.

The principal process wastewaters produced in the plant are generated by equipment cleanout, area washdown, and stripper condensates. Tank cars and tank trucks are rinsed with water and the contaminated water is discharged to the wastewater treatment facility. These wastewaters will contain monomers and uncoagulated latex. Reactors and strippers are cleaned of solid deposits with a high pressure watergun and then water rinsed. Blowdown tanks, filters, compound tanks, and storage tanks are rinsed with water. In all cases the wastewaters discharged to the wastewater treatment facility contain organic compounds and latex. Latex spills and leakages are first coagulated with alum, cleaned up in-place, and finally washed down. The washings are sent to the treatment facility.

Excess monomers are stripped from the latex with steam under vacuum. The vacuum is produced using steam jets and not vacuum pumps. The excess styrene, or acrylonitrile, is condensed and discharged to a receiver. Although the receiver is periodically decanted and the condensed styrene or acrylonitrile drummed for disposal, styrene and acrylonitrile still enter the effluent wastewaters. A caustic scrub solution is used to remove the butadiene inhibitor, which is bled gradually to the final effluent. Characteristics of this stream are high COD, pH, alkalinity, and color.

The plant utility wastewaters enter the storm sewer system. The boiler blowdown has a low flow rate but high total dissolved solids. Demineralizer regeneration wastes are both acidic and alkaline and may potentially produce pH peaks. The cooling tower blowdown is high in total dissolved solids but, because the corrosion inhibitors used are chromium and zinc free, these heavy metals do not appear in the blowdown. The vacuum pump seal water is currently discharged on a once-through basis to the storm sewer system. This water picks up small quantities of organic compounds but has only a moderate COD concentration. Studies are being made to recycle the bulk of the seal water and discharge the blowdown only to the treatment facility.

The plant's treatment facility consists of chemical coagulation and clarification followed by activated sludge secondary treatment. The final effluent after secondary treatment is discharged to a municipal treatment plant. All the latex plant process wastewaters are discharged to two coagulation pits. They operate so that one pit is being filled with wastewater, while water in the second pit is being treated, settled, and emptied. The pH of the wastewater is first adjusted with lime and then treated with ferrous sulphate, a polyelectrolyte, and limestone. The latex solids coagulate around the limestone which serves to sink the solids. The settled solids are removed from the pits periodically when the solids depth becomes excessive. The clarified wastewater enters four aeration basins operated in parallel. The basins are equipped with four 15-horsepower aerators. The aeration basin effluent enters a secondary clarifier and overflows to a sump from which it is pumped to the city treatment plant. The clarifier underflow is sent to a sludge thickener, while the supernatant is returned to the aeration basins. The biological sludge in the thickener is periodically removed and landfilled. The coagulation pit solids and the thickened biological solids are not suitable for satisfactory landfill because of their high water content. Studies are currently underway to determine adequate techniques for dewatering and disposing these sludges. The coagulation pits provide good quality primary effluent. The COD and BOD of this effluent are high, however. The secondary treatment plant produces a final effluent having a COD and BOD of approximately 600 and 50 mg/L respectively. The high COD: BOD ratio indicates high biological resistance of the wastewater constituents from this latex plant. Although the BOD level (50 mg/L) would not be suitable for direct discharge, it is very amenable to acceptable discharge to secondary treatment plants.

## Plant Q

This plant is responsible for the manufacture of styrene-butadiene latexes. The annual production rate is approximately 21,000 metric tons. The plant commenced production in 1952 and is located in an urban area with limited room for expansion. The plant also has a research facility and a pilot plant.

The styrene-butadiene family of latexes produced at the plant can be classified by three groups: styrene-butadiene latex, styrene-butadiene carboxylated latex, and styrene-butadiene-vinyl pyridine latex. All these latexes are produced by similar processing techniques and equipment. The monomers used (styrene, butadiene, organic acids, and vinyl pyridine) are shipped to the plant by tank car and tank truck. The latexes produced are used for tire fabric coating, backing material, and paper coatings.

The plant uses city water for process water, boiler makeup water, and cooling tower makeup. The boiler makeup is softened before injection. The cooling tower makeup is treated with a dispersant, corrosion inhibitor, and slimicide. The process water, used for solution preparation, is deionized before use.

The principal process wastewaters generated in the plant originate from equipment cleanout, area washdown, and stripper condensates. Excess monomers are not recovered. Reactors, strippers and storage tanks are periodically cleaned of rubber build-up by hand and then rinsed with water. Generally, large quantities of water are used for each cleanout. The latex filters are frequently cleaned. This involves first removing the trapped rubber solids and flushing the filter with water. The rinse waters contain suspended solids, COD, and uncoagulated latex. Floors and loading-unloading areas are flushed with water. These wastewaters contain COD, suspended solids, and uncoagulated latex. The vapors from steam stripping operations are condensed and discharge into a receiver. The receiver waters which overflow to the plant sewers have a high organic loading with correspondingly high COD and oil levels. The seal water for the vacuum pump serving the vacuum stripping equipment is slightly contaminated with organics, and presently discharges on a once-through basis. Studies are being made to collect individual seal water discharges and recycle the bulk of them with a controlled blowdown of contaminated water. This will reduce the total volume in the plant's final effluent.

The regeneration waste from the boiler water makeup softener is a concentrated salt solution and therefore contributes high total dissolved solids to the effluent. The process water deionizer is regenerated with sulphuric acid and caustic soda. The discharge of these solutions will produce both acid and alkali peaks in the effluent, although there is generally an excess of sulphuric acid in the daily regeneration discharges. The boiler and cooling tower blowdowns contribute high total dissolved solids and moderate COD to the plant's final effluent.

The treatment of the plant's wastewaters includes equalization, chemical coagulation and settling, and secondary treatment in the local municipality's treatment plant. The wastewaters are first pumped from the plant effluent trench into an equalization basin, which provides approximately 24 hours detention and is aerated with two aerators. The pH of the equalized wastewater is adjusted from normally alkaline by addition of sulfuric acid to the neutralization sump. The wastewaters are pumped from the sump to a reactor-clarifier where alum, coagulant, and polyelectrolyte are added in the mixing chamber. The latex and fine rubber particles are coagulated and collected as a sludge from the bottom of the clarifier. The clarified effluent overflows the clarifier to the city's sanitary sewer for secondary treatment. The clarified sludge is sent to a thickener and finally to a sludge holding tank, and is then loaded into a tank truck for disposal. The supernatant from the thickener is returned to the reactor-clarifier. The treatment

system described above produces a good quality primary effluent. COD and BOD are reduced by approximately 70 and 50 percent, respectively. The suspended solids and oil are decreased by 80 and 50 percent each.

# Summary of Control and Treatment Technology

In-plant control technology covers segregation and measures for handling, reuse, modification of processing, and disposal of various types of wastewaters, including spills and leakage, washdowns, control of runoffs, and housekeeping practices. End-of-pipe treatment technology covers the treatment of various combinations of process and non-process wastewaters. Separate discussions are presented for the Tire and Inner Tube and the Synthetic Rubber segments of the industry.

## Tires and Inner Tubes

## In-Plant Control

In-plant measures included the proper handling of soapstone, of the latex dip, and of discharges from air pollution equipment.

#### Soapstone

Soapstone is a slurry normally consisting of clay, an emulsifying agent, and water. According to one plant representative, scapstone, if continually discharged, will contribute a high solids and BOD loading to the process wastewaters. The standard method of eliminating a continuous discharge of large quantities of soapstone is the use of a closed-loop recirculation system. Such a system needs periodic cleaning, usually on a weekly basis. This cleaning operation can, but does not necessarily, lead to a discharge. Prior to cleaning, the soapstone solution in the system is generally transferred to storage tanks. The alternative to recirculation is to discharge the solution directly into the process sewers. Both practices were observed during the field survey, the first being the better from a wastewater control standpoint. Soapstone washwater is potential discharge which is commonly sent to end-of-pipe treatment. However, it was observed that this washwater could be stored and used as makeup for the soapstone solutions for future operations. Alternative methods for controlling discharges from weekly washdown include the use of substitute solutions which require the system to be cleaned on a less frequent basis.

Control of minor discharges of soapstone, such as spills and leakage, is achieved by the use of curbing and by blocking off drains in the dipping area. In addition, drip pans are provided for stock during the air-drying operation. Soapstone that is spilled into the curbed

area is periodically vacuumed out and sent to a landfill site. Newer plants are constructed without drains in this area, thus eliminating the possibility of soapstone contamination of process wastewaters. Instead of curbing, steel grates are placed on the floor; these can be removed when cleaning the area.

## Latex Dip

The most common practice of the larger manufacturers is to eliminate this operation from the tire facility. Fabric is dipped by a centrally located facility and then shipped to the tire plant. However, in plants that still dip fabric, the accepted procedure is to seal off drains in the immediate area, supply the area with curbing, and drum the waste solutions for disposal at landfill sites. The alternative is to dump the waste solutions into process sewers which are destined for end-of-pipe treatment systems. The amount of waste from this operation is small, less than 230 liters (60 gals) per day. Drumming of the solution is therefore preferred, since treatment of this stream once diluted with other streams is difficult.

## Air Pollution Control Residues

It is not common for manufacturers to use large quantities of wet particulate-collection systems. In the compounding area, in particular, bag-houses, rather than wet scrubbers are used. Wet systems are more common in the tire-finishing area, where they collect the grindings from the white sidewall grinding machines, balancing machines, and the tire-repair area.

Discharges from wet scrubbers contain high loadings of settleable solids, which must be removed before final discharge. The solids collected from the tire-finishing area can be settled out in a small sump. The particulates are large, and with a properly designed separator, the clarified water can be, and frequently is completely reused.

The discharges from wet scrubbers used in the compounding area are much finer and require longer settling times. Only one plant visited used wet scrubbers in this area. This plant used a 2,100 sq. meter (0.52-acre) lagoon to separate the solids from this discharge. Unless specifically required to meet air pollution ordinances, wet scrubbers in this area are not recommended.

Additional air pollution equipment can be found in the tire-painting areas. Stricter air emission standards and OSHA standards are forcing tighter controlls on particulate and solvent emissions from this area. Consequently, the industry is currently attempting to substitute water-

based paints and sprays for solvent-based materials, but with only limited success. Wet air pollution equipment in this area was found at only one plant; there was no wastewater discharge, because all the scrubber water was reused.

## Spills and Leakage

To control oily wastewaters resulting from spills and leakage, the common practice is to provide curbing and oil sumps and to seal drains. In older plants, the roller mills are located in basins. The blocking off of drains in these basins as a control measure is not feasible because electrical machinery is located in the basins. A broken water pipe would fill the basin, thus shorting out the machinery. Curbing is used to keep normal area washdown and periodic leakages and spills from entering the basin and thus contaminating process waters. In newer plants, machinery is located on the floor surface. Updated seal designs prevent the leakage of oil. In many cases, potentially contaminating areas have no drains, thus eliminating the possibility of oil in these process wastewaters.

In plants where recirculated water is the primary source for cooling, the process and non-process sewers are separate. Oil sumps and API separators can therefore be provided to treat oily process wastewaters. The separable oil from these devices is removed either periodically by maintenance people or continuously by a belt filter: the continuous removal is considered the better practice. During periodic removal of oil, the agitation supplied will result in a large quantity of oil being released to the effluent, thus reducing the separator's overall average removal efficiency.

In plants where the primary source of cooling is once-through water, process and non-process sewers are combined. Removal of oil must be accomplished in an end-of-pipe treatment facility. Dilution by non-process wastewaters directly affects the removal efficiencies of oil in the end-of-pipe treatment facility.

## Washdowns and Machine Cleaning

Common practice for prevention of process-area washdowns from contaminating wastewaters is the use of dry sweeping equipment. These include automatic sweepers, brooms, and shovels. Oily spills are cleaned using solvents and rags, the resulting contaminated material being drummed and sent to a landfill. Practices employed in non-process areas (such as the boiler house and storage areas) are similar.

Machines and machinery parts are normally cleaned with solvents or steam. Spent solvents are drummed and sent to a landfill. The use of steam requires a special area supplied with curbing and an API separator to remove separable oil and solids. Discharges of untreated oil— and solid—contaminated steam condensate occur and constitute a significant source of process wastewaters. Although steam cleaning has the disadvantage of having a continued discharge that must be treated, it eliminates the possibility of a careless operator discharging large quantities of organic solvents into an untreated process wastewater stream.

Molds from the curing presses are normally cleaned by sand- or airblasting equipment. These are dry, and involve no wastewater problem.

#### Runoff

Runoff from oil-storage areas occurs due to oil spills, storm water, and various blowdowns which occur in the storage area. Handling practices vary within the industry. Minimal control involves the diking of all oil-storage areas to prevent contamination of wastewater by large oil spillages which can occur during unloading or due to leaking tanks. These dikes generally are provided with drainage ports to prevent normal storm water from filling the diked area. This allows minor oil spills, attributable to operator negligence, to contaminate storm runoff. A better system involves the diking of the storage area, the roofing of storage area to prevent storm runoff contamination, and use of an oil sump to collect minor spills and leakage. Collected oil is drummed and sent to a landfill. To prevent oil from unloading areas from contaminating the wastewaters, drains are diked and covered with straw filters. This control technique suffers from the possibility of storm runoff contamination.

Other treatment schemes include the use of separators to treat oil storage runoff. The primary emphasis here is to treat runoffs due to continual water running through the area. The systems generally are not designed to handle increased loads due to storm runoff.

Solvent storage and maintenance areas are normally confined to buildings. To decrease the possibility of contamination due to operator or maintenance negligence, these areas are not supplied with drains.

#### End-of-Pipe Treatment

End-of-pipe treatment in this segment of the industry generally involves the treatment of combined process and non-process wastewater in a primary sedimentation basin or lagoon. Once-through, non-contact cooling water usually is not treated even though the possibility exists for oil contamination from process wastewater. Primary emphasis is on removal of separable solids from the non-process boiler blowdowns and water treatment wastes and from the process washdown waters (if any) from the soapstone area.

The most effective system, although not generally applicable because of land requirements, is the use of judicious water management techniques to minimize non-process discharges and of holding lagoons to contain all wastes including process, non-process, and storm runoff. Other lagooning systems used for treatment of all process (including once-through cooling water) and non-process wastewaters were observed. Residence times varied from twelve to twenty-four hours with surface loadings as high as 12,000 liters/min/sq meter (1,200 gal/min/sq ft). Auxiliary equipment observed included oil skimmers and sludge handling equipment.

From the standpoint of treating process wastewaters, these systems suffer heavily from dilution, particularly in the treatment of grease or oily wastes. Dilution by process streams was as high as 75 to 1. Dilution by heavy storm runoff was an additional problem at many locations.

#### Synthetic Rubber

#### In-plant Control

Since the synthetic rubber industry is highly technological, involving many proprietary and confidential processing techniques, many potential in-plant wastewater control methods would call for radical changes in processing or product quality. Such techniques are obviously not feasible. However, some potential control methods deserve mention so that their applicability may be evaluated.

#### Crumb Rinse Overflow

It was observed that some crumb rubber plants generate crumb rinse overflows which have a lower loading of rubber fines than other plants. Generally, however, such losses cannot be reduced with finer in-plant screens since they are a function of both the type and the coagulation properties of the rubber. One plant did use a proprietary method to finish the rubber cement in which a water slurry is not used. This system eliminates the crumb slurry overflow and the contained rubber fines. It is not necessarily applicable wholesale to crumb rubber production, but does merit investigation by industry.

#### Coagulation Liquor Overflow

Most emulsion crumb rubber processes use an acid and brine coagulation liquor. One plant, however, coagulates the latex with an acid-polyamine liquor which reduces the quantity of total dissolved solids discharged in the coagulation liquor overflow. The use of this type

of coagulation liquor is not always possible, but if employer could significantly reduce the total dissolved solids in the final effluent.

#### Vacuum Systems

Several plants are converting vacuum systems from steam jet ejectors to vacuum pumps for efficiency and wastewater reasons. In order to maximize the wastewater benefits derived from the use of vacuum pumps, the seal water should be recycled. An overflow is generally required from the seal water recycle system; this overflow is normally slightly contaminated with oil but has a better quality than the steam jet condensate.

## Caustic Scrubbers

In some plants, the caustic soda solution used to remove inhibitors from some monomers (notably butadiene) is replaced batchwise. The spent caustic soda solution, usually 10-20% sodium hydroxide, should not be discharged batchwise. It should be containerized and bled into the total plant effluent, thereby diluting its high pH, alkalinity, COD, and color contributions.

## Carbon Black Slurries

The usual method is to slurry the carbon black for addition to the rubber with water. One plant visited employs a steam grinding-slurrying technique which reduces carbon black spillage and consequently washdown and runoff wastewaters laden with black fines; this technique avoids the need for carbon black settling pits and the associated pit cleaning costs.

## Latex Spills

Latex spills and leakages occur from time to time in all emulsion crumb and latex plants. In most cases, the spill is washed to the nearest plant drain using a water hose. In many cases, this produces unnecessary washdown water and dilutes the latex so that subsequent treatment by coagulation is much more difficult. An alternative technique is to coagulate the latex in situ with alum, for example, and remove the coagulated rubber solids with scrapers. The volume of subsequent washdown water required is less and the latex solids in the washdown water are greatly reduced.

### Baler Oil

As a result of the high hydraulic pressures involved and the continual jarring action of the balers, oil leaks are frequent. Back-welding the hydraulic lines, although more expensive as an initial equipment cost, does significantly reduce the occurrence of baler oil leaks and can produce appreciable savings in baler oil usage. In addition, plant floor drains should be sealed and, if necessary, retention curbing

installed to keep leaked oil from leaving the baler area. Balers using water as the hydraulic fluid are also available and are being used in some plants; oil leakage with this type of machine is obviously eliminated.

#### End-of-Pipe Treatment

#### Emulsion Crumb Plants - Primary

It is normal practice for crumb rubber producers to recycle part of the crumb rinse water. The remainder of the crumb rinse water is discharged in order to blow down accumulating fine rubber solids and dissolved solids and organics. The rinse water discharge or overflow is clarified before final treatment in a crumb separation pit. The trapped rubber solids are removed periodically by scoop. A very common shortcoming of these separators is that they are operated as single units and are not cleaned frequently enough. This results in short-circuiting followed by poor separation. In addition, when the pits are cleaned, the separated rubber solids are disturbed and rubber solids that had previously separated recombine with the pit effluent until the condition of the pit stabilizes. Dual pits would solve this problem: one pit would stay in operation while the other was cleaned and allowed to stabilize.

Since wastewaters from emulsion crumb plants contain considerable quantities of latex, it is necessary to coagulate the latex in order to achieve a good quality effluent. Chemical coagulation by itself is seldom sufficient, because the density of the coagulated rubber is normally close to that of water. Therefore, it is customary to add a "sinker" (clay or limestone) to the coagulation mixture to sink the coagulated rubber and effect the separation. For a small wastewater flow, chemical coagulation using (for example) alum, polyelectrolyte, and clay in a rapid mix tank can be followed by flocculation in a flocculator tank. Clarification can then be accomplished in a rectangular clarifier equipped with solids removal equipment. Larger wastewater flows can be treated in a reactor-clarifier with rim overflow and central sludge draw-off.

The collected sludge can be thickened and dewatered before disposal in a landfill. Dewatering studies on this type of sludge concluded that a plate-and-frame pressure filter performed well. The installed filter was automatically controlled for feed shut-off, silter opening, core blowout, filter closing, precoating, and feed restoration (refer to Plant J).

One plant (Plant K) uses chemical coagulation followed by air flotation for primary clarification (6). Instead of sinking, the rubber solids are floated to the clarifier surface with air bubbles and removed by surface solids removal equipment. This treatment facility is relatively new and has had start-up troubles, although they have been satisfactorily resolved. Air flotation in this application produces primary effluent of good quality.

The collected surface solids are pumped to a sludge impoundment lagoon where they dry out. The use of this lagoon is limited and a long-term solids dewatering and disposal technique will have to be found.

Where adequate land is available, rubber solids separation has been achieved using primary settling ponds. Chemical coagulation of the solids prior to discharge to the ponds is usually necessary. The settled and floating solids (since both types are produced) are removed from the ponds periodically by vacuum truck or scoop.

### Emulsion Crumb Plants - Secondary

Biological oxidation of the primary effluent is achieved in aerated lagoons or in activated sludge plants. Generally, a nutrient must be added. Both technologies obtain satisfactory oxidation of the dissolved contaminants; problems can arise in the clarification of the secondary effluent. Good secondary clarification of effluent from an aerated lagoon has been obtained with the aforementioned air flotation plant, which is a dual system with both primary and secondary air flotation clarifiers.

If sufficient land is available, the effluent from the aerated lagoons can be clarified and stabilized in stabilization ponds. This type of facility is temperature dependent, of course, and performs better in warmer climates.

Clarifiers are commonly used for secondary clarification in activated sludge plants. They are generally adequate, but cases exist where high solids carryover is a problem. Secondary clarification can be assisted with coagulation chemicals in much the same manner as for primary clarification, but the additional chemical cost is high.

One plant in the industry, in an area where water is in short supply, is evaluating evaporation to remove wastewater contaminants (7). Problems encountered have included severe scaling problems and high operating costs. The scaling problems stem from the fact that the scale-producing characteristics of the wastewater vary greatly on a day-to-day basis, and are greatly affected by the inherent operational variations in the rubber plant.

#### Emulsion Crumb Plants - Advanced

After secondary treatment, emulsion crumb wastewaters still contain high levels of COD. A high COD level appears to be a common characteristic of secondary effluents from emulsion crumb, solution crumb, and latex plants, and appears to indicate that certain constituents of the wastewaters generated in synthetic rubber plants are refractory to biological oxidation.

#### Solution Crumb Plants - Primary

Primary clarification of the solution crumb plant wastewater is carried out in crumb pits. These pits are similar in design to those for emulsion crumb production facilities. To avoid re-suspending the separated rubber solids, dual crumb pits should be used.

Other forms of primary treatment are not required for solution crumb wastewaters, since uncoagulated latex is not present and the fine rubber solids separate readily.

#### Solution Crumb Plants - Secondary

Secondary treatment technology uses both activated sludge and aerated lagoon systems. Good BOD removals are achieved, but poor secondary clarification is a problem in most cases. The reasons for this are not certain. A high level of COD remains after biological treatment, indicating that much of the wastewater constituents are biologically refractory.

#### Solution Crumb Plants - Advanced

Advanced or tertiary treatment technologies have not been used on secondary effluents from solution crumb plants. It is very probable that activated carbon treatment would give COD removals similar to those for emulsion crumb wastewater, since the raw wastewater constituents (for example, traces of monomer) are similar for both types of wastewater.

#### Latex Plants - Primary

Since latex plant wastewaters contain uncoagulated latex solids, primary clarification is with chemical coagulation and sinking. In much the same manner as for emulsion crumb wastewaters, clarification can be effected in reactor-clarifiers or systems with separate rapid mix, flocculation, and clarification tanks. Latex wastewaters can also be clarified by air flotation.

#### Latex Plants - Secondary

Activated sludge plants are used for the secondary treatment of latex wastewater. High residual COD levels are a problem. These levels are higher than for either emulsion crumb or solution crumb plants, because the COD loading of the raw wastewater from latex plants is much higher. It is feasible that aerated lagoons and stabilization ponds will produce satisfactory oxidation and stabilization of latex wastewaters.

# Latex Plants - Advanced

Advanced or tertiary treatment technologies have not been used on latex wastewaters. It is probable that COD removals similar to those achieved by emulsion plants could be achieved for latex wastewater by using activated carbon columns.

#### SECTION VIII

### COST, ENERGY AND NON-WATER QUALITY ASPECTS

#### Tire and Inner Tube Industry

# <u>Selection of Control and Treatment Technologies</u> Based on Costs

Two alternative approaches exist for the control and treatment of process wastewaters from both old and new tire and inner tube production plants.

The first approach is to combine process and non-process wastewaters and to treat the entire plant effluent. Where land is available, end-of-pipe treatment is the approach favored by many of the tire manufacturers. Generally, the reasons supporting this approach are as follows:

- In older plants, in-plant sewers for process and non-process wastewaters are usually combined, thus making combined treatment more attractive.
- 2. Process flows are usually small relative to non-process flows.
- 3. The treatment of non-process wastewaters has received the bulk of industry's attention. High suspended solid loadings in blowdown and water treatment wastes are the major pollutant in the combined plant effluent from tire facilities.

However, end-of-pipe treatment systems also have several disadvantages:

- The combined effluent treatment system usually requires one or two lagoons for settlement and retention. Lagooning of the wastes requires large land area, which is not readily available at many plant locations.
- Because of dilution, the effectiveness of treatment for oil removal from process wastewater is reduced. In several of the systems observed, oil passed through untreated (although it was present in significant quantities), because its concentration was below the capabilities of the treatment system employed.

The second approach employed is control and treatment of a segregated and undiluted process wastewater. This approach has been followed in plants having partially or wholly segregated process and non-process sewers. This would, of course, include any plant using recirculated cooling water. The main advantages for this treatment scheme over combined end-of-pipe treatment are:

- 1. Higher pollutant removal rates.
- 2. Smaller land area required for treatment facilities.

The primary disadvantage of a segregated system approach is that separate process and non-process sewers are required.

Upon examining these alternatives, control and treatment of segregated process wastewaters was considered to be most applicable to the tire producing industry. End-of-pipe treatment of combined wastewaters is not feasible for pollution control because of: 1) the ineffectiveness of such systems in removal of process wastewater contaminants; and 2) the large land requirements. All costs, therefore, are related to the treatment of a segregated process waste stream.

With proper in-plant control, the process streams consist of readily separable lubricating and extender oils and settleable solids. Volumetric flow rates for process wastewaters are small. Therefore, the initial treatment applicable from a cost and proven operation basis is an API-type gravity separator. The performance and efficiency of a gravity separator can be improved by addition of an absorbent filter.

Effluent quality data for old tire and inner tube and for new tire facilities are presented (along with cost data) in Tables VIII-1 and VIII-2. The treatment technology involves the isolation of wastes with curbing, the protection of oily areas to prevent storm runoff contamination, and the separation of settleable solid and oily material from the wastewater.

A more detailed description of recommended facilities is presented in the tire and inner tube portion of Section IX, and a flow diagram of the system used as a basis for costing is presented in Figure IX-1.

#### Treatment Cost Data

Data from Corps of Engineers permit applications and plant data obtained during inspection visits were used to obtain the average or typical plant size and wastewater discharge flows, and raw waste loadings as described in Section V.

From these data, a typical process wastewater flow was estimated to be 3.785 liters/sec (60 gal/min) for a plant consuming 205,000 kg (450,000 lbs) of raw materials per day. For the old tire and inner tube plant sub-category the average oil loading is 0.246 kg/1,000 kg of raw material consumed. The suspended solids loading for this sub-category is estimated to be 0.319 kg/1,000 kg of raw material.

TABLE VIII - 1

Old Tire and Inner Tube Production Facility Subcategory

Estimated Wastewater Treatment Costs for Different Degrees of Treatment based on a Typical Raw Material Consumption of 205 metric tons/day

	Treatment or Control Technology 1		
Investment <sup>2</sup>	\$299,000	\$328,000	
Annual Costs			
Capital Costs	\$ 30,000	\$ 33,000	
Depreciation	60,000	66,000	
Operating and Maintenance Costs (excluding energy and power costs)	24,000	27,000	
Energy and Power Costs	1,000	1,000	
Total Annual Costs <sup>2</sup>	\$115,000	\$127,000	

Parameters	Raw	Eff	luent Quality
(kg/10 <sup>3</sup> kg raw material)	Waste Loads	A	<u>B</u>
Suspended Solids	0.319	0.064	.064
Oil and Grease	0.120	0.048	.008

Technology A is Isolation of Wastewaters followed by API Gravity Separator Technology B is Technology A followed by an Absorbent Filter

August 1971 Dollars

# New Tire Production Facility Subcategory

Estimated Wastewater Treatment Costs for Different Degrees of Treatment based on a Typical Raw Material Consumption of 205 metric tons/day

	Treatment or Control Technology			
Investment <sup>2</sup>	<u>A</u> \$276,000	<u>B</u> \$305,000		
Annual Costs				
Capital Costs	\$ 28,000	\$ 31,000		
Depreciation	55,000	61,000		
Operating and Maintenance Costs 'excluding energy and power costs)	22,000	25,000		
Energy and Power Costs	1,000	1,000		
Total Annual Costs <sup>2</sup>	\$106,000	\$118,000		

Parameters	Raw	E	ffluent Quality
(kg/10 <sup>3</sup> kg raw material)	Waste Loads	<u>A</u>	<u>B</u>
Suspended Solids	0.319	0.064	0.064
Oil and Grease	0.083	0.048	0.008

Technology A is Isolation of Wastewaters followed by API Gravity Separator Technology B is Technology A followed by an Absorbent Filter

August 1971 Dollars

Based on these typical profiles for old and new production facilities, treatment cost data were generated and are presented in Tables VIII-1 and VIII-2. Costs typically are higher for older production facilities, primarily due to the fact that a new in-plant process sewer system would be needed. Separation of the present combined system was considered unrealistic for older production plants.

Investment costs have been factored to August 1971 dollars using Engineering News Record cost indices. Depreciation was calculated on the basis of straight-line depreciation with a five year life and zero salvage value.

Designs for the proposed model treatment systems were costed out in order to aid EPA in its efforts to evaluate the economic impact of the proposed effluent limitations. The design considerations (i.e., the influent raw waste loads) were selected to represent the expected raw waste load within each sub-category. This results in the generation of cost data which should be conservative when applied to most of the plants in this category. Relatively conservative cost figures are preferred for this type of general economic analysis.

The capital costs were generated on a unit process basis, with the following "percent add on" figures applied to the total unit process costs in order to develop the total installed capital cost requirements.

Item	Percent of Unit Process Capital Cost
Electrical	12
Piping	15
Instrumentation	8
Site work	3
Engineering Design and Con- struction Supervision Fees	10
Construction Contingency	15

Since land costs vary appreciably between plant locations, it was decided to exclude land cost from the total capital cost estimates. Land costs must be added on an individual case basis.

Annual costs were computed using the following cost basis:

Item

#### Cost Allocation

Capitalization

10 percent of investment

Depreciation

5-yr straight line with zero salvage value

Operations and Maintenance

Includes labor and supervision, chemicals, sludge hauling and disposal, insurance and taxes (computed at 2 percent of the capital cost), and maintenance (4 percent of capital cost)

Power.

Based on \$0.01 kw-hr for electrical power.

The short-term capitalization and depreciation write-off period is what is currently acceptable under current Internal Revenue Service Regulations pertaining to pollution control equipment.

All costs were computed in terms of August, 1971 dollars, which correspond to an Engineering News Record Index (ENR) value of 1580.

#### **Energy Requirements**

Energy input is related to the need for electric pumps to pump process wastewaters from the plant area and through the treatment system. Electricity costs are estimated at one cent per kilowatt hour. The extra power required for treatment and control systems is negligible compared to the power requirement of the tire manufacturing equipment.

#### Non-Water Quality Aspects

The primary non-water quality aspect deriving from use of a separator is the need for disposal of oil and solids. Additional solid waste results from the use of a non-regenerative type absorbent filter.

Solid waste disposal is a major problem confronting the industry as a whole. Typically, 3,100 kg (6,800 lbs) of solid waste are generated by a tire plant each day. Additional solid waste results from the drumming of the waste solutions for off-site disposal. Many manufacturing plants, particularly in the northern states, are finding it difficult to locate and arrange for service at satisfactory landfill sites. Fortunately, the additional solid waste generated by the proposed treatment technology is very small relative to the normal solid waste generated by the production facility; consequently, the impact will not be significant.

Land requirements for the treatment system are small; nevertheless, certain older facilities located in highly congested urban areas will find it difficult to allocate space for even this minimal treatment facility. These plants may be forced to turn to other control measures and/or to pre-treat for disposal and discharge of the process wastewaters to publically owned treatment works.

#### Synthetic Rubber Industry

#### Emulsion Crumb Sub-category

# <u>Selection of Control and Treatment Technologies</u>

Four degrees of control and treatment were considered in weighing treatment effectiveness versus cost of treatment: primary clarification; biological oxidation; and advanced treatment to two levels of COD removal.

Since emulsion crumb wastewaters contain uncoagulated latex solids, it is necessary to coagulate these solids prior to clarification. The cost alternatives for the primary clarification of emulsion crumb wastewater have been developed on the basis of a treatment model involving chemical coagulation, with a sinking material such as clay to sink the coagulated solids. This, however, is only one of several possible methods of achieving primary clarification. Air flotation is another approach to primary clarification which has been applied to emulsion crumb wastewaters with success. Chemical coagulation has been used to develop the cost data because there are more cases of its successful application for this type of wastewater, and, therefore, there is less uncertainty about the effectiveness of this technology for this subcategory.

After primary clarification, emulsion crumb rubber wastewaters invariably have high BOD and COD concentrations. Biological treatment is necessary (and is commonly practiced by the industry) to remove these contaminants. In order to develop the cost alternatives for biological treatment, activated sludge processes were used as a model treatment. It is, of course, only one method for obtaining biological oxidation, since other comparable technologies, such as aerated lagoons and stabilization ponds exist and are used to some extent by the industry. The activated sludge process was chosen as a model treatment because its performance is not as temperatureand climate-dependent as is an aerated lagoon or stabilization pond system and because the resulting cost data are independent of geographic location. In addition, an aerated lagoon or stabilization pond system requires considerably larger areas, which are not always available. Activated sludge facilities, by contrast, require minimal land.

The major pollutant remaining in emulsion crumb wastewaters after biological treatment is COD. Its concentration is much higher than the other principal parameters and if advanced wastewater treatment is to be carried out, it is logical that the treatment technology should be applied to reduction of the high COD levels. For the wastewater flow rates involved in emulsion crumb rubber production, activated carbon

treatment is the only technology applicable for COD removal. In order to prevent blinding of the carbon beds and columns with fine suspended solids, a dual-media filtration system is required upstream of the columns. Activated carbon adsorption of emulsion crumb secondary effluent has been studied in pilot-scale test equipment. However, because of the technical risk with respect to performance and the uncertainty of the associated capital and operating costs, two levels of activated carbon treatment have been modeled. These two levels are equivalent to overall COD reductions of 75 and 90 percent.

#### Basis of the Treatment Cost Data

An emulsion crumb industry profile was made, based on industry production capacity data, to determine the typical size of an emulsion crumb production facility. The average, or typical, plant is rated at 128,000 metric tons per year. The wastewater flow for such a plant would approximate 66 liters/second (1,050 gallons per minute). The model treatment plant, using chemical coagulation and clarification followed by activated sludge biological treatment, is shown in Figure IX-2. The degree of treatment afforded by this technology is equivalent to Level I Control and Treatment. The recommended treatment technology to attain Level II control and treatment is presented in Figure X-1. This treatment technology includes dual-media filtration followed by activated carbon adsorption.

Designs for the proposed model treatment systems were costed out in order to aid EPA in its efforts to evaluate the economic impact of the proposed effluent limitations. The design considerations (i.e. the influent raw waste loads) were selected to represent the highest expected raw waste load. This results in the generation of cost data which should be conservative when applied to most of the plants in the emulsion crumb sub-category. Relatively conservative cost figures are preferred for this type of general economic analysis.

The capital costs were generated on a unit process basis, with the following "percent add on" figures applied to the total unit process costs in order to develop the total installed capital cost requirements.

<u>  tem</u>	Percent of Unit <pre>Process Capital Cost</pre>
Electrical	12
Piping	15
Instrumentation	8
Site Work	3
Engineering Design and Con-	
struction Supervision Fees	. 10
Construction Contingency	15

Since land costs vary appreciably between plant locations, it was decided to exclude land cost from the total capital cost estimates. Land costs must be added on an individual case basis.

Annual costs were computed using the following cost basis:

Item Cost Allocation

Capitalization 10 percent of investment

Depreciation 5-yr straight line with zero salvage value

Operations and Includes labor and supervision, chemicals,
Maintenance sludge hauling and disposal, insurance and
taxes (computed at 2 percent of the capital

costs), and maintenance (computed at 4 percent of the capital cost).

Power Based on \$0.01/kw-hr for electrical power.

The short-term capitalization and depreciation write-off period is what is currently acceptable under current Internal Revenue Service Regulations pertaining to industrial pollution control equipment.

All costs were computed in terms of August, 1971 dollars which correspond to an Engineering News Record Index (ENR) value of 1580.

The total capital and annual costs for the model treatment technologies are presented for a typical emulsion crumb plant in Table VIII-3, together with raw waste load and treated effluent quality.

#### Energy Requirements

The primary clarification and biological oxidation treatment technologies require electrical energy only for operation of equipment such as pumps and aerators. The filtration and activated carbon treatment system, in addition to power requirements, needs a fuel source to regenerate the carbon. The energy and power needs of the recommended treatment technologies are deemed to be modest.

#### Non-Water Quality Aspects

Sludge cake is produced by vacuum filtration of the primary coagulation solids and the digested biological solids. Sludge disposal costs were based on sanitary landfill. Sludge incineration costs were not evaluated because the economics depend, to a large degree, on the accessibility of a landfill site and on the relative costs for sludge haulage and site disposal. The annual quantities of solid waste generated are:

		·	Tr	eatment or Contr	ol Tec	hnologies 1		
		_A_		<u> </u>		<u> </u>		D (Level 11)
Investment <sup>2</sup>	\$ 1	,180,000	\$ 2	2,002,000	\$ 2	2,907,000	\$2	2,993,000
Annual Costs								
Capital Costs	\$	118,000	\$	200,000	\$	291,000	\$	299,000
Depreciation		236,000		400,000		581,000		599,000
Operating and Maintenance Costs (excluding energy and power costs)		147,000		230,000		349,000		396,000
Energy and Power Costs		10,000		20,000		25,000		29,000
Total Annual Costs <sup>2</sup>	\$	511,000	\$	850,000	\$1	,246,000	\$1	,323,000

Parameters	Raw		Effluent Cuality		
(kg/10 <sup>3</sup> kg production		Α	B (Level I)	<u>C</u>	D (Level II)
COD	20.00	12.80	8.00	5.04	2.08
BOD	2.13	2.00	0.40	0.08	0.08
Suspended Solids	7.20	1.29	0.65	0.08	0.16
Oil and Grease	1.40	0.32	0.16	0.08	0.08
Flow (L/10 <sup>3</sup> kg produ	uction) 16.600				

<sup>1</sup> Technology A is Chemical Coagulation followed by Clarification.

Technology B is Technology A followed by Activated Sludge Secondary Treatment

Technology C is Technology B followed by Dual Media Filtration plus Activated Carbon Treatment to produce 75% overall COD reduction.

Technology D is Technology B followed by Dual Media Filtration plus Activated Carbon Treatment to produce 90% overall COD reduction.

<sup>&</sup>lt;sup>2</sup> August 1971 Dollars.

Primary coagulated solids

2,940 cu. meters (3,900 cu. yds)

Biological solids

245 cu. meters (325 cu. yds)

### Solution Crumb Sub-category

#### Selection of Control and Treatment Technologies

Only two degrees of control and treatment have been considered in the evaluation of treatment effectiveness versus cost data. Since latex solids are not contained in wastewaters from solution crumb plants, clarification with chemical coagulation is not required; clarification in crumb pits is sufficient. In addition, after biological treatment, the residual COD concentration is much lower than is the case in the emulsion crumb couterpart. Consequently, carbon adsorption to only one level of overall COD reduction (65 percent removal) is reasonable. COD reductions greater than this would involve additional risk and uncertainty in the costing processes.

The first degree of treatment proposed includes primary clarification of crumb-laden wastewater in dual-unit crumb pits, followed by biological treatment to remove soluble organics. The cost data have been developed on the basis of an activated sludge system for the same reasons as given previously for the emulsion crumb sub-category. Depending on land availability, biological treatment could be aerated lagoons and stabilization ponds. The second degree of treatment consists of dual-media filtration followed by activated carbon adsorption. Carbon adsorption was selected because it is the most feasible technique for reducing the soluble COD content.

#### Basis of the Treatment Cost Data

A profile of the solution crumb rubber industry defined the typical size of a solution crumb production facility as 30,000 metric tons per year. The wastewater flow for such a plant would approximate 15.75 liters/second (250 gallons per minute).

The model treatment plant using activated sludge biological treatment is shown in Figure IX-2. The treatment given by the proposed system is equivalent to Level I Control and Treatment.

The recommended treatment technology to attain Level II Control and Treatment, presented in Figure X-1, consists of dual-media filtration followed by activated carbon adsorption.

The influent raw waste loads upon which the treatment system designs were based were selected to represent the highest expected raw waste load in this sub-category. The same cost criteria used for emulsion crumb plants were applied for solution crumb rubber facilities.

The total capital and annual costs for the model treatment techniques for a typical solution crumb plant are presented in Table VIII-4, together with the raw waste loads and treated effluent qualities.

#### Energy Requirements

The only energy or power need is electricity, and electricity consumption is moderate. The carbon is not regenerated on-site because of the unfavorable economics of small-scale carbon regeneration systems.

#### Non-Water Quality Aspects

Solid waste generation with this treatment system is associated with biological solids and spent activated carbon. The activated carbon canisters may be returned for regeneration off-site by the supplier. However, annual operating data have been based on disposal of the spent carbon at a landfill site. The annual quantities of solid waste generated are:

Biological solids

102 cu. meters (135 cu. yds)

Spent carbon

140 cu. meters (185 cu. yds)

Air quality and noise levels will not be significantly affected by the operations proposed in these treatment systems.

#### Latex Sub-category

#### Selection of Control and Treatment Technologies

Four degrees of control and treatment were considered in weighing the treatment effectiveness versus cost of treatment. These degrees of treatment are the same as for emulsion crumb wastewater and include primary clarification, biological oxidation, and advanced treatment to two levels of COD removal.

Latex rubber wastewaters contain uncoagulated latex solids and the proposed primary treatment (chemical coagulation and clarification) is similar to that recommended for emulsion crumb wastewaters. The biological treatment cost data have been based on activated sludge for the same reasons as were cited for the emulsion crumb sub-category. The advanced treatment cost data were modeled on two levels of overall COD reduction, 87 and 95 percent. Overall removals greater than 95 percent would call for undue technical risk, and uncertainty about capital and operating costs.

# TABLE VIII-4 Solution Crumb Rubber Subcategory

Estimated Wastewater Treatment Costs for Different Degrees of Treatment based on a Typical Production Capacity of 30,000 metric tons/year

	Treatment or Control Technologies 1				
investment <sup>2</sup>	\$810,000	<u>B</u> (Level II \$1,182,000			
Annual Costs					
Capital Costs	\$ 81,000	\$ 182,000			
Depreciation	162,000	236,000			
Operating and Maintenance Costs (excluding energy and power costs)	68,000	145,000			
Energy and Power Costs	4,000	6,000			
Total Annual Costs <sup>2</sup>	\$315,000	\$ 569,000			

Parameters	Raw	Effluent (	Quality
(kg/10 <sup>3</sup> kg production)	Wastewaters	A (Level I)	B (Level II)
COD	6.00	3.94	2.08
BOD	0.80	0.40	0.08
Suspended Solids	2.20	0.65	0.16
Oil and Grease	0.25	0.16	0.08

<sup>&</sup>lt;sup>1</sup>Technology A is Primary Clarification of Crumb Rinse Wastewaters followed by Activated Sludge Secondary Treatment.

Technology B is Technology A followed by Dual Media Filtration plus Activated Carbon Treatment to produce 65% overall COD reduction.

August 1971 Dollars.

### Basis of the Treatment Cost Data

A latex rubber industry profile was made to determine the typical size of a latex rubber production facility. The average, or typical, plant has an annual capacity of 10,000 metric tons, and its wastewater flow approximates 4.4 liters/second (70 gallons per minute).

The model treatment plant, consisting of chemical coagulation and clarification followed by activated sludge biological treatment, is illustrated in Figure IX-2. This is equivalent to Level I Control and Treatment.

The recommended treatment technology to achieve Level II Control and Treatment technology, presented in Figure X-1, includes dual-media filtration followed by activated carbon adsorption.

The treatment designs upon which the cost data are based correspond to the highest expected raw waste load within each category.

The same cost criteria used for the emulsion crumb sub-category were applied to latex rubber. See Table VIII-5.

#### Energy Requirements

Since on-site carbon regeneration is not proposed for economic reasons, the only power or energy requirement of these treatment systems is electric power for pumps and other motive equipment.

#### Non-Water Quality Aspects

Solid wastes are produced by chemical coagulation and clarification, wasted biological sludge, and spent activated carbon. For cost purposes, it is proposed that these all be hauled to a landfill. The annual quantities of solid wastes are listed below:

Primary coagulated solids 214 cu. meters (283 cu. yards)

Biological solids 62 cu. meters (82 cu.yards)

Spent carbon 126 cu. meters (167 cu. yards)

Neither air quality nor noise levels will be adversely affected by the proposed treatment technologies.

# TABLE VIII-5 Latex Rubber Subcategory

Estimated Wastewater Treatment Costs for Different Degrees of Treatment based on a Typical Production Capacity of 10,000 metric tons/yr.

_		A	<u>B</u> (Level 1)	C	<u>D</u> (Level 11)
Investment <sup>2</sup>		\$361,000	\$637,000	\$784,000	\$784,000
Annual Costs					
Capital Costs		\$ 36,000	\$ 64,000	\$ 78,000	\$ 78,000
Depreciation		72,000	127,000	157,000	157,000
Operating and Mainten excluding energy and		33,000	57,000	100,000	117,000
Energy and Power Cost	s	1,000	3,000	3,000	3,000
Total Annual Costs <sup>2</sup>		\$142,000	\$251,000	\$338,000	\$355,000
<u>&lt;</u>					
n Parameters	Raw		Effluent Cualit	.y	
(kg/10 <sup>3</sup> kg production)	Wastewater	<u>A</u>	B (Level I)	<u>_C</u> _	<u>D</u> (Level 11)
COD	33.52	14.75	6.85	4.31	1.78
BOD	5.61	4.77	0.34	0.07	0.07
Suspended Solids	5.63	0.93	0.55	0.07	0.14
Oil and Grease	0.70	0.34	0.14	0.07	0.07

Technology A is Chemical Coagulation followed by Clarification.

Technology B is Technology A followed by Activated Sludge Secondary Treatment.

Technology C is Technology B followed by Dual Media Filtration plus Activated Carbon Treatment to produce 37% overall COD reduction.

Technology D is Technology B followed by Dual Media Filtration plus Activated Carbon Treatment to produce 95% overall COD reduction.

August 1971 Dollars.

#### SECTION IX

# BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE -- EFFLUENT LIMITATIONS

# Tire and Inner Tube Facilities

# <u>Identification of Best Practicable Control Technology</u> <u>Currently Available</u>

The best control and treatment technologies currently in use emphasize in-house control of solution wastes with end-of-pipe treatment of combined process and non-process wastewaters. However, as discussed previously, end-of-pipe treatment of process wastewaters after combination with non-process wastewaters is considered ineffective.

Of the exemplary plants visited, only one plant performs a totally adequate end-of-pipe treatment of all process wastewater streams. The treatment facility involves the use of holding lagoons for combined process and non-process effluents and the re-use of the wastewater for irrigation of farm land. The very large land requirements involved keep this type of treatment from being applied to the industry as a whole. Other end-of-pipe treatment facilities examined were not very effective in removal of the oil constituent in the wastes, due to dilution by non-process wastewaters.

There are many in-plant control and treatment facilities. Recirculation of the soapstone solution was considered adequate and effective. However, the weekly washing and dumping of the system in most plants reduced this effectiveness. Oil sumps and separators are common to the tire industry, but their effectiveness is reduced by dilution with other wastes or by improper maintenance.

Since process wastes are best treated before dilution with non-process wastewaters and because no plant obtained effective control and treatment for all the wastewaters it generated, the proposed Level 1 treatment technology for a typical plant is a combination of the best features of various plants examined and visited.

Since only the loadings vary between the Old Tire and Inner Tube Production Facilities sub-category and the New Tire Production Facilities sub-category, the treatment schemes described below will be the same for both.

Basically, the technology employed consists of:

- 1. Elimination of any discharge of soapstone or latex-dip solution.
- 2. Segregation, control, and treatment of all oily waste streams.

A flow diagram of the proposed system is shown in Figure IX-1.

Zero discharge of soapstone and latex solutions is currently practiced by production facilities in each of the sub-categories. Elimination of soapstone solution discharges involves:

- 1. Recycle of soapstone solution.
- 2. Installation of curbing around the soapstone dipping area.
- 3. Sealing of drains in the dipping area.
- 4. Re-use of the recirculating system washwater as make-up for fresh soapstone solution.

The re-use of the recirculating system washwater is the key to zero discharge of this waste. In emptying the system for cleaning, the soapstone used should be stored in tanks. The washwater used should also be collected and stored. Once the system is cleaned, stored soapstone can then be returned to the system for use in the new production batch. The collected and stored washwater can then be re-used as make-up water to the soapstone bath during the normal production run.

Eliminating the discharge of latex solution is achieved by:

- 1. The use of curbing around the latex dipping area.
- 2. Sealing of all drains in the dipping area.
- 3. Containment of all wastewaters from the area.

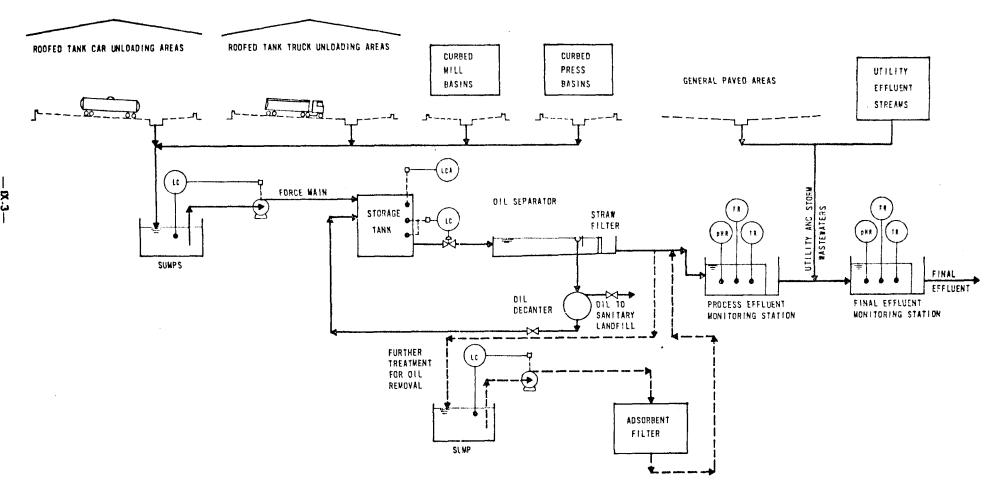
Several plants have already achieved zero discharge by these methods. The contained and collected wastes are disposed of off-site in a landfill.

Control and treatment of oily waste streams involves segregation, collection, and treatment of these wastes. The wastes to be segregated include runoff from oil storage and unloading areas and leakage and spills in the process areas, as shown in Figure IX-1. Press and mill basins, when present, are included in the process area.

To achieve proper segregation of wastes, any possibility of mixing process and non-process streams must be eliminated. This requires two completely segregated sewer systems, proper plant piping, and good housekeeping and employee awareness. As a basis for this study, it was assumed that plants categorized as "old" have combined sewers. To segregate sewers properly in plants of the "old" sub-category, it was deemed necessary to install completely new drains and sewer lines; existing drains would be sealed off. Older plants often have a significant number of drains and sewer runs in which the location and interconnection are often doubtful because of outdated engineering and installation drawings. It would, therefore, be less costly to install new plant sewers properly segregated than attempt to redirect the existing ones.

FIGURE IX.1

HYPOTHETICAL WASTEWATER SEGREGATION AND TREATMENT FACILITY FOR TIRE AND INNER TUBE PLANTS



Once isolated, these wastewaters are collected in sumps located in strategic areas throughout the plant. Waste flows will be intermittent by nature and, therefore, a sizable flow rate will hardly ever be obtained without first collecting all wastes in centralized locations. Wastewaters collected in these sumps will be periodically pumped to an API-type gravity separator, where the separable oil and solids fraction is removed. To provide for large spills or leakage of a major water supply line, a 37,850-liter (1,000-gal.) storage tank is provided.

Separated oil is removed by a manually operated slotted pipe. A decant tank is provided to allow water removed with the oil to settle out. Concentrated oil-water mixtures are then removed from the decant tank, drummed, and sealed, and sent to a landfill. Water removed from the tank is pumped back to the separator.

Settleable solids collected in the separator are periodically removed and also sent to a landfill. The separator is provided with two dualoperating chambers in order to provide for uninterrupted service during clean-out.

The gravity separator is provided with a straw filter to remove any large oil globules still remaining due to possible short circuiting or unforeseen peak overload conditions. Additional treatment for oil removal is obtained by passing the effluent from the separator through an absorbent filter.

#### Effluent Loadings Attainable With Proposed Technologies

Based on the control technology data obtained from tire manufacturer sources, and treatment data obtained from industries having similar wastewater problems, it was determined that the proposed Level 1 control and treatment technologies will result in the following effluent quality for both Old Tire and Inner Tube and New Tire Facilities:

Oil and Grease 5 mg/L Suspended Solids 40 mg/L

It is expected that the use of an API separator will result in an effluent oil concentration of 30 mg/L. The use of an absorbent filter will further reduce the effluent oil concentration to 5 mg/L.

A reduction in suspended solids concentration will result from the use of the proposed API-type gravity separator. Additional reduction in suspended solids is deemed likely after passage through the absorbent filter. However, no reliable data are available for making such a determination. As a result, recommended standards for Level 1 are as follows:

Suspended Solids 0.64 kg/10<sup>3</sup> kg raw material 0.008 kg/10<sup>3</sup> kg raw material

#### Synthetic Rubber Industry

# <u>Identification of Best Practicable Control Technology</u> Currently Available

In view of the fact that all sub-categories of the synthetic rubber industry are highly technical and proprietary in nature, it is not possible to base effluent limitation guidelines and standards of performance on in-plant control technologies which might impact on processing procedures and product quality. Instead, these guidelines have been formulated around the best practicable end-of-pipe treatment technologies employed by the synthetic rubber industry. In order to achieve the contaminant reductions recommended for this guideline, the synthetic rubber industry will require better housekeeping and maintenance practices, as well as in-plant processing modifications, to assist the end-of-pipe treatment plant in attaining the required reductions. The effluent limitations have been based on the effluent quality and contaminant removal efficiencies of well-designed and properly-operated treatment facilities. Level I technology has been defined as equivalent to secondary treatment.

#### Emulsion Crumb Sub-category

The coagulation liquor and crumb rinse overflow stream should be passed through crumb pits to remove crumb rubber fines. These pits should be be dual units so that good crumb separation can be achieved during pit unit cleaning operations. Figure IX-2 shows a hypothetical end-of-pipe secondary treatment facility applicable to the treatment of emulsion crumb wastewaters. This treatment includes chemical coagulation and clarification, and biological treatment. The total plant effluent should be passed through an equalization basin, providing approximately 24 hours detention, to smooth out waste load peaks and to equalize hydraulic flow. The equalization basin should be aerated to insure good mixing, prevent anaerobic conditions, and assist in the biological oxidation removal process.

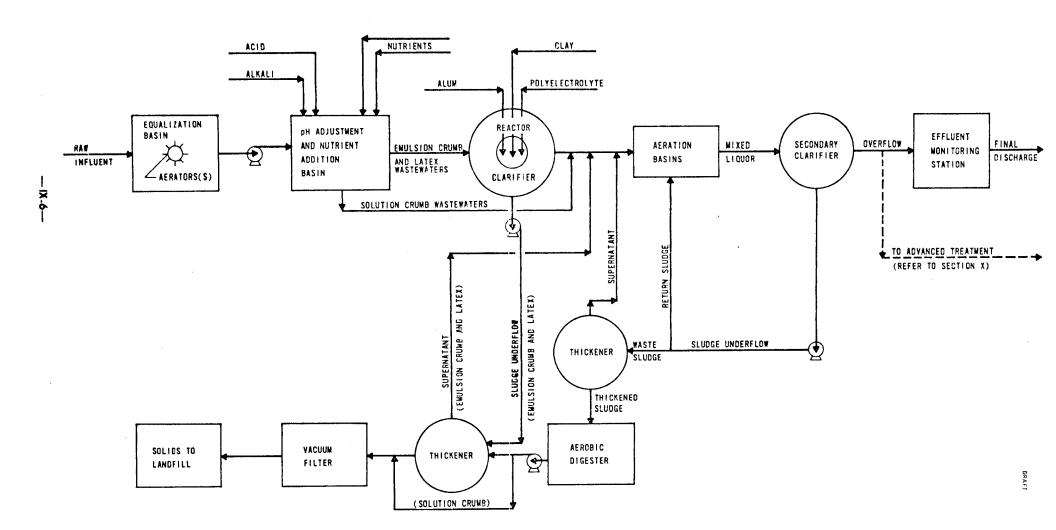
From the equalization basin, the wastewaters are pumped to a mixing basin, where the pH of the wastewaters is adjusted to achieve optimum coagulation conditions. The desired pH value is approximately neutral (pH=7) and is suitable for biological treatment with no changes. Nutrients to facilitate biological treatment will also be added in this basin.

After pH adjustment, the wastewaters flow into a reactor-clarifier, where coagulating chemicals (alum and polyelectrolyte) are added in the reactor compartment. A clay slurry is also added, to weight down the coagulated rubber solids. The wastewater flows from the reactor compartment to the clarifier, where the settleable solids and coagulated solids settle and are removed. The clarified wastewater overflows the clarifier and enters the bioligical treatment system.

FIGURE IX-2

HYPOTHETICAL END-OF-PIPE SECONDARY WASTEWATER TREATMENT FACILITY

FOR SYNTHETIC RUBBER PLANTS



The clarified wastewater flows into aeration basins where it is well mixed with biological solids. Micro-organisms synthesize new biological solids from organic matter contained in the wastewater. At the same time, some soluble matter is consumed for energy purposes using oxygen supplied by aerators in the basin. The result is that soluble material is converted to insoluble biological solids and the BOD of the wastewater is reduced. The mixed liquor containing biological solids suspended in the wastewater overflows the aeration basin to the secondary clarifier.

The solids in the mixed liquor are settled in the secondary clarifier, and the clarified wastewater overflows and enters an effluent monitoring station, where the flow is recorded and an automatic 24-hour composite sample is collected.

Part of the settled biological solids is returned to the aeration basins to maintain the mixed liquor solids concentration in the basin. The remainder of the bio-solids must be wasted from the system as a sludge.

The waste sludge is first thickened in a gravity thickener with the supernatant returning to the head of the aeration basins. The thickened sludge underflow enters an aerobic digestor, where the biological sludge is wasted by endogenous respiration utilizing oxygen to aerate and reduce the bio-solid bulk. This process is referred to as aerobic digestion.

This digested sludge is then mixed with the primary solids underflows from the reactor-clarifier unit and enters a secondary thickener. The clear supernantant from this thickener is also recycled to the aeration basins. The thickened underflow is then discharged to a vacuum filter for further conditioning and concentration.

A drum-type vacuum filter separates thickened sludge into a dewatered cake, which discharges by belt conveyor to a dumpster bin and into a filtrate that is recycled to the aeration basin. The dewatered sludge cake is biologically stable and can be disposed of at a sanitary landfill. Filter aid and precoat preparations are used to assist and maintain the quality of the filtrate.

#### Solution Crumb Sub-category

The plant wastewaters are first passed through crumb pits to remove rubber crumb fines. As previously noted in the discussion of the emulsion crumb sub-category, these pits should be dual units.

Figure IX-2 represents a hypothetical secondary treatment alternative which is applicable to solution crumb rubber wastewaters, as well as to the emulsion crumb wastewaters previously discussed. Since solution crumb wastewaters do not contain uncoagulated latex solids, and if ade-

quate separation of the rubber fines has been achieved in the crumb pits, neither the chemical coagulation process nor the primary clarifier is required. The wastewaters can then pass from the pH and nutrient addition basin directly into the aeration basin (refer to Figure IX-2). In addition, since there are no primary solids, the second thickener is not necessary and the wasted biological sludge passes directly from the digester to the vacuum filter. The solution crumb secondary wastewater treatment facility is similar to the emulsion crumb wastewaters in all other aspects.

#### Latex Sub-category

The model secondary wastewater treatment facility illustrated in Figure IX-2 is also applicable at latex rubber plants. Since latex plant wastewaters contain uncoagulated latex solids, primary clarification assisted by chemical coagulation is required. However, because latex plants are considerably smaller than emulsion crumb plants, the wastewater flow rate is much lower. The lower flow rates indicate the use of separate rapid-mix, flocculator, and clarifier units, since small reactor-clarifiers are not practicable in small diameters due to reduction in efficiency, mixing, and settlement of solids.

Other than this basic difference (due to flow rate only) in the design of the primary clarification equipment, the secondary treatment facility for latex plant wastewaters is identical to that described for emulsion crumb wastewater.

### Effluent Loadings Attainable With Proposed Technologies

#### Emulsion Crumb Sub-category

Based on raw waste load and the control and treatment data from emulsion crumb plants, it was determined that the described proposed control and treatment technologies will result in the following effluent quality:

COD	500	mg/L
BOD	25	mg/L
Suspended Solids	40	mg/L
Oil and Grease	10	mg/L

Effluent quality can also be expressed in terms of effluent waste loads, which are independent of wastewater flow. These effluent waste loads, resulting from the application of treatment technologies equivalent to chemical coagulation with clarification and biological treatment, constitute the best practicable control and treatment technology standards currently available (Level 1) for the emulsion crumb sub-category. Recommendations for proposed limitations for Level 1 are:

COD	$8.00 \text{ kg/}10^3$	kg production
BOD	$0.40 \text{ kg/}10^3$	kg production
Suspended Solids	$0.65 \text{ kg/}10^{2}$	kg production
Oil and Grease	$0.16 \text{ kg}/10^3$	kg production

# Solution Crumb Sub-category

Industry raw waste load and the control and treatment data indicate that proposed control and treatment technologies for solution crumb rubber wastewater will achieve the following effluent quality:

COD	245	mq/L
BOD	25	mg/L
Suspended Solids	40	mg/L
Oil and Grease	10	mq/L

Effluent quality can also be expressed in terms of effluent waste loads, which are independent of wastewater flow. These effluent waste loads, resulting from the application of treatment technologies equivalent to primary clarification and biological treatment, constitute the best practicable control and treatment technology standards currently available (Level 1) for the solution crumb sub-category. Recommendations for proposed limitations for Level 1 are:

COD	$3.94 \text{ kg/}10_3^3 \text{ kg production}$
BOD	0.40 kg/103 kg production
Suspended Solids	$0.65 \text{ kg/}10^3 \text{ kg production}$
Oil and Grease	$0.16 \text{ kg/}10^3 \text{ kg production}$

#### Latex Sub-category

Raw waste load and the control and treatment data indicate that the proposed control and treatment technologies for latex rubber wastewaters will achieve the following effluent quality:

COD	500 mg/L
BOD	25 mg/L
Suspended Solids	40 mg/L
Oil and Grease	10 mg/L

Effluent quality can also be expressed in terms of effluent waste loads, which are independent of wastewater flow. These effluent waste loads, resulting from the application of treatment technologies equivalent to primary clarification with chemical coagulation followed by biological treatment, constitute the best practicable control and treatment technology standards currently available (Level 1) for the latex rubber sub-category. Recommendations for proposed limitations for Level 1 are:

COD BOD Suspended Solids	0.34 kg/10 <sup>3</sup> 0.55 kg/10 <sup>3</sup>	kg production kg production kg production
Oil and Grease	$0.14 \text{ kg/}10^3$	kg production

#### CHAPTER X

# BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE -- EFFLUENT LIMITATIONS

#### Tire and Inner Tube Industry

Effluent limitations commensurate with best available technology economically achievable and best practicable technology currently available are identical.

# Old Tire and Inner Tube Production Facilities

Suspended Solids  $0.064 \text{ kg/}10^3 \text{ kg raw materials}$  0.11 and Grease  $0.008 \text{ kg/}10^3 \text{ kg raw materials}$ 

# New Tire Production Facilities

Suspended Solids  $0.064 \text{ kg/}10\frac{3}{3} \text{ kg raw materials}$  0.108 kg/ $10^3 \text{ kg raw materials}$ 

Based on a typical plant size of 205 metric tons of raw materials per day, and process wastewater flow rate of 3.785 liters/sec (60 ppm), a loading of .008 kg/l000 kg raw materials results in an effluent concentration of 5 mg/L.

This concentration of oil represents the lower accuracy limit based on currently approved EPA analytical techniques. Further reductions would therefore be academic, and cost data could then not be equated to additional beneficial reduction.

A suspended solids loading of .064 kg/1000 kg of raw material consumed is equivalent to a concentration of 40 mg/L. This concentration is not significant and will have minimal impact on the receiving stream. Further reduction in suspended solids does not appear to be justified either on a cost or on a benefit basis.

#### Synthetic Rubber Industry

# <u>Identification of Best Practical Control Technology</u> Currently Available

After review of the data and control and treatment technologies, it is clear the principal pollutant load after biological treatment, for all sub-categories in the Synthetic Rubber Industry waste, is due to COD. The other parameters (BOD, suspended solids, and oil and grease) are reduced to comparatively low levels. Therefore, advanced treatment should be addressed to COD removal and reduction.

None of the end-of-pipe systems observed in use by this industry was considered completely adequate for establishing effluent limitations commensurate with the best available technology economically achievable (Level II).

#### Emulsion Crumb Sub-category

After biological treatment, emulsion crumb wastewaters have low BOD, suspended solids, and oil and grease concentrations, and high COD concentrations (about 500 mg/L). The most feasible technique to reduce residual COD content after biological treatment is by using an activated carbon adsorption technique. This technology has been studied in pilot scale apparatus using as feed stock emulsion crumb wastewaters which had been subjected to secondary treatment. After treatment with carbon, the resultant COD level was reduced to about 130 mg/L. This degree of removal has been used to establish Level II COD effluent limitations and standards of performance for the emulsion crumb sub-category.

Because both the quantity and quality of the data available for supporting the adoption of this level of treatment for secondary wastewaters from emussion crumb facilities are sparse, the proposed limitations of performance will be confirmed by the EPA National Environmental Research Center, Cincinnati, Ohio prior to approval of this document by the EPA. The technology proposed here involves no more than acceptable technical risk and uncertainty of costs.

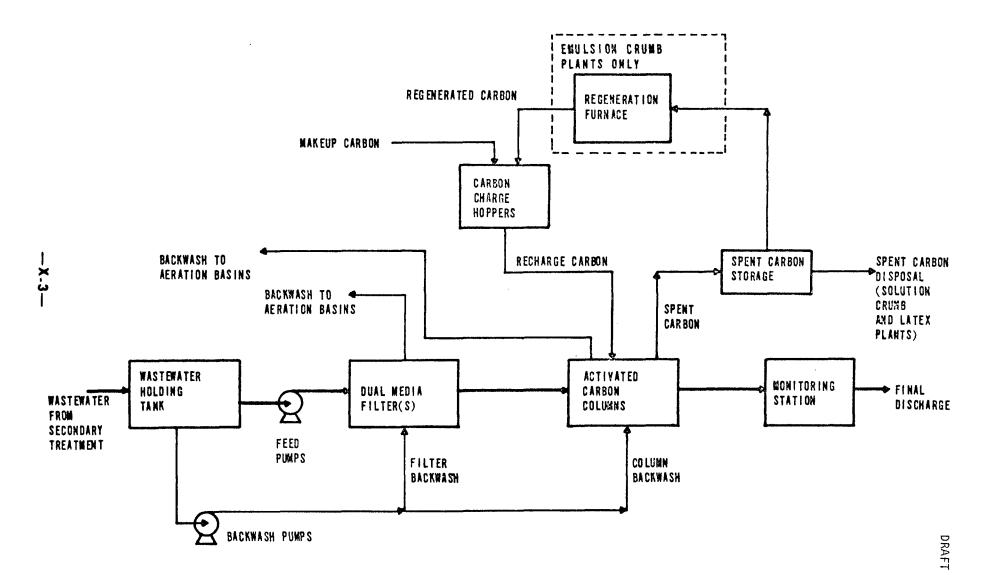
Figure X-1 shows a hypothetical advanced wastewater treatment facility using activated carbon treatment to achieve COD removals adequate for Level II control and treatment technology.

The secondary effluent discharges into a holding tank which is normally maintained full by a level-control signal to the feed pumps. The feed pumps produce sufficient line pressure to pump the wastewater through the dual multi-media filters and the carbon columns.

FIGURE X-1

HYPOTHETICAL END-OF-PIPE ADVANCED WASTEWATER TREATMENT FACILITY

FOR ALL SUB-CATEGORIES OF SYNTHETIC RUBBER PLANTS



DRAFT

The wastewater is first filtered to remove the residual suspended solids from secondary treatment. Filtration before the carbon bed will prevent fine particles from plugging the carbon. The filtration media used generally are anthracite and fine graded sands. The filters are dual or multiple units depending on the wastewater flow rate and standard equipment sizes available. Periodically, these filters require backwashing indicated by a pressure buildup upstream or a pressure drop across the filter bed. When filter backwashing is necessary, the feed is switched to the dual unit, the backwash pumps are activated, and the unit undergoes the complete backwash cycle. Backwash water containing trapped solids is piped to the aeration basins of the secondary treatment facility. The backwash cycle usually includes an air scour and a final service flow period for resettlement of the filter media. The flow rate during the backwash cycle is considerably higher than during the normal service cycle and therefore requires a holding tank of sufficient capacity to furnish the necessary water for the backwash operation.

The filtered wastewater flows down through the activated carbon columns. Depending on the wastewater flow rate, two or more parallel carbon bed columns may be required. Due to solids builup in the carbon columns, periodic backwashing is also required. Each column is backwashed when the pressure drop across the column exceeds a pre-set value. The backwashing water is discharged to the aeration basins of the secondary treatment facility.

The carbon in the columns is replaced with fresh or regenerated carbon when its activity is depleted. This is indicated by breakthrough or leakage as detected in an automatic total carbon analyzer. The spent carbon is discharged to a spent carbon storage bin, and a regenerated or fresh charge of carbon is provided to the columns from a charge hopper.

The effluent from the carbon bed columns has low COD, BOD, suspended solids, and oil and grease. The flow of this effluent is monitored through a monitoring station where a 24 hour composite sample is collected.

In most emulsion crumb plants, the carbon usage is sufficiently high to justify on-site regeneration. Regeneration may be carried out in an oil-fired, multiple-hearth furnace. The spent carbon is continuously fed from the spent carbon storage bin to the furnace. The regenerated and cooled carbon is then returned to a carbon charge hopper and is ready for re-charging. Overflow carbon quench and slurry waters from the regeneration process are discharged to the aeration basins of the secondary treatment plant. Makeup carbon (to replace carbon lost during unloading, transfer, loading, and regeneration) is added at the charge hopper. Losses normally amount to approximately 5 percent of the regenerated carbon weight.

In smaller emulsion crumb production facilities, carbon usage is low and on-site regeneration may not be feasible. The carbon can then either be returned to the supplier for regeneration or can be disposed of as solid waste in a landfill site.

# Solution Crumb Sub-Category

The hypothetical advanced wastewater treatment facility illustrated in Figure X-1 is also applicable to a secondary effluent from solution crumb wastewater. The illustrated facility will produce an effluent satisfactory for Level II control and treatment technology.

Although this technology has not been used by plants in the solution crumb sub-category, it has been studied for emulsion crumb secondary effluent. Because of the many similarities between solution crumb and emulsion crumb wastewater (e.g., use of the same monomers and similar processing techniques by the two sub-categories), it is reasonable to propose this advanced treatment technology for secondary solution crumb wastewater. The level of treatment representative of this technology will be confirmed by the EPA National Environmental Research Center, Cincinnati, Ohio prior to approval of this document by the EPA. The technology proposed here to achieve Level II involves no more than acceptable technical risk and cost uncertainty.

The advanced treatment facility for solution crumb is similar to that for emulsion crumb, except that in most cases the carbon will be disposed of or regenerated off-site, instead of being regenerated on-site. This is due primarily to the fact that solution crumb plants are generally smaller than emulsion crumb plants, and on-site carbon regeneration is not economically feasible.

# Latex Sub-Category

Again, the hypothetical advanced wastewater treatment facility illustrated in Figure X-1 is recommended for treatment of secondary effluent latex rubber wastewaters. This facility corresponds to the proposed Level II control and treatment technology for latex rubber plants.

This technology has not been used by latex rubber plants, but it has been studied, on a pilot scale, for the advanced treatment of secondary effluent emulsion crumb rubber wastewaters. There are many similarities in materails used and processing operations between latex and emulsion crumb production, and hence similarities in their wastewaters. Differences tend to revolve around the level of loadings rather than the characteristics and constituents. It is, therefore, reasonable to recommend this advanced treatment technology for secondary effluent latex rubber wastewaters. The level of treatment attainable by this technology will be confirmed by the EPA National Environmental Research Center, Cincinnati, Ohio prior to approval of this document by the EPA. This technology involves no more than acceptable technical risk and cost uncertainty.

The hypothetical facility will be similar to that proposed for emulsion crumb wastewaters. However, it is most probable (because of unfavorable economics) that on-site carbon regeneration will not be practiced. Off-site regeneration by the carbon supplier or landfill disposal of the exhausted carbon appears more feasible from a technology and cost basis.

# Effluent Loading Attainable with Proposed Technologies

# Emulsion Crumb Sub-category

Based on secondary treatment data and pilot studies of activated carbon adsorption, the proposed control and treatment technologies will result in effluent quality better than or equal to the following values:

COD	130	mg/L
BOD	5	mg/L
Suspended Solids	10	mg/L
Oil and Grease	5	mg/L

The proposed treatment will probably produce an effluent of higher quality for BOD, Suspended Solids, and Oil and Grease than the above values. However, the resultant limitations on these parameters are governed by the accuracy of the analytical methods.

Effluent quality can also be defined in terms of effluent waste loads, which are independent of wastewater flow. These effluent waste loads, resulting from the application of treatment technologies equivalent to multi-media filtration and activated carbon adsorption, constitute the best available treatment economically achievable (Level II) for the emulsion crumb sub-category. The proposed limitations for Level II are as follows:

COD	$2.08 \text{ kg}/10^{3} \text{ kg production}$
BOD	$0.08 \text{ kg}/10^3 \text{ kg production}$
Suspended Solids	$0.16 \text{ kg}/10^3 \text{ kg production}$
Oil and Grease	$0.08 \text{ kg}/10^3 \text{ kg production}$

### Solution Crumb Sub-category

Industry secondary treatment data and data extrapolated from the pilotscale activated carbon adsorption studies on secondary effluent emulsion crumb wastewaters were used to quantify the effluent quality of solution crumb wastewaters following advanced treatment. The effluent quality is given as follows:

COD	130	mg/L
BOD	5	mg/L
Suspended Solids	10	mg/L
Oil and Grease	5	mg/L

The effluent values for BOD, Suspended Solids, and Oil and Grease are dictated by the lower limit of accuracy for the currently accepted analytical methods.

Effluent quality can also be expressed in terms of effluent waste loads, which are independent of wastewater flow. The effluent waste loads following multi-media filtration and activated carbon adsorption constitute the best available treatment economically achievable (Level II) for the solution crumb sub-category. The proposed limitations for Level II are as follows:

COD	2.08 kg/10 <sup>3</sup> kg production 0.08 kg/10 <sup>3</sup> kg production 0.16 kg/10 <sup>3</sup> kg production 0.08 kg/10 <sup>3</sup> kg production
BOD	$0.08 \text{ kg/}10^3 \text{ kg production}$
Suspended Solids	$0.16 \text{ kg}/10^{3} \text{ kg production}$
Oil and Grease	$0.08 \text{ kg/}10^3 \text{ kg production}$

# Latex Sub-category

Latex industry secondary treatment data and data extrapolated from pilotscale plant studies on the activated carbon adsorption treatment of emulsion crumb secondary effluent were used to formulate the following effluent qualities:

COD	130 mg/L
BOD	5 mg/L
Suspended Solids	10 mg/L
Oil and Grease	5 mg/L

The effluent levels for BOD, Suspended Solids, and Oil and Grease are dependent on the accuracy of the best accepted analytical methods.

Effluent quality can also be expressed in terms of effluent waste loads which are independent of wastewater flow. The effluent waste loads resulting from the application of treatment technologies equivalent to multimedia filtration and activated carbon adsorption form the basis for the best available treatment economically available (Level II) for the latex sub-category. The proposed limitations for Level II are:

COD	1.78 kg/10 <sup>3</sup> kg production 0.07 kg/10 <sup>3</sup> kg production 0.14 kg/10 <sup>3</sup> kg production
BOD	$0.07 \text{ kg}/10^3 \text{ kg production}$
Suspended Solids	$0.14 \text{ kg}/10^3 \text{ kg production}$
Oil and Grease	$0.07 \text{ kg}/10^3 \text{ kg production}$

### SECTION XI

#### NEW-SOURCE PERFORMANCE STANDARDS

# Tire and Inner Tube Production Facilities

Recommended effluent limitations for new sources are identical and commensurate with best available technology economically achievable and best practicable technology currently available. These effluent limitations are presented in Sections IX and X of this report.

# Synthetic Rubber Industry

Because all stated sub-categories of the synthetic rubber industry are highly technical and involve proprietary processes, in-plant control technologies cannot be fully defined or enumerated; such in-plant measures might impact on manufacturing practices and product quality.

Since advanced wastewater treatment technologies have been proposed for the best available end-of-pipe treatment economically achievable by existing plants, no improvement upon those standards can be recommended for new sources. No additional treatment technologies or controls are proposed for beyond Level II. It should be noted at this time that the application of activated carbon adsorption for COD removal after secondary treatment involves acceptable but certain technical risks and unconfirmed costs. The performance of this proposed advanced treatment technology will be confirmed by the EPA National Environmental Research Center, Cincinnati, Ohio, prior to approval of this document by EPA.

The effluent waste loads resulting from the application of the best available treatment economically achievable for new sources (Level III) for synthetic rubber plants are as follows:

# Emulsion Crumb Sub-category

COD	2.08 kg/10 <sup>3</sup> kg production
BOD	0.08 kg/10 <sup>3</sup> kg production
Suspended Solids	0.16 kg/10 <sup>3</sup> kg production
Oil and Grease	0.08 kg/10 kg production
UII and Grease	0.00 kg/10 kg production

### Solution Crumb Sub-category

COD	$2.08 \text{ kg}/10^{3}$	kg production
BOD	$0.08 \text{ kg/}10^{3}$	kg production
Suspended Solids		kg production
Oil and Grease	$0.08 \text{ kg}/10^3$	kg production

# Latex Sub-category

COD	$1.78 \text{ kg/}10^{3} \text{ kg production}$
BOD	$0.07 \text{ kg/}10^{3} \text{ kg production}$
Suspended Solids	$0.14 \text{ kg/}10^{3} \text{ kg production}$
Oil and Grease	$0.07 \text{ kg/}10^3 \text{ kg production}$

# Pretreatment Recommendations

A minimum level of pretreatment must be given to new production facilities which will discharge wastewater to a publicly owned treatment works. In addition, potential pollutants which will inhibit or upset the performance of publicly owned treatment works must be eliminated from such discharges.

# Tire and Inner Tube Industry

Pretreatment recommendations for process wastewaters from the tire and inner tube industry include the separation of oils and solids in an API gravity separator and the use of an equalization basin to prevent shock loads of oil, suspended solids or batch dumps of dipping solutions from entering and upsetting the performance of a publically owned treatment works. Oily wastes, after dilution in a public sewer system, will remain untreated and therefore must be controlled before discharge from the plant boundaries.

Pretreatment of other non-process wastewaters from the tire and inner tube industry will pose more difficult problems. These include alkalinity in boiler blowdowns and both acidity and alkalinity in water treatment wastes. Both boiler blowdowns and water treatment wastes will contain high concentrations of suspended and dissolved solids. Cooling tower water treatment wastes may contain heavy metals such as chromium and zinc used for corrosion inhibition. Potential problems such as acidity, alkalinity, solids, oils, and heavy metals may require control at the plant to conform to local ordinances for discharge to a publicly owned treatment works. The control techniques and treatment methods are described in earlier sections of this report. Equalization of the waste load and wastewater flow is the key step in the control of batch dumps of production chemicals and solutions.

# Synthetic Rubber Industry

Emulsion crumb and solution crumb slurry overflow wastewaters should be passed through crumb pits to remove floatable rubber crumb. Few publicly owned treatment works have primary clarification equipment adequate to handle large quantities of agglomerated rubber crumb solids.

Wastewaters from emulsion crumb and latex production facilities are invariably laden with uncoagulated latex solids. Since publicly owned treatment works do not generally have coagulation capabilities, these wastewaters should, at least, be chemical coagulated with a sinking agent and clarified.

Utility wastes often exhibit extreme pH peaks which should be neutralized or, at least equalized, prior to discharge to the publicly owned treatment works. This problem is not so severe with emulsion crumb and latex plants, where pH adjustment is required prior to chemical coagulation, as it is with solution crumb production facilities where adjustment of the wastewater pH is normally not necessary. Heavy metals, present in cooling tower blowdowns for example, should be eliminated by substitution of inhibitor or equalized prior to discharge to a publicly owned treatment works.

No compounds or species present in synthetic rubber wastewater can be considered toxic or inhibitory to the performance of publicly owned treatment works.

In summary, the following pretreatment requirements apply to wastewater discharges to publicly owned treatment works from synthetic rubber plants:

Emulsion Crumb Subcategory - Gravity separation of crumb fines in crumb pits, chemical coagulation and clarification of latex-laden wastewaters, and neutralization or equalization of utility wastes.

Solution Crumb Subcategory - Gravity separation of crumb fines in crumb pits, and neutralization or equalization of utility wastes.

Latex Subcategory - Chemical coagulation of latex-laden waste-waters, and neutralization or equalization of utility wastes.

#### SECTION XII

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#### SECTION XIII

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# SECTION XIV GLOSSARY

### <u>Act</u>

The Federal Water Pollution Control Act Amendments of 1972.

# Activator

A metallic oxide that makes possible the crosslinking of sulfur in rubber vulcanization.

# Antioxidant

An organic compound added to rubber to retard oxidation or deterioration.

# Accelerator Agents

A compound which greatly reduces the time required for vulcanization of synthetic or natural rubber.

# <u>Banbury Mixer</u>

Trade name for a common internal mixer manufactured by Farrel Corporation used in the compounding and mixing of tire rubber stock.

# Best Available Technology Economically Achievable (BATEA)

Treatment required by July 1, 1983 for industrial discharges to surface waters as defined by Section 301 (b) (2) (A) of the Act.

### Best Practicable Control Technology Currently Available (BPCTCA)

Treatment required by July 1, 1977 for industrial discharges to surface waters as defined by Section 301 (b) (1) (A) of the Act.

### Best Available Demonstrated Control Technology (BADCT)

Treatment required for new sources as defined by Section 306 of the Act.

# BOD

Biochemical Oxygen Demand.

#### Bag House

An air emission control device used to collect intermediate and large particles (greater than 20 microns) in a bag filter. A bag filter is constructed of fabric. Common usage in the tire industry is to control and recover carbon black in a dry state from vapors leaving the compounding area.

# Butyl Rubber

A synthetic rubber made by the solution polymerization of isobutylene and isoprene.

#### Camelback

Tire tread used in the retreading of tire carcasses.

# Capital Costs

Financial charges in August 1971 dollars which are computed as the cost of capital times the capital expenditures for pollution control. Cost of capital is assumed to be 10 percent.

# Carbon Black

A reinforcing agent used in large quantities in tire rubber compounds.

### Catalyst

A substance that initiates a chemical reaction and enables it to proceed at a greatly accelerated rate.

### Category and Subcategory

Divisions of a particular industry which possess different traits which affect water quality and treatability.

#### Cement

A solution of synthetic rubber particles.

# Chain

A revolving metal belt upon which the newly formed glass fibers fall to form a thick mat. There are two general types of chains: wire mesh chains and light conveyors. The latter are hinged metal plates with several holes to facilitate the passage of air.

#### Coaquiation

The combination or aggregation of previously emulsified rubber particles into a clot or mass.

#### COD

Chemical Oxygen Demand.

#### Crumb

Small coagulated particles of synthetic rubber.

# Curing Agent

Curing or vulcanization agents are substances which bring about the rubber crosslinking process. The most important agent is sulfur. See vulcanization.

# Depreciation

Accounting charges reflecting the deterioration of a capital asset over its useful life. Reported as straight line over five years with zero salvage value.

# Dry Air Pollution Control

The technique of air pollution abatement without the use of water.

#### Emulsion

A stable mixture of two or more immersible liquids held in suspension by small percentage of substances called emulsifiers.

# Endogenous Respiration

Auto-oxidation of the microorganisms producing a reduction and stabilization of biological solids.

#### **EPDM**

A synthetic rubber based on ethylene-propylene and a controlled amount of non-conjugated diene. Polymerization is carried out in solution.

#### Extender

A low specific gravity substance used in rubber formulations chiefly to reduce costs.

#### Extrude

To shape by forcing a material through a die. The operation is carried out in a device known as an extruder. In tire and inner tube manufacture treads and inner tubes are formed by extrusion.

# Filler

A high specific gravity (2.00-4.50) compound used in rubber mixtures to provide a certain degree of stiffness and hardness and used to decrease costs. Fillers have neither reinforcing or coloring properties and are similar to extenders in their cost-reducing function.

#### gpm

Gallons per minute.

### IR

Polyisoprene rubber, the major component of natural rubber, made synthetically by the solution polymerization of isoprene.

# Investment Costs

The capital expenditures reported in August 1971 dollars required to bring the treatment or control technology into operation. Included are expenditures for design, site preparation, purchase of materials, construction and installation. Not included is the purchase of land on which the system is to be built.

# L

Liter

#### Latex

A suspension of rubber particles in a water solution. Coagulation of the rubber is prevented by protective colloids. A colloid is a surface active substance that prevents a dispersed phase of a suspension from coalescing by forming a thin layer on the surface of each particle.

# Masterbatch

A compounded rubber stock applicable to a wide variety of uses. Main ingredients are rubber, carbon black and extender oil.

#### mg/1

Milligrams per liter. Nearly equivalent to parts per million concentration.

### Modifier

An additive which adjusts the chain length and molecular weight distribution of the rubber during polymerization.

#### Monomer

A compound of a relatively low molecular weight which is capable of conversion to polymers or other compounds.

### NBR

Nitrite rubber, a synthetic rubber made by emulsion polymerization of acrylonitrile with butadiene.

#### New Source

Any building, structure, facility, or installation from which there is or may be a discharge of pollutants and whose construction is commenced after the publication of the proposed regulations.

# Non-Productive Rubber Stock

Rubber stock which has been compounded but which contains no curing agents. Synonym for non-reactive rubber stock.

# Non-Reactive Rubber Stock

Rubber stock which has been compounded but which contains no curing agents. Synonym for non-productive rubber stock.

#### Operations and Maintenance

Costs required to operate and maintain pollution abatement equipment. They include labor, material, insurance, taxes, solid waste disposal, etc.

#### PBR

Polybutadiene rubber, a synthetic rubber made by solution polymerization of butadiene.

#### pН

A measure of the relative acidity or alkalinity of water. A pH of 7.0 indicates a neutral condition. A greater pH indicates alkalinity and a lower pH indicates acidity. A one unit change in pH indicates a 10 fold change in acidity and alkalinity.

# <u>Pigment</u>

Any substance that imparts color to the rubber. Pigment substances such as zinc oxide or carbon black also act as reinforcing agents.

# <u>Plastic</u>

Capable of being shaped or molded with or without the application of heat.

# Process Water

All waters that come into direct contact with the raw materials, intermediate products, final products, or contaminated waters or air.

### Productive Rubber Stock

Compounded rubber which contains curing agents and which can be vulcanized. Synonym for reactive rubber stock.

# Reactive Rubber Stock

Compounded rubber which contains curing agents and which can be vulcanized. Synonym for productive rubber stock.

# Reinforcers or Reinforcing Agent

Fine powders used to increase the strength, hardness and abrasion resistance of rubber. Reinforcing agents used in the rubber processing include carbon black, zinc oxide and hydrated silicas.

# SBR

Styrene Butadiene Rubber, a synthetic rubber made either by emulsion or solution polymerization of styrene and butadiene.

### Soapstone

A substance used to prevent tire and inner tube rubber stocks from sticking together during periods of storage. Used in both a dry and solution form. The major ingredient is usually clay.

#### Solution

A uniformly dispersed mixture of the molecular level of one or more substances in one or more other substances.

#### Stripper

A device in which relatively volatile components are removed from a mixture by distillation or by passage of steam through the mixture.

# Surface Waters

Navigable waters. The waters of the United States including the territorial seas.

# Tire Bead

Tire beads are coated wires inserted in the pneumatic tire at the point where the tire meets the steel rim on which it is mounted. They insure an air tight seal between the tire and rim.

# Tire Cord

Woven synthetic or natural fabrics impregnated with rubber. They form the body of the tire and supply it with most of its strength.

# Tire Tread

Tire tread is riding surface of the tire. Their design and composition are dependent on the end use of the tire.

# Vulcanization

Vulcanization is the process by which plastic rubber is converted into the elastic rubber or hard rubber state. The process is brought about by linking of macro-molecules at their reactive sites.

### Wet Air Pollution Control

The technique of air pollution abatement utilizing water as an absorptive media.

SECTION XV
METRIC UNITS AND CONVERSION FACTORS

English Unit	Abbreviation	Conversion Factor by	Metric Unit	Abbreviation
acre	ac	0.405	hectares	ha
acre - feet	ac ft	1233.5	cubic meters	cu m
cubic feet	cu ft	0.028	cubic meters	cu m
cubic feet	cu ft	28.32	liters	1
cubic inches	cu în	16.39	cubic centimeters	cu cm
cubic yards	cu yđ	0.7646	cubic meters	cu m
feet	ft	0.3048	meters	m
gallon	gal	3.785	liters	1
gallon/minute	gpm	0.0631	liters/second	1/sec
horsepower	hp	0.7457	kilowatts	kw
inches	in	2.54	centimeters	cm
pounds	16	0.454	kilograms	kg
million gallons/day	mgd	3,785	cubic meters/day	cu m/day
square feet	sq ft	0.0929	square meters	sq m
square inches	sq In	6.452	square centimeters	sq cm
tons (short) (2,000 lbs)	t	0.907	metric tons (1000 kilograms)	) kkg
tons (long) (2,240 lbs)	t	1.016	metric tons (1000 kilograms)	) kkg
yard	У	0.9144	meters	m

NOTE: Multiply the value of the English Unit by the indicated conversion factor to get the value of the corresponding Metric Unit.