

# Water Requirements of the Styrene, Butadiene and Synthetic-Rubber Industries

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WATER REQUIREMENTS OF SELECTED INDUSTRIES

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*A study of manufacturing processes,  
with emphasis on present water uses and  
future requirements*



**UNITED STATES DEPARTMENT OF THE INTERIOR**

**STEWART L. UDALL, *Secretary***

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## WATER REQUIREMENTS OF SELECTED INDUSTRIES

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### WATER REQUIREMENTS OF THE STYRENE, BUTADIENE, AND SYNTHETIC-RUBBER INDUSTRIES

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By CHARLES N. DURFOR

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#### ABSTRACT

About 710 million gallons of makeup water is withdrawn daily by the styrene, butadiene, styrene-butadiene rubber (SBR), and specialty-rubber industries; 88 percent of this water is used only for once-through cooling. About 429 million gallons of water daily (mgd) is withdrawn by the butadiene industry; 158 mgd is withdrawn by the styrene industry; 94 mgd is used to make special-purpose synthetic rubber; and 29 mgd is used in the direct manufacture of SBR.

The amount of makeup water withdrawn to produce SBR ranges from 11,400 to 418,000 gallons per long ton of finished rubber. The amount of makeup water withdrawn depends upon the type of rubber, the processes used to make SBR and its intermediates (styrene and butadiene), and the availability of water at the styrene, butadiene, and SBR plants. The amount of makeup water used to make styrene ranged from 2.19 to 123 gallons per pound; to make butadiene, ranged from 5.38 to 22.0 gallons per pound; and in the direct manufacture of SBR, ranged from 0.883 to 10.2 gallons per pound of finished rubber. The amount of makeup water withdrawn for use in the manufacture of special-purpose synthetic rubber ranged from 8.45 to 104 gallons per pound.

About 64 percent of the makeup water was obtained from salty water sources. These waters, which were used only in once-through cooling, contained as much as 35,000 ppm of dissolved solids. About 26 percent of the makeup water was obtained from fresh-water streams and lakes, and most of the other makeup waters were obtained from ground water. Less than 1 percent of the makeup water was obtained from reprocessed municipal sewage. Most makeup water from fresh-water streams, lakes, and wells contained less than 1,000 ppm of dissolved solids, and most makeup water used in the manufacture of SBR contained less than 500 ppm of dissolved solids. The maximum hardness of the untreated fresh makeup waters used in the manufacture of SBR was less than 500 ppm.

About 97 percent of the makeup water withdrawn was discharged to surface waters; the warmed salty waters were returned to their source. The remaining 3 percent, or about 23.6 mgd, of makeup water was used consumptively. The styrene industry consumptively used about 2.0 percent of its intake; the butadiene industry, about 4.5 percent; the specialty-rubber industry, about 9.1 percent; and the SBR industry, about 11 percent. The water shipped in the synthetic-rubber products increased the consumptive use of water by these industries.

## INTRODUCTION

### PURPOSE AND SCOPE

This report describes the uses of water and the ranges of makeup water required in the production of styrene, butadiene, and synthetic rubbers in the United States. It is one of a series describing the water requirements of selected industries that are of national importance and has been prepared at the request of and in consultation with the Water and Sewerage Industry and Utilities Division, Business and Defense Services Administration, Department of Commerce. It is designed to serve the dual purpose of providing basic information for national defense planning and, at the same time, of providing assistance to business and industry.

This investigation consisted of a field survey and a literature survey of the uses of water in the manufacture of styrene, butadiene, styrene-butadiene rubber, and other synthetic rubbers. The field survey was made during the summer of 1959. Information was obtained on the sources, quantity, chemical character, temperature, and required treatment of makeup waters<sup>1</sup> supplied to plants making these products. The adequacy of water supply for present capacity production and for future expansion was determined.

Special acknowledgment is given to the officials and management of companies manufacturing styrene, butadiene, and synthetic rubber who permitted the author to visit their plants and who supplied information on the use of water in their plants. Photographs were furnished by the Texas-U.S. Chemical Co. and Firestone Synthetic Rubber and Chemical Co.

The amounts of water and the quality of the water withdrawn for cooling, process, boiler-feed, sanitary, and other uses in the manufacture of these products were determined. The consumptive use<sup>2</sup> and the amount of water discharged to waste after being used for cooling, process, boiler feed, sanitary, and other services were balanced against the water intake. Information was also obtained on the treatment and disposition of waste water from each plant.

The uses of the makeup water were classified according to the definitions of O. D. Mussey (1961).

Process water is water that comes in contact with an end product or with materials incorporated in an end product. Cooling water is water that is used only for cooling. Water used to cool a product by being brought into contact with it is classified as process water, not as cooling water. Boiler-feed water is that introduced into boilers for conversion into steam. Sanitary and service water

<sup>1</sup> Makeup water is water added to a system to make up for the water consumed or discharged to waste.

<sup>2</sup> The quantity of water discharged to the atmosphere or incorporated in the products of the process in connection with . . . an industrial process (MacKichan, 1957, p. 2).



is that used for drinking, showers, general cleaning, flushing wastes, and company cafeterias and housings.

Water for steam brought into contact with a product is classified as boiler-feed water and not as process water.

### TYPES OF SYNTHETIC RUBBER

Only one synthetic rubber has been developed as a general-purpose replacement for natural rubber. This rubber is composed principally of about one part of styrene and about three parts of butadiene and is known as styrene-butadiene rubber, or SBR; it was formerly known as Buna-S and GRS. About 80 to 90 percent of the synthetic rubber produced in the United States is SBR.

No synthetic rubber has the chemical composition or all the properties of natural rubber. However, some special-purpose synthetic rubbers have been developed which have particular properties that are superior to natural rubber for specific purposes. The four principal special-purpose synthetic rubbers are nitrile, neoprene, butyl, and thiokol.

Thiokol is used where high resistance to oils and chemicals, which attack natural rubber, are desired and where its unpleasant odor is not objectionable. It retains rubbery characteristics to  $-60^{\circ}\text{F}$ . Neoprenes have high resistance to mineral oils, heat, oxidation, ozone, sunlight, and burning. Nitrile rubber competes with neoprene where resistance to oil and gasoline is desired. Almost all nitrile rubber produced during World War II was used in self-sealing fuel tanks, gaskets, cable covers, and similar equipment for military aircraft. Butyl rubber is markedly superior to natural rubber in air retention and is used for inner tubes (Whitby, 1954).

### HISTORY OF SYNTHETIC RUBBER IN UNITED STATES

The water requirements of the synthetic rubber industry have changed since the first batch of SBR was made just prior to World War II. A brief examination of the history of the industry will help in understanding the variations in water requirements in the manufacture of synthetic rubbers.

The unavailability of natural rubber in 1942 and the demands of an expanding Army and Navy made rubber a critical defense material. Of the million long tons of rubber consumed in 1941, only 6,260 long tons were synthetic rubber. Plants had to be built to manufacture SBR, which was selected as the general-purpose rubber substitute for natural rubber. Styrene had been made commercially, and additional plants were built using, mainly, a process developed by the Dow Chem-

ical Co. The Carbide and Carbon Company at Institute, W. Va., built a plant to produce styrene by another process.

New techniques were developed to produce butadiene, another essential product for the production of SBR. Plants using the process of making butadiene by dehydrogenation of grain alcohol were built quickly and supplied about 64 percent of the butadiene made in 1944. After the war, these plants could not compete unsubsidized with plants manufacturing butadiene from petroleum and were shut down. No plants were producing butadiene from alcohol at the time of this survey. However, "in case of another general war, the production of SBR might again need to depend heavily upon butadiene-from-alcohol plants" (U.S. National Production Authority, 1952).

In the latter part of World War II, plants were built to produce butadiene by the dehydrogenation of butylene and butane, which are obtained from petroleum. These plants are still in operation.

Most SBR plants originally were built of a standard design and used a standard formula to combine styrene and butadiene into SBR. Since 1944, the individual operating companies have modified the SBR formula and operating techniques to incorporate some of the following improvements:

In 1944, carbon-black slurry was introduced into SBR latex prior to coagulation. This procedure was initiated because of the lack of facilities at the rubber finishing plants to incorporate carbon black into the SBR crumb and to overcome the lack of tackiness of SBR crumb. The introduction of carbon-black slurries into the latex increased (a) the amount of process water used to prepare the slurry and to wash the increased volume of rubber crumb and (b) the amount of steam needed to dry the increased volume of rubber crumb.

In the same year, 1944, operating techniques were devised to manufacture SBR by a continuous process that levels off the peak demands for steam, process, and cooling water.

In 1947, "cold rubber" was manufactured at 41°F; initially all SBR had been manufactured at a reaction temperature of 121°F (hot rubber). This cold rubber was superior to hot rubber in resistance and wear and became the principal rubber for passenger tires. SBR manufactured at 41°F requires vastly more cooling water than rubber made at 121°F.

In 1951, "oil-extended" SBR was made by mixing an extender oil with the latex prior to coagulation. This oil-extended rubber had improved tread wear and resistance. It required less reactor charge water but required more washing water and steam to dry the apparent increase in volume of rubber crumb.

**BASIS FOR REPORTING WATER-USE DATA**

In this report the uses of water in the styrene, butadiene, SBR, and specialty-rubber industries are considered separately. The water-use data for the manufacture of styrene and butadiene represent the total water use by these industries. The amounts of water required by these intermediate materials for use in the manufacture of SBR are discussed under "Aggregate quantity of water required to produce styrene-butadiene rubber (SBR)." The amounts of makeup water used in these industries were reported as being typical for capacity production. Production in excess of design capacity decreases the makeup water requirements, and production below design capacity increases the makeup water requirements. Makeup water requirements in gallons per unit of product may be higher in summer and lower in winter than the data reported.

Although styrene is made by several different processes, the water requirements have been summarized for the entire industry; data are not given for the various processes. Water use is reported in gallons of water per pound of styrene.

Butadiene is manufactured from petroleum by two principal processes and from two principal feed stocks. Small amounts of butadiene are produced as a byproduct from other industrial operations. Water requirements have been summarized for the entire industry and are not given for the various operating techniques. Water use is reported in gallons of water per pound of butadiene.

Styrene-butadiene rubber is manufactured as SBR latex, SBR crumb, oil-extended SBR, carbon-black crumb, and oil-extended carbon-black crumb. It is manufactured at 41°F and 121°F by batch and continuous processes. Some plants use several operating processes and produce a variety of products. Water-use data were not available for each type of rubber produced. Thus, the water required for the direct manufacture of SBR is reported in gallons of water per pound of finished rubber crumb. For latex plants, the water use is reported on the basis of gallons of water per pound of rubber solid.

The water required to produce 1 pound of SBR is approximately the sum of the water required to produce one-fourth pound of styrene plus three-fourths pound of butadiene, plus the water required in the direct manufacture of 1 pound of SBR. The amount of water required to produce 1 pound of extended rubber depends upon the amount of styrene, butadiene, extender oil, and carbon black in the finished product.

During this water-use survey 2 butyl, 2 neoprene, 2 thiokol, and 3 nitrile rubber plants and 1 specialty-rubber plant were visited.

## USE OF WATER IN THE MANUFACTURE OF STYRENE

Most producers of styrene use a method developed by the Dow Chemical Co., but some styrene is made by a process developed by the Carbide and Carbon Chemicals Corp., and some by a process developed by the Cosden Petroleum Co.

### HOW WATER IS USED

#### DOW PROCESS

Most of the styrene manufactured in the United States in 1959 was made by the Dow Chemical Co. process. In this process ethylene, an unsaturated gas commonly obtained from petroleum, reacts with benzene to form ethylbenzene. Purified ethylbenzene, diluted with superheated steam, is catalytically dehydrogenated to form styrene. Figure 33 is a flowsheet of the manufacture of styrene, showing these steps. The use of water in these operations is shown in shading; the use of steam is shown in dotted lines.

About 98 percent of the makeup water is used to cool gases and liquids and to condense vapors from distillation columns and reactors. Less than 1 percent of the makeup water is used for washing ethylbenzene and for quenching gases from the ethylbenzene dehydrogenation reactor. Less than 3 percent of the water is used for makeup to the steam boilers. Superheated steam is used for heating and for diluting the ethylbenzene feed to the dehydrogenation reactor.

The uses of water can best be understood by dividing the process into three parts: (a) formation of ethylbenzene, (b) dehydrogenation of ethylbenzene to styrene, and (c) purification of styrene.

#### FORMATION OF ETHYLBENZENE

High-purity benzene, recycle benzene, and catalyst "mud" are pumped continuously to a large brick-lined cylindrical reactor containing liquid about 30 feet deep. Ethylene gas is pumped into the bottom of the reactor and reacts with benzene to form ethylbenzene. Heat is evolved and the reaction is maintained at about 200°F by the evaporation of benzene and the refluxing of the condensate. The benzene is condensed and cooled in heat exchangers in which water is circulated.

The crude alkylate overflows from the reactor, is cooled by water in a heat exchanger, and is pumped to a settling tank where the entrained catalyst mud precipitates. The oil layer is decanted and washed with water and caustic solution. After it has settled, the water layer is decanted and discharged to waste. The neutralized crude ethylbenzene is distilled to a purity of more than 99 percent in a series of fractionating towers. The unreacted benzene is recovered by distil-

lation, condensed and cooled in water-cooled heat exchangers, and mixed with fresh benzene.

In the fractionating system, a part of the benzene vapors from the benzene column and a part of the vapors from the ethylbenzene column are condensed and cooled in water-cooled heat exchangers and returned to the column. This cooled condensate regulates the operating temperature of the top of the column. A part of the higher boiling materials discharged from the bottom of each distillation column (called "bottoms") is reheated in steam reboilers and returned to the column. This reheated bottom material is the source of heat for the distillation operation.

The purified ethylbenzene is cooled by water and sent to be dehydrogenated to styrene.

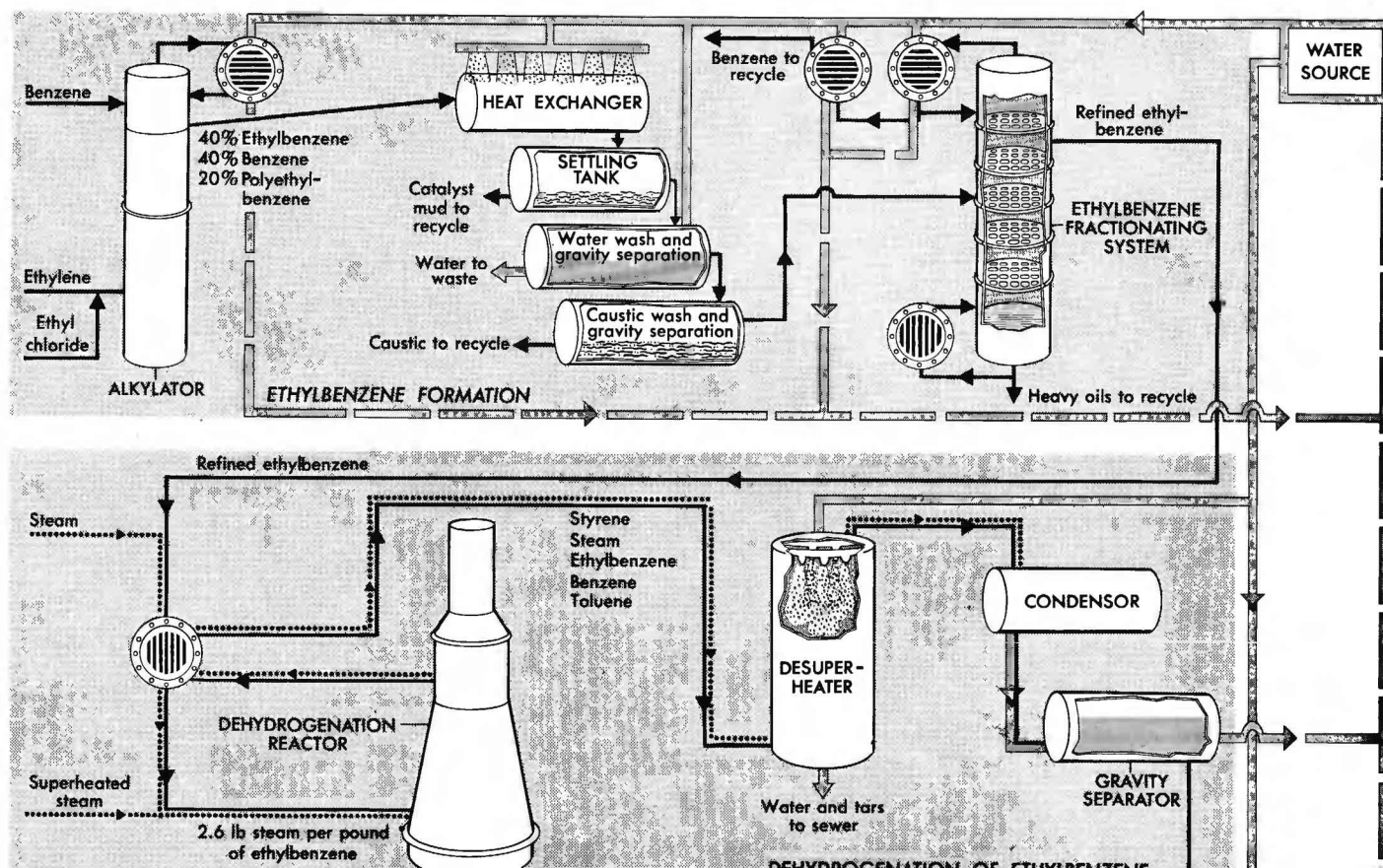
#### DEHYDROGENATION OF ETHYLBENZENE TO STYRENE

Purified ethylbenzene is mixed with and heated by superheated steam to 1,170°F and injected into a dehydrogenation reactor. As the vaporized ethylbenzene flows up through the catalyst bed and out of the reactor, a part of it is dehydrogenated to styrene. The hot reactor gases are cooled by heat exchange with the incoming ethylbenzene and steam, and are quenched in a desuperheater by a water spray. After the oil-water mixture has condensed and settled, part of the water layer is recycled to the water spray, and the rest of the water layer is discharged to waste (Mitchell, 1946); or the water layer is stripped of organic materials by steam distillation, and the recovered water is sent to the steam plant (Smith, 1947, and Martin and Rostenbach, 1953). The oil layer, containing about 40 percent styrene and 59 percent ethylbenzene, is sent to storage prior to distillation of the styrene.

#### PURIFICATION OF STYRENE

Crude styrene is purified by a series of distillations that separate styrene from benzene, toluene, and ethylbenzene. The benzene and toluene phase is vacuum distilled from the crude styrene and then further fractionated to yield benzene and toluene. The ethylbenzene-styrene phase is fractionated in a two-stage ethylbenzene distillation column. Ethylbenzene is distilled from the first stage, condensed in water-cooled heat exchangers, and recycled to the dehydrogenation reactor. The bottoms from the second stage, containing 98 percent styrene, is further distilled to 99.5 percent of purity.

The purified styrene is stabilized to inhibit polymerization, which is the linking together of a large number of molecules to form a polymer. The polymer formed has a molecular weight much higher than and properties different from the constituent links of styrene molecules (called monomers).



**EXPLANATION**

Water

Returned cooling water

Product

Water-cooled heat exchanger

Steam-heated reboiler

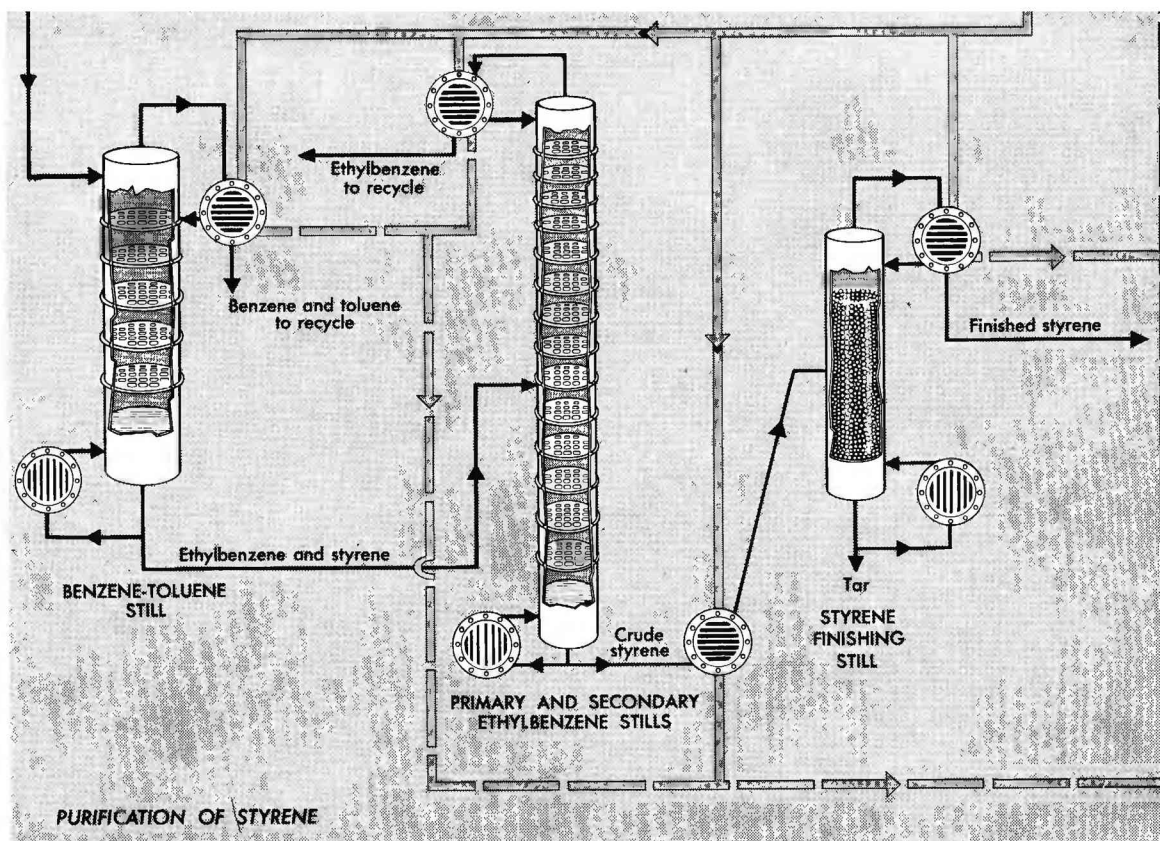


FIGURE 33.—Flowsheet illustrating the use of water in the manufacture of styrene.

Each distillation tower used in the fractionation and purification of crude styrene is equipped with water-cooled heat exchangers to condense the vapors from the tower and to regulate the temperature of the refluxed condensate. These distillations are operated at low temperatures maintained by cooling water and at subatmospheric pressures maintained by steam jet ejectors. A portion of the bottom material from each column is reheated by steam to supply the heat needed for the distillation operation.

#### **CARBIDE AND CARBON PROCESS**

As in the Dow process, ethylbenzene is formed from ethylene and benzene. The liquid ethylbenzene is oxidized catalytically by air to acetophenone. The temperature of this exothermic reaction is controlled at about 260°F by water circulating in cooling coils around the reactor. Steam in the reactor gases is condensed in water-cooled heat exchangers and is used to prepare caustic solutions.

The reactor liquor, which is principally acetophenone, phenylethyl alcohol, and unreacted ethylbenzene, is cooled to about 81°F in heat exchangers circulating water, mixed with a 10 percent caustic solution, and sent to a settling tank. The aqueous (bottom) layer in the tank is withdrawn, stripped of organic material by steam distillation, and sent to waste. The organic layer from the settling tank is washed by a spray of water in a scrubbing tower. The resultant water phase is sent to waste.

The organic layer containing ethylbenzene, acetophenone, and phenylethyl alcohol is stripped of ethylbenzene by distillation. The resultant acetophenone-phenylethyl alcohol fraction is further refined in another distillation tower. The distillate is catalytically hydrogenated to phenylethyl alcohol, which is then dehydrated catalytically to styrene. The crude styrene is distilled to a purity of more than 99 percent styrene.

The vapors from each distillation column are condensed and cooled in water-cooled heat exchangers. The refluxing of these condensates controls the temperature of the top of the distillation column. The heat to each column is supplied by a portion of the bottoms, which is returned to the column after being heated in steam reboilers.

#### **COSDEN PROCESS**

In this process, ethylbenzene is obtained by the "ultrafractionation" of a mixed xylene stream containing about 30 percent ethylbenzene obtained from certain petroleum fractions (Chemical and Engineering News, 1960b). The recovered ethylbenzene is diluted with steam and dehydrogenated catalytically to styrene. Data on water requirements for the recovery of ethylbenzene from the xylene

steam and for the dehydrogenation of ethylbenzene to styrene were not available. However, the major use of water is in the dehydrogenation of ethylbenzene to styrene.

## FINDINGS OF THE SURVEY

### SOURCES

At capacity production, about 158 million gallons of water is withdrawn daily from wells, lakes, streams, and ocean bays, and purchased from private water companies and from municipal water and sewage supplies for use in the manufacture of styrene. About 155 million gallons is obtained from surface-water sources and about 3 million gallons is withdrawn from ground-water sources. A small fraction of the total makeup water is obtained from municipal sewage. The sources of makeup water used in the styrene industry are summarized in table 1.

TABLE 1.—*Sources of makeup water used in the manufacture of styrene*

Source	Number of plants being served by indicated source				
	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water
Well water:					
Self-supplied.....	2	1	1	1	1
Water company.....	-----	1	1	1	-----
Surface water:					
Self-supplied.....	2	3	1	4	2
Water company.....	-----	-----	-----	-----	2
Municipal water supply.....	-----	-----	-----	-----	1
Bay or ocean water.....	1	-----	-----	-----	-----
Municipal sewage.....	-----	1	-----	2	-----

About two-thirds of the styrene plants use more than one source of water supply. At only two plants is surface water used as the sole source of supply; the other plants supplement the surface-water supply with well water, sewage, or bay water. At only one plant is ground water used as the only source of supply; the other plants supplement the ground water with surface water or municipal sewage. At some plants, the secondary source of supply was maintained only as a standby source for emergencies. At plants using sewage and bay water, it was necessary to use another source of water for sanitary use. The plants located in the northeastern part of the United States and along the Gulf Coastal Plain use predominately surface water. The styrene plants at Big Spring, Tex., and at Odessa, Tex.,



use treated municipal sewage for a substantial part of the water supply (Connell and Berg, 1958). Galveston Bay is a source of cooling water at Texas City, Tex. (Hebbard, Powell, and Rostenback, 1947).

The amounts of water available at the individual establishments are adequate for capacity production. Many styrene plants are near or are a part of a large petroleum refinery or a chemical complex. These styrene plants commonly use the electricity, power, water, and sewer facilities of the larger operation. The water used by some of these styrene plants is only a small part of the total water used in the larger operation.

#### CHEMICAL QUALITY

The chemical quality of the makeup water from streams and wells is determined to a large extent by the environs of the watershed and the aquifer. Well waters are usually higher in pH, hardness, alkalinity, and dissolved solids than most rivers and lakes. Waters from estuaries, bays, and the ocean contain very high concentrations of chloride, sulfate, and other dissolved solids. The chemical quality of municipal sewage depends to a large extent upon the constituents in the water prior to treatment at the municipal sewage treatment plant.

The chemical quality of the untreated ground water, surface water, and sewage used for makeup to cooling towers and steam boilers has been summarized in table 2. This table presents the minimum, maximum, median, lower, and upper quartile values of the more important constituents in the untreated makeup waters used at styrene plants. These data do not represent any specific analysis; for example, the water with the minimum hardness is not the water with the minimum sodium and potassium content.

The chemical composition and the amount of dissolved solids in the makeup water influence the rate of corrosion, the rate of scale formation, and the chemical treatment required. Most natural waters have calcium and magnesium as the principal cations and minor amounts of sodium and potassium. Where natural softening occurs, the principal cation will be sodium, with minor amounts of calcium, magnesium, and potassium also present. The principal anions present in most natural waters are generally carbonate and bicarbonate. Minor amounts of sulfate, chloride, fluoride, and nitrate are commonly present.

Waters containing large amounts of calcium and magnesium ions form insoluble curds with soap and are classified as hard waters: the more calcium and magnesium, the harder the water. Waters containing large quantities of calcium, magnesium, bicarbonate, car-

TABLE 2.—*Chemical properties of untreated makeup water used in the manufacture of styrene*

[Chemical analyses were furnished by plants manufacturing styrene and by the U.S. Geological Survey]

Constituent or property	Cooling						Boiler feed					
	Number of samples	Parts per million					Number of samples	Parts per million				
		Minimum	Lower quartile	Median	Upper quartile	Maximum		Minimum	Lower quartile	Median	Upper quartile	Maximum
Silica (SiO <sub>2</sub> )	7	5.7	6.0	13	25	31	8	0.5	5.8	6.8	24	31
Calcium (Ca)	8	1.1	19	32	66	118	8	1.1	19	32	36	118
Magnesium (Mg)	7	2.2	2.8	8.0	26	28	7	2.2	2.8	8.0	9.0	26
Sodium (Na) and potassium (K)	6	9.2	21	58	121	218	7	9.2	21	55	121	218
Bicarbonate (HCO <sub>3</sub> )	9	22	84	151	201	251	9	22	84	124	192	251
Carbonate (CO <sub>3</sub> )	11	0	0	0	2	27	9	0	0	0	1	27
Sulfate (SO <sub>4</sub> )	9	8.6	17	42	101	270	8	8.6	17	36	92	270
Chloride (Cl)	9	4.8	17	33	238	351	9	4.8	17	27	204	351
Dissolved solids:												
Residue on evaporation at 180°C	7	107	242	356	726	1,120	8	107	188	320	645	1,120
Hardness as CaCO <sub>3</sub>	9	2	60	117	288	404	9	2	60	114	183	404
Noncarbonate hardness as CaCO <sub>3</sub>	9	0	0	28	123	320	9	0	0	28	88	320
pH	9	6.9	7.0	7.5	8.2	9.1	9	5.6	7.0	7.4	8.2	9.1

bonate, and sulfate ions have a tendency to form coatings on metal pipes. At temperatures below boiling, waters containing large amounts of calcium and carbonate ions deposit coatings of scale. At temperatures above boiling, waters containing large amounts of calcium and bicarbonate ions deposit coatings of calcium carbonate scale, and waters containing large amounts of calcium and sulfate ions deposit an extremely hard scale that is difficult to remove. Scale acts as an insulator that lowers the rate of heat transfer and reduces the effective pipe diameter; this reduction decreases the pumping efficiency. Water used for makeup to steam boilers should be low in hardness and should contain no calcium sulfate. The "Progress report of the committee on quality tolerances of water for industrial uses" recommended that boiler-feed water for boilers operated at pressures below 150 psi (pounds per square inch) have a hardness less than 80 ppm (as CaCO<sub>3</sub>), and for boilers operated at pressures in excess of 400 psi have a hardness less than 2 ppm (Moore, 1940).

Waters that contain low concentrations of calcium and magnesium and whose predominant anions are sulfate and chloride can cause metallic corrosion. The greater the concentration of sulfate and chloride and the higher the temperatures, the greater the corrosion. The presence of large amounts of dissolved gases, particularly dissolved oxygen, also accelerates corrosion.

Large amounts of sodium and potassium salts in boiler-feed water, in the presence of suspended matter, are believed to cause foaming, which accelerates scale formation and corrosion in the boilers (Powell, 1954). Salts of sodium and potassium carbonate in recirculating cooling water can cause the delignification of wood in cooling towers. When the deterioration of the wood is extreme, the remaining cellulose cannot hold nails or support other fastenings (Blohm and Frazier, 1950).

Most natural waters contain silica in excess amounts; it can cause problems in steam generation. At elevated temperatures and pressures, especially in the presence of calcium, silica forms a low thermal-conductivity, hard, glassy scale that causes structural failures. Silica also is deposited on turbine blades as a scale that is difficult to remove and that causes operating difficulties (Nordell, 1951).

Phosphate is usually not present in natural waters but, as a result of the use of household detergents, is commonly present in municipal sewage. Although phosphate is added to cooling-tower and boiler-feed waters to control scale and corrosion, excessive amounts of it can form an undesirable scale in cooling towers and steam boilers (Sullivan, 1958).

The presence of iron is undesirable and, fortunately, is seldom found in most surface waters; but concentrations of iron in excess of 1 ppm are common in ground water and acid surface water (Rainwater and Thatcher, 1960). Excessive amounts of iron cause staining of porcelain fixtures and increase the hardness, turbidity, and color of natural waters.

Many types of water were supplied to plants making styrene; figure 34 illustrates two types. The percentages of the reacting weights of the more important constituents are plotted as fractions of the circle. The radius of these composition diagrams was drawn in proportion to the dissolved-solids content. The diagram on the right represents a water containing sodium and potassium and chloride as the principal constituents. Smaller amounts of calcium, magnesium, bicarbonate, chloride, and nitrate also were present. This type of water was obtained from some coastal streams, ground waters, and municipal sewage in Texas. These sodium chloride waters had a dissolved-solids content that ranged from 100 to 1,120 ppm. The diagram on the left represents a water containing calcium and bicarbonate as the principal constituents. Minor amounts of magnesium, sodium and potassium, sulfate, chloride, and nitrate also were present. This type of water contained much less dissolved solids and represented the less mineralized type of makeup water used in the styrene industry.

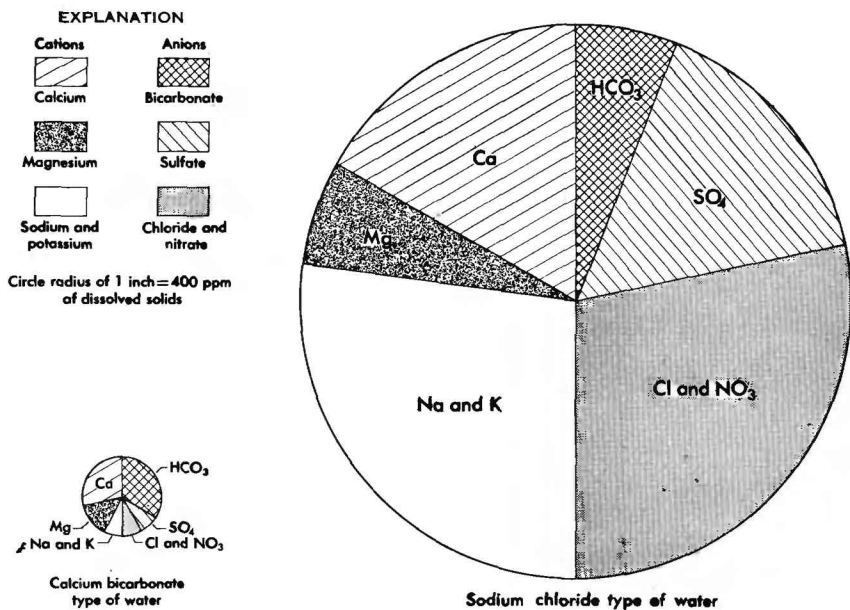


FIGURE 34.—Types of makeup water used in the manufacture of styrene.

Other types of water used contained sodium and bicarbonate, sodium and sulfate, calcium and sulfate, and calcium and chloride, respectively, as their principal constituents. In summary, many chemical types of water were used. All waters contained less than 1,150 ppm of dissolved solids, with the exception of salty water that was used only for once-through cooling.

#### TREATMENT OF MAKEUP WATER

The type and degree of treatment given to makeup water are governed by the chemical composition of the water and its use in the plant. The types of treatment given makeup water in the styrene industry are summarized in table 3.

The minimum requirements for cooling water are that the water should be free of sediment, debris, and algae that could clog pipes. As indicated in table 3, waters used for once-through cooling are given a minimum of treatment—generally clarification and chlorination. Chlorine and chlorine compounds reduce growths of slime and algae that reduce the effective pipe diameter and the rate of heat transfer.

Water used as makeup to cooling towers, such as the one shown in figure 35, requires additional treatment. In these cooling towers the warmed water is cooled by heat exchange with air and by evaporation of the water spray. In the process of being cooled, the water



FIGURE 35.—Cooling tower to lower the temperature of warmed recirculating cooling water.

becomes saturated with oxygen from the air, and this accelerates metallic corrosion. The dissolved oxygen is removed usually by deaeration or by such chemical inhibitors as chromates and phosphates.

About 0.2 percent of the water circulating through the tower is lost as spray to the wind, and about 1 percent of the water is evaporated and lost for each 10°F drop in water temperature (DeFlon, 1950, p. 790). The evaporation of the water increases the dissolved-solids content and causes the recirculated water to have higher dissolved solids than the makeup water. Water that does not form scale when used only once may become scale forming after it has been concentrated several times in cooling-tower use. To reduce the formation of scale, a fraction of the recirculated water is discharged to waste as blowdown. The treatment of makeup waters with sulfuric acid, which converts calcium carbonate into the more soluble calcium sulfate, and the softening of the makeup water also reduces scale formation.

TABLE 3.—*Treatment of makeup water at styrene plants*

[Does not include prior treatment of purchased water]

Treatment	Number of plants using indicated treatment				
	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water
None			2		
Clarification (screening, coagulation, settling, and filtering)	3	3		1	2
Disinfection: chlorine or chlorine compounds	3	5	2	3	4
Prevention of corrosion and scale:					
Chromate and phosphate		3			
pH adjustment		1		2	
Softening:					
Lime soda		2		3	1
Ion exchange		2	1	5	
Phosphate				4	

The Dow Chemical Co., at Freeport, Tex., uses sodium pentachlorophenate to control algae and slime and to eliminate delignification of cooling-tower wood. "When alkalinity is high and excessive amounts of chlorine are used, the chlorine can react with the lignin in the wood, and the wood quickly deteriorates due to separation of celluloid fibers" (Chem. Eng. Prog., 1960).

The temperatures in high-pressure steam boilers favor the formation of scale and corrosion; therefore, makeup water for them commonly is treated by ion exchange, lime, and phosphate. The dissolved gases in boiler-feed makeup are eliminated to prevent corrosion and pitting.

Treatment of water varies with its use. Water for sanitary purposes is commonly treated with a disinfectant to ensure that the water is safe for human consumption. The dissolved-solids content and the hardness are reduced by chemical treatment, where necessary, to make the water palatable and usable for showers. Waters used for scrubbing tanks and floors, and other services, usually receive a minimum of water treatment.

Owing to the presence of high concentrations of phosphate, detergents, and fluctuating chemical concentrations, the treatment of municipal sewage is usually more complex than the treatment of water obtained from surface- and ground-water sources. The use of municipal sewage presents problems that require individual attention. However, at Big Spring, Tex., the treatment of this sewage is cheaper than the treatment of the available ground water, which is highly mineralized (McCormick and Wetzel, 1954).

## QUANTITY OF WATER WITHDRAWN AND CONSUMED

The quantity of water withdrawn for use in the styrene industry varies with the local availability of water. In parts of the country where large amounts of surface water are available, water is used once for cooling and then discarded. In other parts of the country, where water supplies are not plentiful, the cooling water is recirculated and the water use decreases. In the High Plains of Texas, municipal sewage is the principal source of plant water, and all uses of water are carefully inventoried. In these areas of low availability of water, air cooling is supplementing or replacing cooling by water. Table 4 summarizes the quantities of water withdrawn for cooling, process, boiler feed, and sanitary and service uses by the styrene industry.

The largest withdrawals are used for cooling water. Although only four plants use once-through cooling water, more than 95 percent of the water withdrawn is used once in a heat exchanger and then discharged to waste. No water was used consumptively for once-through cooling.

About 5.7 million gallons of water is withdrawn daily at capacity production and used as makeup to cooling towers. Cooling water is circulated through cooling towers, on the average, about 65 times; at one plant it is circulated about 160 times. Of the water circulating through the cooling tower, 0.276 to 1.59 gallons of water per pound of styrene is lost by evaporation or as wind spray, or is otherwise consumed.

TABLE 4.—Quantity of makeup water used, in gallons per pound, in the manufacture of styrene

Water use	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water	All uses
Number of plants.....	4	7	3	8	9	9
Minimum.....	2. 75	. 496	. 002	. 319	. 003	2. 19
Lower quartile.....		. 981		. 450	. 064	2. 26
Median.....		1. 42		. 926	. 209	4. 86
Upper quartile.....		1. 88		1. 52	. 385	60. 8
Maximum.....	121	3. 31	. 190	1. 86	. 711	123

At most plants the amount of process water used is negligible; the maximum reported value is 0.190 gallon of water per pound of styrene. No process water is consumed.

About 4.43 million gallons of water is withdrawn daily and used as makeup to steam boilers. About 40 percent of this makeup water is consumed. Because of the high quality of water required in steam boilers, the water is used, on the average, less than five times.

Some of the steam condensate is not returned to the boiler house but is used as makeup to the cooling tower or as process water. Some steam becomes contaminated with oils and cannot be reused for boiler feed until the oils are removed. For example, in the dehydrogenation of ethylbenzene, about 2.6 pounds of steam is mixed with each pound of ethylbenzene and must be discarded unless the oil is removed. The amount of makeup water for boiler feed ranges from 0.319 to 1.86 gallons of water per pound of styrene.

Water for sanitary and other services is used once and discharged to waste; the amounts of these waters range from 0.003 to 0.711 gallon of water per pound of styrene.

#### **TREATMENT OF WASTE WATERS**

Waste waters from styrene plants that are a part of large chemical complexes are combined with waste waters from other parts of the complex. The combined waste waters are then treated according to their composition.

At some styrene plants the oils and tars in waste waters are separated by gravity, and the resultant water phase is neutralized. The settleable solids in the waste water are then precipitated in a series of settling basins. The water is then filtered through hay or straw (Martin and Rostenback, 1953). At other styrene plants, the waste waters containing oils and tars are steam distilled. The 150 million gallons of water withdrawn daily, used once in cooling equipment, and then discharged is given almost no waste treatment before being discharged to surface waters. Although the dissolved-solids content has increased, the 4.8 million gallons of waste water discharged daily from cooling towers and boilers commonly is given no waste treatment. All sanitary-waste waters are discharged to municipal sanitary sewers or are treated in company-owned Imhoff tanks or septic tanks.

### **USE OF WATER IN THE MANUFACTURE OF BUTADIENE**

#### **HOW WATER IS USED**

##### **BUTADIENE FROM PETROLEUM**

Most butadiene is produced by cracking *n*-butylene, diluted with steam, and by cracking *n*-butane in the absence of steam. Butadiene is also produced by cracking *n*-butane to *n*-butylene, in the absence of steam, and cracking the *n*-butylene, in the presence of steam, to butadiene.



A flowsheet of the manufacture of butadiene by dehydrogenating purified n-butylene is shown in figure 36. The uses of water in this process are shown in shading; the uses of steam are shown in dotted lines. About 96 percent of the water withdrawn is used for cooling; about 91 percent is used once for cooling and then discarded; about 4.7 percent is used for makeup to cooling towers. Large amounts of cooling water are used to cool and condense the overhead fractions from distillation columns, to quench the products from the dehydrogenation reactors, and to maintain the extraction solvents at about 10°F.

About 2.7 percent of the water withdrawn is used for makeup to steam boilers. Steam is used to (a) supply the heat required for the cracking of n-butylene to butadiene, (b) eliminate the necessity of dehydrogenating in a vacuum, (c) decrease the amount of cracking in the furnace, (d) regenerate the catalyst, and (e) supply heat in the distillation towers.

The uses of water in the manufacture of butadiene can best be understood by separating the process into (a) feed preparation, (b) dehydrogenation, and (c) purification.

#### FEED PREPARATION

The purpose of feed preparation is to separate n-butylene from the other constituents in the butane-butylene (B-B) stream and to concentrate the n-butylene. The degree of feed preparation varies with the concentration of n-butylene in the B-B feedstream. Isobutylene is removed from the B-B stream by dissolving the isobutylene in sulfuric acid. The acid layer is then processed to recover the acid and the isobutylene. Cooling water is used in this separation to remove the heat evolved in the dissolving of isobutylene in the acid. Water is also used to cool and wash the recovered isobutylene. Butane is commonly removed from the B-B stream by extractive distillation. These distillation towers use steam reboilers to supply heat to the column and use water-cooled reflux condensers. The lower the concentration of n-butylene in the B-B stream, the more water is required in the concentration of the n-butylene.

The butane feed stock for the catalytic dehydrogenation of butane to butadiene requires no feed preparation.

#### DEHYDROGENATION

In the steam-dilution method, prepared butylene is mixed with 10–20 volumes of steam which has been preheated to about 1,300°F. The hot butylene-steam mixture enters the top of a large brick-lined vertical drum and passes down through a shallow bed of catalyst with little

drop in temperature. Immediately below the catalyst bed, the gases are quenched with sprays of water to suppress polymerization of butadiene. The hot reactor gas is further cooled in waste heat boilers, where the heat of the gas is used to generate steam that is further heated in superheaters and used for diluting the butylene feed to the reactor.

The hot reactor gases are further cooled in an oil quench tower by passing them up through a spray of cooling oil. The heated oil is cooled by water in heat exchangers and recirculated. The product stream from the oil quench tower is cooled by water in heat exchangers and is further cooled in a water quench tower. Heated oil and water from these quench towers are cooled by water in heat exchangers and reused in the quench towers. At some plants this system of oil-and-water quench towers is replaced by a series of oil quench towers and at other plants by a series of water quench towers. At all plants using quench towers, the cooling liquid in the towers is cooled by water in heat exchangers. At some plants, water-cooled heat exchangers instead of quench towers are used to cool the gas from the reactor.

The cooled reactor gas and steam condensates are compressed to a liquid, cooled by water, and allowed to separate in a vapor-condensate separator. The water layer is withdrawn and after treatment is reused as cooling-tower makeup or discarded.

The hydrocarbon layer from the condensate separator is fractionated in a series of distillation towers, where crude butadiene is separated from hydrocarbons having lower and higher boiling points. These towers operate with water-cooled reflux condensers to control the tower temperature and the quality of the distillate, and with steam-heated reboilers to maintain the distillation temperature. The crude butadiene, containing butane, n-butylene, isobutylene, and butadiene is sent to be purified to SBR-grade butadiene.

In the Houdry process, butane is dehydrogenated catalytically to butadiene in the absence of steam. Butane, mixed with recycle butylene, is vaporized, heated, and passed through a layer of catalyst in an insulated horizontal drum reactor. Immediately below the catalyst bed, the hot reactor gas is quenched by sprays of water. The reactor gas is further cooled in waste-heat boilers where the heat of the reactor gas is used to generate steam.

The hot reactor gas is then cooled to about 100°F in oil quench and water quench towers. The cooling liquids in these quench towers are cooled by water in heat exchangers. The cooled reactor gas is then compressed, cooled, and fractionated to recover the crude butadiene, as in the steam-dilution method.

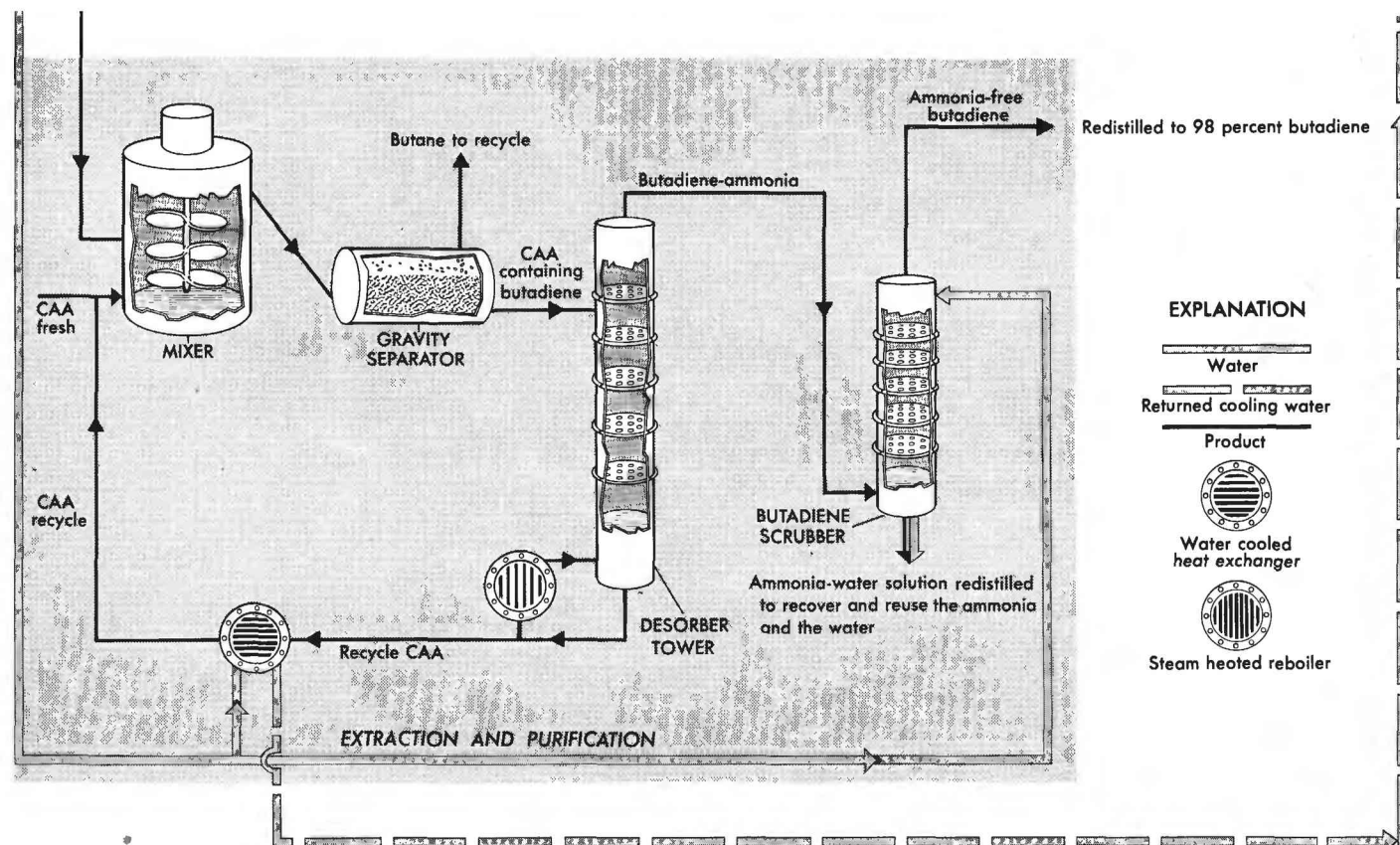
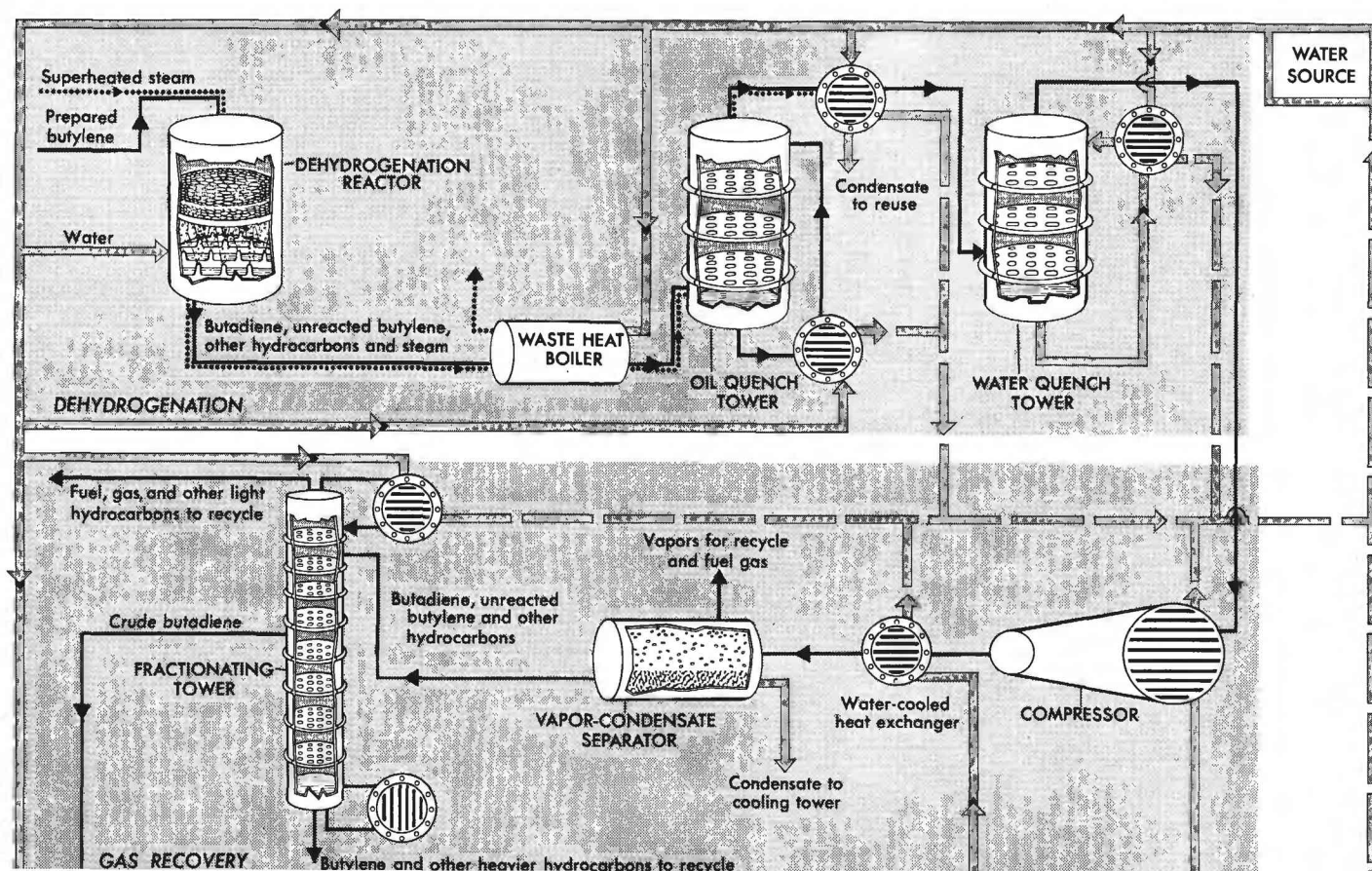


FIGURE 36.—Flowsheet illustrating the use of water in the manufacture of butadiene.

After about 8–10 minutes of cracking, the reactor is purged by steam to remove oil from the catalyst. Heated air is then passed over the catalyst to burn off the carbon, which reactivates the catalyst. The hot flue gases from this regeneration operation are pumped through water-cooled quench tanks, water-cooled heat exchangers, waste-heat boilers, and barometric condensers, which intimately mix the hot gases with cooling water. At some plants the cooling water from the barometric condensers is used as cooling-tower makeup; at others, it is discarded to waste.

In the combined steam-dilution and Houdry process, some plants use butane and butylene as raw materials and operate the Houdry process to crack butane to butylene and the steam-dilution method to crack butylene to butadiene.

#### BUTADIENE PURIFICATION

Butadiene is commonly extracted from the crude butadiene by cold solutions of aqueous cuprous ammonium acetate (CAA). (See fig. 36.) The crude butadiene steam is mixed with CAA, and the butadiene is absorbed by the solution of CAA. The butadiene-free hydrocarbon phase and the CAA phase containing butadiene are separated by gravity. The hydrocarbon phase is washed with water and recycled. The CAA layer is sent to a distillation tower where the butadiene is distilled from the CAA. The heat for this distillation is supplied by reheating a portion of the CAA bottoms in steam-heated reboilers. The remainder of the CAA is cooled by water and recycled.

The butadiene distillate contains ammonia, which is removed by passing the butadiene-ammonia mixture up through a spray of water in a scrubbing tower. The ammonia-free butadiene is then redistilled to a purity of 98 percent butadiene. The SBR-grade butadiene is stabilized to prevent the formation of higher molecular-weight polymers that range in consistency from a tacky liquid to a resinous solid.

The ammonia water is distilled to remove the volatile ammonia and is then reused to dissolve ammonia from the butadiene-ammonia mixtures.

The distillation towers are operated by condensing the distillate in water-cooled heat exchangers and by reheating the bottoms in steam reboilers. The extraction of butadiene with cuprous ammonium acetate (CAA) is commonly operated at about 10°F and requires large amounts of cooling water for the refrigeration equipment.

Butadiene is also commonly purified by extractive distillation with furfural. The crude butadiene is stripped, by distillation, of n-butyl-

ene and then pumped to an extractive-distillation tower where the butadiene is absorbed by furfural. The butadiene-furfural phase is distilled to separate the furfural, which is recycled to the solvent tower, from the butadiene, which is redistilled to a purity of better than 98 percent butadiene. The refined butadiene is stabilized to prevent polymerization. Each of these distillation towers operates with water-cooled reflux condensers and steam-heated reboilers.

#### BUTADIENE FROM ALCOHOL

Butadiene was not manufactured from alcohol commercially at the time of this survey. However, because butadiene was made from alcohol during World War II and because alcohol may be an important source in the event of another national emergency (U.S. National Production Authority, 1952), a brief discussion of this method and of the water requirements is included.

The vapors of ethyl alcohol are catalytically dehydrogenated to acetaldehyde. The crude acetaldehyde is scrubbed with water to recover the acetaldehyde and ethyl alcohol. This acetaldehyde-alcohol phase is then distilled from the water and catalytically dehydrogenated to butadiene. In this process the main use of water is for cooling and for makeup to steam boilers.

#### FINDINGS OF THE SURVEY

##### SOURCES

At capacity production, about 429 million gallons of makeup water is withdrawn each day in the manufacture of butadiene. A large part of this water is salty and is obtained from the Gulf of Mexico, bays, estuaries, and the Pacific Ocean. About 25.6 million gallons a day (mgd) is withdrawn from ground-water supplies and about 14 mgd is obtained from nonsaline surface-water sources. A small part of the water is obtained by processing municipal sewage. The sources of makeup water used in the manufacture of butadiene are summarized in table 5.

Most butadiene plants use more than one source of water supply. Of the 12 butadiene plants visited, 10 use ground water for all or part of the water supply. One of the other plants supplements its surface-water supply with estuarine waters. Those plants using salty water for once-through cooling use it for no other purpose. At Odessa, Tex., municipal sewage is used as makeup for cooling towers and steam boilers, well water is used for sanitary purposes, and drinking water is purchased (Chemical and Engineering News, 1957a).

Many plants use the same source of water for more than one use. Of the 12 plants visited, 9 use the same source of water for makeup to

steam boilers and cooling towers; 6 plants use the same source of water for process and cooling-tower makeup; 7 plants use the same source of water for sanitary and service purposes and for cooling-tower makeup.

TABLE 5.—*Source of makeup water used in the manufacture of butadiene*

Source	Number of plants being served by indicated source				
	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water
Well water:					
Self-supplied.....	2	6	4	5	9
Water company.....		1	1	1	
Surface water:					
Self-supplied.....		2	2	2	1
Municipal water supply.....	1	1		2	1
Water authority.....	2	1	2	2	1
Sewage.....		1		1	
Bay, estuary, ocean.....	3				

Most butadiene plants are a part of a complex that produces more than one petrochemical. Many of these establishments have a central water intake, treatment, and disposal system. At a few complexes the makeup water used for butadiene is a small part of the total water intake. At the present time all producers are obtaining sufficient water for capacity production; however, at some plants the present sources of water would not be adequate if production were increased or if the allowable intake of water were reduced.

If ground water is available, it is used for sanitary purposes because less treatment is required. Where ample supplies of ground water and surface water are available, the selection of the source to be used for the various purposes is dictated by the chemical quality and the temperature.

#### CHEMICAL QUALITY

The chemical analyses of water withdrawn for use in the manufacture of butadiene are summarized in table 6. This table contains the minimum, lower quartile, median, upper quartile, and maximum values of each constituent. These data include chemical analyses of the municipal sewage used but do not include a chemical analysis of water from any estuary, bay, or ocean.

The significance of the more important chemical constituents in water has been discussed on page 232. Four companies manufacturing butadiene also make styrene and use the same sources of water for both petrochemicals. In addition, some butadiene plants are near

styrene plants and use the same type of water as used in the manufacture of styrene. The chemical quality of the makeup water used to make butadiene is similar to that of the makeup water used to make styrene.

TABLE 6.—*Chemical properties of untreated makeup water used in the manufacture of butadiene*

[Chemical analyses were furnished by plants manufacturing butadiene and by the U.S. Geol. Survey]

Constituent or property	Number of samples	Parts per million				
		Minimum	Lower quartile	Median	Upper quartile	Maximum
Silica (SiD <sub>2</sub> )-----	14	5. 0	10	18	31	53
Iron (Fe)-----	6	. 04	. 07	. 10	. 14	. 40
Calcium (Ca)-----	13	4. 7	7. 9	33	40	91
Magnesium (Mg)-----	13	1. 2	2. 0	7. 5	14	28
Sodium (Na) and potassium (K)-----	9	9. 2	36	60	166	207
Bicarbonate (HCO <sub>3</sub> )-----	20	15	112	170	232	445
Carbonate (CO <sub>3</sub> )-----	18	0	0	0	4	12
Sulfate (SO <sub>4</sub> )-----	17	0. 0	2. 7	17	168	325
Chloride (Cl)-----	20	8. 5	26	51	108	362
Fluoride (F)-----	5	. 1	. 1	. 3	. 4	. 4
Nitrate (NO <sub>3</sub> )-----	5	. 5	. 8	1. 5	1. 7	1. 7
Dissolved solids:						
Residue on evaporation at 180°C-----	18	107	276	382	553	1, 010
Hardness as CaCO <sub>3</sub> -----	18	12	29	74	154	342
Noncarbonate hardness as CaCO <sub>3</sub> -----	20	0	0	8	40	170
pH-----	20	6. 9	7. 2	8. 0	8. 2	8. 6

With the exception of the saline waters, most makeup waters contained less than 1,000 ppm of dissolved solids. Although most of the butadiene plants are in Texas and Louisiana, the composition of the makeup water varies widely. Plants in the Houston and Baton Rouge area withdraw ground waters of low hardness, whose principal constituents are sodium and bicarbonate. The natural softening is the result of cation exchange in the aquifer (Meyer and Turcan, 1955). These waters have a dissolved-solids content of about 250–550 ppm.

Plants withdrawing fresh water from the Neches, Sabine, and Brazos Rivers in Texas and from aquifers near Odessa and Orange, Tex., use sodium-chloride waters. The municipal sewage water at Odessa also contains sodium and chloride as the principal constituents but contains appreciable amounts of sodium phosphate from detergents (Sullivan, 1958). The plants obtaining salty water from Neches River, Gulf of Mexico, and Pacific Ocean use water which may contain as much as 35,000 ppm of dissolved solids, 19,000 ppm of

chloride, and 11,000 ppm of sodium and potassium. Because of the high concentration of salts, these salty waters are used only for once-through cooling.

#### **TREATMENT OF MAKEUP WATER**

Salty waters used for once-through cooling are treated with chlorine to suppress the growth of algae and slime, but no treatment is given to the other waters used only once for cooling.

Table 7 summarizes the treatment methods used on makeup water at butadiene plants. Water used as makeup to cooling towers is given considerably more treatment than water used for once-through cooling. The majority of the butadiene plants that recirculate cooling water treat the makeup water to the cooling towers with chlorine to reduce the growth of algae and slime, adjust the pH, and treat the cooling-tower makeup water with phosphate and chromate to prevent corrosion. A few of the plants reduce the hardness and the dissolved solids of the cooling tower makeup water by treating the water with lime-soda and by ion exchange.

The principal treatment given to makeup water for steam boilers is softening by ion exchange, lime-soda, and phosphate to suppress the formation of scale. As indicated in table 7, most waters are treated by ion exchange. Many of the surface-water supplies and none of the ground-water supplies are given a clarification treatment before the water is sent to the boilers.

The majority of the waters withdrawn for sanitary and other services are obtained from ground-water sources, and many of these ground-water supplies are given no treatment. The treated ground waters generally are given only a chlorination treatment. The surface-water supplies for sanitary and other services commonly are clarified and chlorinated.

#### **QUANTITY OF WATER WITHDRAWN AND CONSUMED**

The few published quantities of makeup water required in the butadiene industry have been summarized in table 8. All plants that made butadiene from alcohol used once-through cooling water, and the amount of cooling water used at Kobuta, Pa., should be representative of the amounts of makeup water used at the three plants that made butadiene from alcohol during World War II.

The amount of makeup water withdrawn varies with (a) composition of the feedstock, (b) process used, (c) method of purification of crude butadiene, and (d) availability of water supply. The amounts of makeup water withdrawn for once-through cooling, recirculated cooling, process, boiler-feed, and sanitary and service uses



TABLE 7.—*Treatment of makeup water at butadiene plants*

[Does not include prior treatment of purchased water]

Treatment	Number of plants using indicated treatment				
	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water
None.....	4	—	2	—	6
Clarification:					
Sedimentation.....	—	—	1	1	—
Filtration.....	—	2	—	1	1
Coagulation and filtration.....	—	—	1	2	—
Disinfection: chlorine and chlorine compounds.....	2	7	3	1	5
Prevention of scale and corrosion:					
Chromate and phosphate.....	—	8	—	—	—
pH adjustment.....	—	7	—	—	—
Softening:					
Lime soda.....	—	1	2	6	—
Ion exchange.....	—	2	1	10	—
Phosphate.....	—	—	1	3	—

in the butadiene industry are summarized in table 9. Water used to generate steam that is not used somewhere in the butadiene plant is not included in this summary, but some butadiene plants sell steam.

Butadiene plants located near an ample supply of salty water use this source for once-through cooling, withdrawing more once-through cooling water per pound than plants withdrawing from fresh-water sources. Neches Butane Products Co., one of the large producers of butadiene, states in a company brochure that it withdraws enough water to supply a city the size of Cleveland, Ohio. More than 98 percent of this water, which is obtained from the Neches estuary, is used for once-through cooling. In all, less than 1 percent of the water used in the butadiene industry for once-through cooling comes from fresh-water supplies.

Butadiene plants circulate water through cooling towers about 45 times on the average. At one plant the cooling water is circulated about 83 times. The amount of water lost by evaporation, wind spray, or other consumptive uses ranges from 0.750 to 10.1 gallons per pound of finished butadiene. Most makeup to the cooling towers is obtained from fresh-water supplies; but a few plants use makeup water which has been used elsewhere in the plant. The amount of makeup withdrawn from fresh-water supplies ranges from 1.19 to 11.3 gallons per pound of finished butadiene. Plants that use a combination of once-through cooling water and recirculated cooling water require smaller amounts of cooling-tower makeup water per pound of finished butadiene. Plants extracting the crude butadiene

TABLE 8.—*Published quantities of makeup water required in the manufacture of butadiene in the United States*

Location	Use	Water required (gallons per pound)	Source reference
Toledo, Ohio-----	Recirculated cooling-	5. 2	Thayer and others, 1942.
Los Angeles, Calif.---	Boiler feed-----	2. 8	Chem. Eng., 1954.
Kobuta, Pa.-----	Once-through cooling.	144	Stein, 1945.
	Boiler feed-----	4. 2	Do.
Entire industry (U.S.)-	All uses-----	160	Gorman, 1943.
Entire industry (U.S.)-	-----do-----	11. 0-363	United Nations, 1958.
Los Angeles, Calif.---	-----do-----	3. 65-105	O'Connell and Gregory, 1944.

TABLE 9.—*Quantity of makeup water used in the manufacture of butadiene*

Water use	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water <sup>1</sup>	All uses
Number of plants-----	6	11	8	12	12	12
<b>Gallons per pound</b>						
Minimum-----	0. 392	1. 19	0. 020	0. 045	0. 023	5. 38
Lower quartile-----	2. 94	1. 65	. 110	1. 08	. 115	7. 21
Median-----	9. 88	3. 60	. 172	1. 47	. 402	9. 60
Upper quartile-----	48. 6	4. 84	. 218	2. 57	. 752	14. 6
Maximum-----	217	11. 3	1. 31	5. 85	1. 72	221
<b>Million gallons per day</b>						
Total for industry-----	391	20. 1	2. 10	11. 6	4. 10	429

<sup>1</sup> Includes water supplied to company town.

with CAA use less cooling-tower makeup water than plants extracting crude butadiene with furfural.

Some plants use no process water; some use water that has been used elsewhere for process water; some use a mixture of water used elsewhere and new makeup water; and others use only new makeup water. The amount of process water withdrawn from surface- and ground-water supplies ranges from 0.020 to 1.31 gallons per pound of finished butadiene. Plants using butane-butylene feed stock withdraw less process water per pound of finished butadiene than plants using butane as the feed stock.

Most plants operate steam-generating boilers; and a part of the steam condensate, commonly, is collected and returned to the boiler-

house. The water in the steam system is circulated, on the average, about four times: at one plant the boiler water is circulated about 15 times. The amount of steam lost by evaporation or otherwise consumed ranges from 0.087 to 1.36 gallons per pound of finished butadiene. To replace the boiler feed consumed and the blowdown from the boilers requires between 0.045 to 5.85 gallons of water per pound of finished butadiene.

Plants manufacturing butadiene by mixing about 10 to 20 volumes of steam to each pound of hydrocarbon sent to the dehydrogenation reactor require larger amounts of boiler-feed makeup than plants making butadiene by the Houdry process. Plants using a combination of Houdry and steam-dilution methods require less boiler-feed makeup than plants manufacturing butadiene by the steam-dilution method, but more than plants using the Houdry process.

Water for sanitary and other services commonly is used once and discharged to waste. At one plant these services include supplying water to a company-operated town. The amount of water for sanitary and service ranged from 0.023 to 1.72 gallons per pound of finished butadiene.

#### **TREATMENT OF WASTE WATERS**

The butadiene industry at capacity production discharges about 410 million gallons of waste water each day to surface waters. Most of this effluent is salty and is returned to its source without any waste treatment. Some waste waters from cooling towers and steam boilers are discharged also without any waste treatment.

Most butadiene plants operate oil-separation systems to remove oily hydrocarbons from waste waters. Usually the waste waters are neutralized by adjusting the pH, and the settleable solids are removed in a series of settling basins. At some plants the waste waters are neutralized, freed of oil and settleable solids, diluted with cooling water, and discharged to waste.

All sanitary waste waters are discharged to sanitary sewers or treated in company-operated Imhoff tanks or septic tanks. Blue water leakages from CAA equipment contain copper and usually are treated to recover the copper.

### **USE OF WATER IN THE MANUFACTURE OF STYRENE-BUTADIENE RUBBER**

#### **HOW WATER IS USED**

Styrene-butadiene rubber (SBR) is made by forcing styrene and butadiene to react in a soapy water solution and form minute particles of synthetic rubber. This suspension of rubber in soapy water, called

latex, is coagulated to form a rubber crumb that is washed and dried. Aqueous solutions of oil and carbon black may be added to the latex before coagulation, to extend the volume of rubber.

About 61 percent of the water withdrawn for use in the manufacture of SBR comes into direct contact with the rubber. Most of this process water is used to (a) make the aqueous solutions of soap and other chemicals, (b) make carbon-black slurries and oil solutions, and (c) wash the rubber crumb. About 17 percent of the water withdrawn is used for cooling polymerization reactors and heat exchangers used in the recovery of unreacted butadiene and styrene. Makeup water to the boilers generating steam for use in the styrene stripping column and in drying the rubber crumb requires about 11 percent of the water withdrawn. The remainder of the water is used for general services in the plant.

The amount and quality of water used in the manufacture of this synthetic rubber can be best described by dividing the process into four phases: (a) feed preparation, (b) latex formation, (c) recovery of butadiene and styrene, and (d) conversion of latex into dry rubber. Figure 37 is a simplified flowsheet of the manufacture of SBR with the uses of steam shown by dotted lines and the uses of water by shading.

#### FEED PREPARATION

The principal raw materials pumped to the reactor are styrene, butadiene, and aqueous solutions of soap and other chemicals. Styrene requires no feed preparation, and it and butadiene are stored in steel tanks that, at some plants, are sprayed with cooling water during hot weather to reduce polymerization. The small amount of polymerization inhibitor in styrene is not removed. Butadiene received from a distance contains a polymerization inhibitor that is removed by (a) mixing butadiene with a caustic solution, (b) allowing the solutions to separate by gravity, (c) decanting off the butadiene, (d) mixing the butadiene with water, (e) allowing the solutions to separate by gravity, and (f) decanting off the butadiene.

The solutions of soap and other chemicals are generally prepared in waters containing less than 10 ppm of hardness.

#### LATEX FORMATION

Styrene, butadiene, soapy water, and other aqueous solutions are cooled and pumped into temperature-regulated, glass-lined pressure reactors. The thoroughly agitated emulsions of styrene and butadiene polymerize and form minute particles of SBR. Butadiene enters the reaction first, but as the polymerization proceeds the rubber formed contains increasing amounts of styrene. Increasing the sty-

rene content increases the tensile strength of the rubber; decreasing the styrene content favors the retention of resilience and flexibility at low temperatures. SBR is composed of about 6 butadiene units to each styrene unit. The styrene units may enter the system singly or in clumps and are randomly located in the chain. After the reaction has proceeded to the desired degree of completion, the catalyst is destroyed and the reaction stops.

The conversion of butadiene and styrene into SBR generates considerable heat that is dissipated throughout the agitated soap solution. In the manufacture of hot rubber, the temperature of the reaction is controlled to about 120°F by circulating cooling water in a jacket around the reactor. In the manufacture of cold rubber, the reaction temperature is regulated near 41°F. At some plants this temperature is regulated by circulating brine or methanol-water solution in a jacket around the reactor; the brine and methanol-water solutions are then cooled by water in heat exchangers. At some plants the temperature is regulated to 41°F by the direct evaporation of ammonia in cooling coils inside the reactor; the ammonia is recondensed in water-cooled heat exchangers.

At some plants the raw materials are charged into the reactor, the reaction proceeds to the desired stopping point, and the batch is then dropped into a blowdown tank. This batch type of operation requires a large amount of process water and steam only at the start of the reaction and cooling water only during polymerization. The operation of a large number of reactors eliminates the surges of water demand.

At some plants butadiene, styrene, and aqueous solutions are pumped continuously into the top and out the bottom of a series of reactors. The flow rates of the raw materials are adjusted to obtain the desired viscosity or monomer conversion in the last reactor of the series. The continuous process allows about a 20 percent increase in effective reactor capacity (Whitby, 1954); therefore more steam, process, and cooling water is required as the result of the increased production.

#### RECOVERY OF BUTADIENE AND STYRENE

The latex in the blowdown tanks contains considerable amounts of unreacted butadiene and styrene that are recovered by flash evaporation and steam distillation. The recovery of these monomers requires large amounts of steam and cooling water. Steam is injected into the latex in the blowdown tanks. The heated latex and unrecovered monomers are transferred to butadiene "flash" tanks, where butadiene is evaporated or "flashed" from the latex. The butadiene vapors are compressed to a liquid and blended with fresh butadiene for reuse.

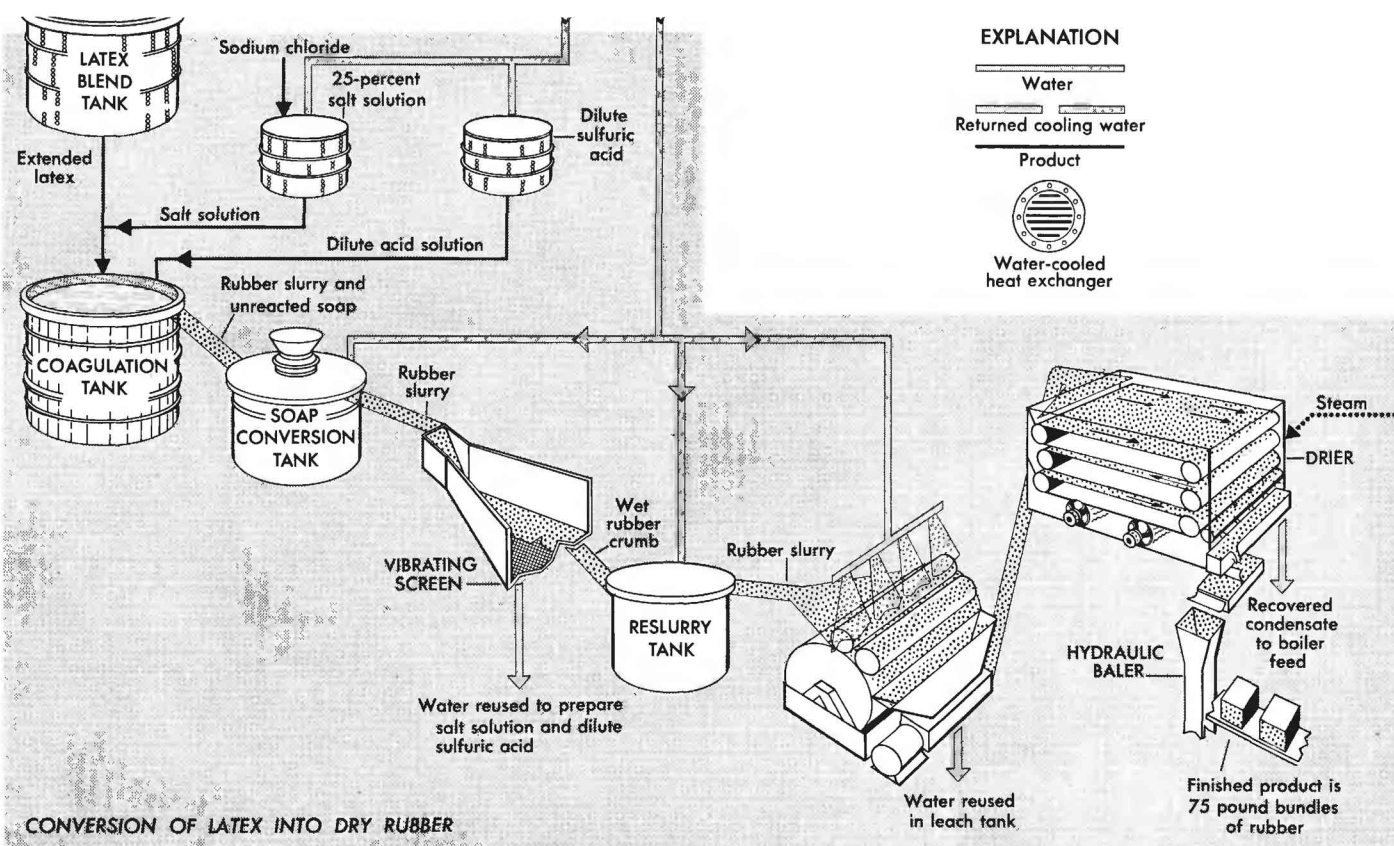
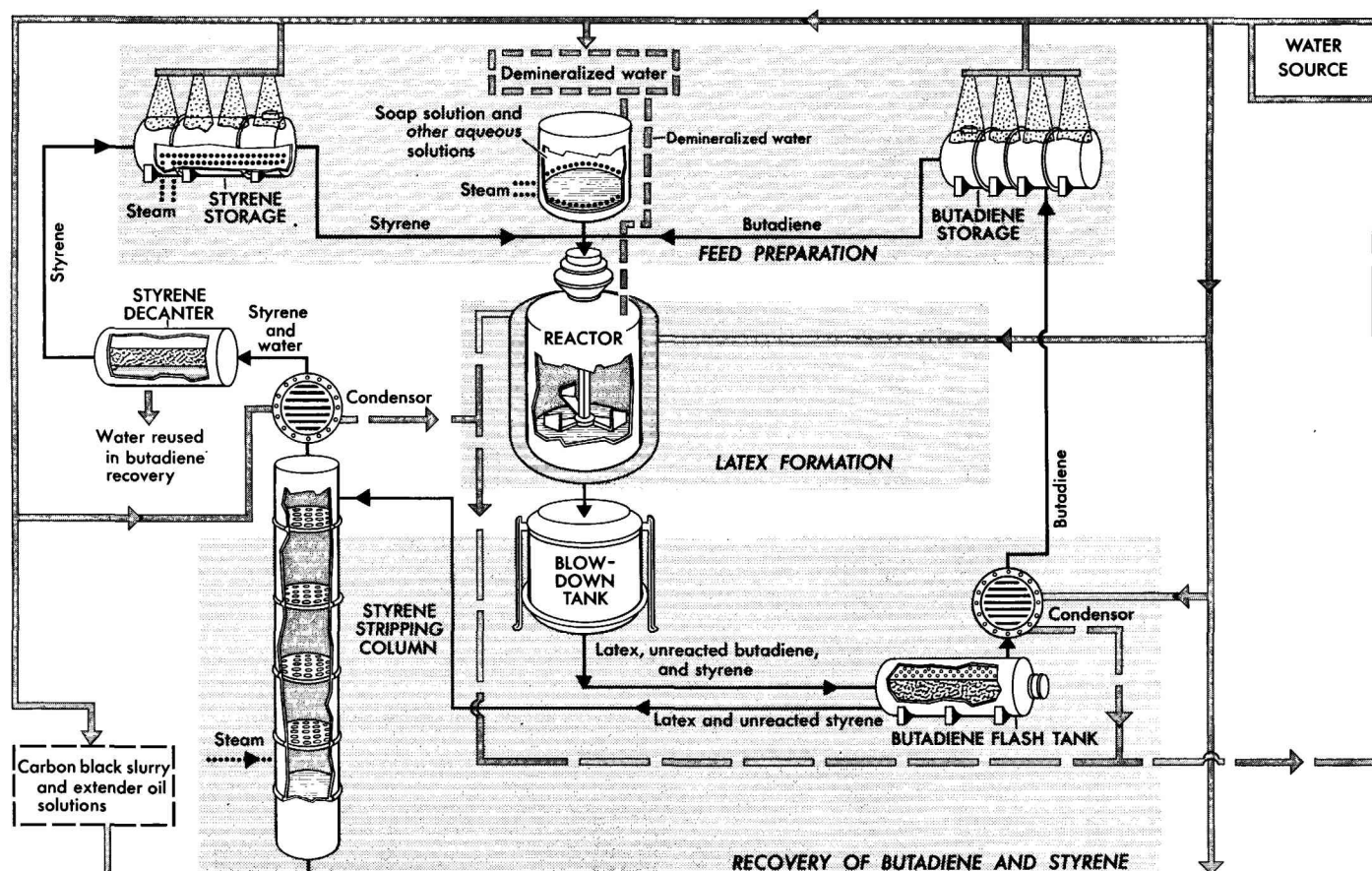


FIGURE 37.—Flowsheet illustrating the use of water in the manufacture of styrene-butadiene rubber (SBR).

The latex and unrecovered styrene are pumped from butadiene flash tanks to the top of a styrene stripping column. The recovery of styrene from the latex is illustrated in figure 38. A stream of low-pressure desuperheated steam is injected into the bottom of the tower, passes up through the falling latex, and strips the vaporized styrene from the latex. The vapors of styrene and steam flow to a water-cooled heat exchanger, where the steam and styrene are condensed. The condensed styrene and water flow to a styrene decanter tank, where the liquids are separated by gravity. Styrene overflowing from the decanter tank is blended with fresh styrene of higher purity

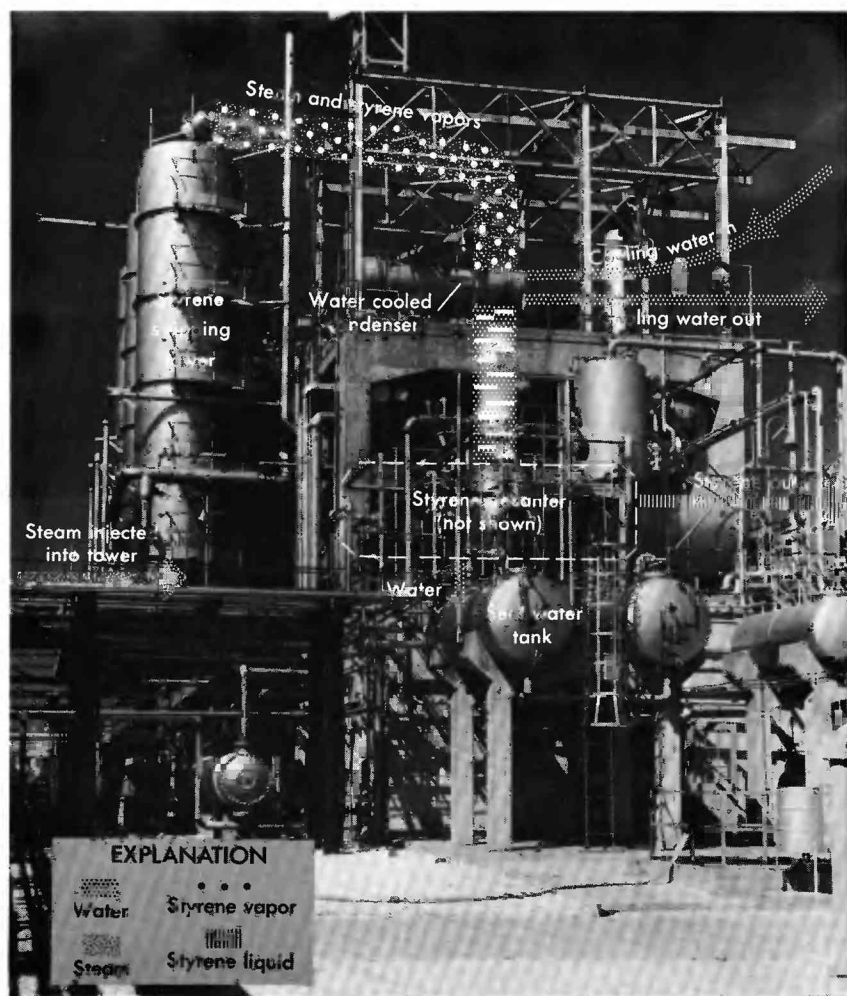


FIGURE 38.—Water use in the recovery of styrene from latex.

for reuse. Part of the water from the decanter is used in the "seal water system" of the butadiene recovery system, and part is released to waste. Water in the "seal water system" is used to seal and compress butadiene vapors in vacuum pumps and compressors.

The latex, stripped of monomers, is blended with latexes from several batches or production lines. About 7 percent of the latex produced in 1959 was sold before coagulation into the rubber crumb. The rubber content in the latex to be sold is commonly increased by evaporating water from the latex with steam heat.

#### CONVERSION OF LATEX INTO DRY RUBBER

To prevent deterioration of the rubber, aqueous emulsions of anti-oxidant are added in the blend tank to latex that is to be coagulated and dried. The methods of coagulating and drying SBR vary from plant to plant. The following description, which emphasizes the use of water, is a composite of the techniques used in the industry.

Oil-extended SBR is made by adding an emulsion of oil, caustic, and water to the latex in the blend tank. SBR is master batched by mixing a slurry of 20 percent carbon black with the latex in the blend tank. Oil-extended master batch is made by adding extender oil and a slurry of carbon black to the latex. If the rubber is to be extended with oil and carbon black, the finished rubber may contain more than 100 pounds of extender oil and carbon black for each 100 pounds of standard SBR.

Latex with carbon black, oil-extended latex, and latex extended with oil and carbon black are coagulated and dried in the same manner as standard SBR latex, except that additional water is required for washing and additional steam for drying the larger volume of apparent rubber.

Latex is pumped from the blend tank and mixed with a water solution of sodium chloride in the coagulation tank. The brine causes a partial flocculation of the latex particles, which changes the consistency of the latex to that of a heavy cream. The coagulation of the crumb is completed by the addition of dilute sulfuric acid to the latex in the coagulation tank. After the flocculation is completed, the crumb overflows to the soap-conversion tank, where any residual soap is converted to fatty acid. The slurry of coagulated rubber overflows from the soap-conversion tank to a vibrating screen or to a skimmer tank, where the rubber crumb is separated from the water serum. The serum which contains about 4 percent sodium chloride and residual sulfuric acid, is reused in the preparation of the brine solution and the dilute acid solution. Excess serum is sent to the sewer.



The rubber crumb is reslurried with fresh water to wash out residual salts and acids. As illustrated in figure 39, the overflow from the reslurry tank flows by gravity onto a large rotating vacuum drum, where the wash water is removed. The friable crumb shown in figure 39 is washed with hot water at some plants and with cold water at other plants to reduce even further any residual salt and acid. The large rollers compress the rubber crumb and water is drawn by vacuum through the screen. This wash water is recovered and used to reslurry the rubber crumb before it contacts the rotating filter.



FIGURE 39.—Dewatering of styrene-butadiene-rubber (SBR) crumb.

The rubber, which comes from the filter and contains about 25-30 percent water, is shredded and blown into a large dryer which is usually heated by steam. The water is evaporated from the rubber crumb and, at some plants, is condensed and reused as boiler-feed water. The crumb, which comes from the drier and contains less than 0.5 percent water, is compressed in a hydraulic baler. The 75-pound bales of rubber are then sprayed with talc or wrapped in polyethylene film.

## FINDINGS OF THE SURVEY

### SOURCES

At capacity production about 15.9 million gallons of ground water and about 12.8 million gallons of surface water are withdrawn each day in the production of styrene-butadiene rubber. The 28.7 million gallons of water required each day is obtained (a) by pumping from ground or surface water sources or (b) by purchasing from municipal supplies, water authorities, public utility companies, or neighboring industries. No water from the ocean or other saline sources was used in the manufacture of the styrene-butadiene rubber. The sources of supply used for cooling water, process water, boilerfeed water, and sanitary and service water by the SBR plants are summarized in table 10. Municipal sewage water was used only for boiler-feed makeup water.

TABLE 10.—*Sources of makeup water for styrene-butadiene rubber*

Source	Number of plants being served by indicated sources				
	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water
Well water:					
Self-supplied.....	1	7	7	4	6
Water company.....		2	2	2	1
Neighboring industry.....					1
Surface water:					
Self-supplied.....		2	1	2	1
Water company.....					1
Water authority.....		2	2		2
Municipal water supply.....	2	3	4	1	
Neighboring industry.....					4

The majority of the SBR plants obtain ample water from present sources of supply; however, some plants are obtaining just enough water for present capacity production. If the amount of water available at present should be reduced or if production should be greatly increased, these plants would have difficulty in obtaining sufficient

water from the present sources of supply; therefore these plants are planning to develop additional supplies.

Two-thirds of the plants visited used more than one source of supply. The other third used only ground-water supplies. Of the 15 SBR plants, 14 used the same source of water for process use and for makeup to the cooling towers. Five of the plants purchased steam, and all the other plants used the same source of water for boiler-feed makeup and for makeup to the cooling towers.

#### CHEMICAL QUALITY

The chemical properties of untreated makeup water used in the manufacture of SBR are summarized in table 11. The table contains the minimum, lower quartile, median, upper quartile, and maximum values of each constituent in the makeup water for recirculated cooling water, process water, and boiler-feed water. Because 14 out of 15 plants use the same sources of water for cooling and process use, the analytical data for these 2 uses were combined. The data for boiler-feed makeup water included the chemical analyses, where available, of the raw water used to generate the purchased steam. The chemical analyses of sewage water have been included in the preparation of this table. The significance of the more important chemical constituents were discussed on page 232.

TABLE 11.—*Chemical properties of untreated makeup water used in the manufacture of styrene-butadiene rubbers*

[Chemical analyses were furnished by plants manufacturing SBR and by the U.S. Geol. Survey]

Constituent or property	Cooling and process						Boiler feed					
	Number of samples	Parts per million					Number of samples	Parts per million				
		Min-imum	Lower quar-tile	Med-ian	Upper quar-tile	Max-imum		Min-imum	Lower quar-tile	Med-ian	Upper quar-tile	Max-imum
Silica (SiO <sub>2</sub> ).....	13	1.8	7.8	14	26	40	10	4.5	9.0	14	24	40
Iron (Fe).....	13	.00	.06	.10	.80	1.9	5	.08	.08	.10	.82	1.5
Calcium (Ca).....	15	4.0	7.8	25	34	139	10	4.0	7.8	15	32	139
Magnesium (Mg).....	15	1.0	2.2	5.2	8.0	36	10	1.0	1.5	2.8	7.3	36
Sodium (Na) and potassium (K).....	15	4.1	19	38	70	129	6	13	21	22	55	61
Bicarbonate (HCO <sub>3</sub> ).....	16	8	42	133	241	366	13	8	31	144	224	366
Carbonate (CO <sub>3</sub> ).....	16	0	0	0	0	5	13	0	0	0	0	8
Sulfate (SO <sub>4</sub> ).....	15	0.0	4.4	17	50	213	11	.0	4.4	17	95	213
Chloride (Cl).....	16	3.5	9.7	25	36	52	13	6.7	9.8	27	44	298
Nitrate (NO <sub>3</sub> ).....	5	.0	.2	1.0	16	32						
Dissolved solids:												
Residue on evaporation at 180° C.....	10	38	107	223	335	526	89	38	107	236	309	900
Hardness as CaCO <sub>3</sub> .....	16	16	34	77	135	495	13	16	31	65	326	495
Noncarbonate hardness as CaCO <sub>3</sub> .....	16	0	2	17	40	231	12	0	2	12	54	231
pH.....	13	6.7	7.0	7.5	7.8	8.6	11	6.7	6.9	7.2	7.6	8.6

The makeup water, exclusive of municipal sewage, generally was of good quality and had maximum dissolved solids of about 526 ppm; the sewage water had dissolved solids of 900 ppm. Most makeup waters were of a calcium bicarbonate type, but the hardness was less than 500 ppm and the bicarbonate less than 370 ppm. A few water supplies in Texas and Louisiana, where natural ion exchange may have occurred, had sodium and bicarbonate as the principal constituents. In these waters the maximum sodium reported was 129 ppm, and the maximum bicarbonate was 317 ppm. The principal constituents of the makeup water from municipal sewage and the Lower Neches Valley Authority were sodium and chloride. In these waters the maximum chloride was 298 ppm.

The median hardness of recirculated cooling and process water is about 77 ppm. At some plants the hardness in the makeup water for process use was reported to cause problems. D. W. Cate (1958?) in advising on the handling and storage of Firestone latices states, "Polyvalent ions such as iron, calcium, magnesium or aluminum cause coagulation of latex." The rubber plant at Institute, W. Va., reported that waters having a hardness in excess of 50 ppm caused rubber latex to coagulate in tanks, pipelines, and other pieces of plant equipment (Borg, 1945).

#### TREATMENT OF MAKEUP WATER

The treatment given to makeup waters withdrawn for cooling, process, boiler-feed, and sanitary and service uses is summarized in table 12. Of the 15 plants manufacturing SBR, only 2 plants use once-through cooling water. One plant adjusts the pH clarifies by the addition of alum and filtration, and chlorinates the makeup water. The other plant purchases the makeup water that had been similarly treated by a municipality; this plant does not treat the makeup water further.

The makeup water for cooling towers is given more extensive treatment. All SBR plants recirculate cooling water through cooling towers; of 15 plants, 11 add chromates or phosphates to the cooling-tower makeup water to suppress corrosion; 4 treat the makeup water with lime or ion exchange resins to lower the hardness and to prevent the formation of calcium carbonate scale; 11 chlorinate the cooling-tower makeup water; and 2 of the remaining 4 plants purchase water that has been chlorinated.

As indicated in table 12, the principal treatment given to process water is lowering the hardness by ion exchange. Most plants reduce the hardness of part or all of the process water to less than 10 ppm; a few plants lower to near zero the hardness of the water used

TABLE 12.—*Treatment of makeup water at styrene-butadiene rubber plants*

[Does not include prior treatment of purchased water]

Treatment	Number of plants using indicated treatment				
	Once-through cooling water <sup>1</sup>	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water
None .....	1	-----	1	-----	6
Clarification:					
Filtration .....				2	-----
Coagulation and filtration .....	1	2	3	2	2
Coagulation and settling .....		2	1	1	1
Coagulation, settling and filtration .....		2	2	-----	2
Disinfection: chlorine or chlorine compounds .....	1	11	7	3	7
Prevention of corrosion and scale:					
Chromate and phosphate .....		11	-----	-----	-----
pH adjustment .....	1	5	2	-----	2
Softening:					
Lime-soda .....		3	5	9	3
Ion-exchange .....		1	14	9	1
Phosphate .....		-----	-----	4	-----

<sup>1</sup> Only 2 plants use once-through cooling water.

to make reactor water solutions. Plants producing only SBR latex deionize all process water; plants producing dry SBR deionize between 10 and 50 percent of the process water. The water used to wash the rubber crumb, which is a large part of the process water, generally comes from the same source as the reactor charge water but is not demineralized.

Almost all plants reduced the hardness and the dissolved-solids content of the makeup water for boiler feed by ion exchange or by lime-soda treatment. Of all plants, 7 chlorinated the water for sanitary purposes, and 6 additional plants purchased water for sanitary purposes from municipalities that chlorinate the water before selling it to the plants. A few plants soften water for sanitary use in the locker rooms.

#### QUANTITY OF WATER WITHDRAWN AND CONSUMED

The author was unable to find published information on the quantity of makeup water used in the direct manufacture of SBR. Published values of the aggregate amounts of water used to produce SBR and to produce its required amounts of styrene and butadiene are discussed later.

At capacity production, about 28.7 million gallons of water is withdrawn daily for use in the direct manufacture of SBR; about 15.9 million gallons is obtained from ground-water supplies, and about 12.8 million gallons is withdrawn from surface-water supplies. The

amount of water withdrawn varies with the process of manufacture of SBR and the availability of water supply at the plant. The amounts of makeup water withdrawn for recirculated cooling water, process water, boiler feed, and sanitary and service water are summarized in table 13.

Only two plants use once-through cooling water as well as recirculating cooling water. All SBR plants recirculate part of or all the cooling water through cooling towers. The recirculated cooling water does not come into contact with the product and is used as many as 240 times. Recirculated cooling-water losses due to evaporation, wind spray, or other consumptive uses range from 0.054 to 2.6 gallons of water per pound of finished rubber. To replace consumptive losses and water discarded to waste from the cooling towers requires from 0.065 to 4.71 gallons of water per pound of finished rubber. Rubber extended with oil and carbon black uses less makeup water per pound of finished rubber for cooling than latex or nonextended SBR. The seeming decrease in water use by the extended rubbers is due to the added weight of extender oil and carbon black in the finished apparent rubber. The three companies using the largest amounts of makeup water for recirculated cooling are located in areas of plentiful water supply.

TABLE 13.—Quantity of makeup water used in the manufacture of styrene-butadiene rubber

Water use	Recirculated cooling water <sup>1</sup>	Process water	Boiler-feed water	Sanitary and service water	All uses
Number of plants.....	15	15	15	15	15
Gallons per pound					
Minimum.....	0. 065	0. 122	0. 087	0. 022	0. 883
Lower quartile.....	. 351	1. 31	. 210	. 109	2. 52
Median.....	. 402	2. 33	. 406	. 431	3. 45
Upper quartile.....	. 954	2. 88	. 672	. 830	5. 42
Maximum.....	4. 71	3. 91	1. 21	1. 25	10. 2
Million gallons per day					
Total for industry.....	-----	-----	3. 12	3. 06	28. 7

<sup>1</sup> In addition, 2 plants used once-through cooling water.

The amount of water withdrawn for process use ranges from 0.122 to 3.91 gallons per pound of finished rubber. Most plants have two types of process water: deionized process water and nondeionized process water. The deionized water is used for reactor charge and other

uses where the minerals in the water could cause coagulation of the latex. The minimum amount of deionized water required for standard SBR formulas is 0.22 gallon per pound of finished rubber. The amount of process water treated by ion exchange in most plants ranged from 0.25 to 0.78 gallon per pound of finished rubber. Some plants mix recovered steam condensate with deionized water for process use.

Plants making only latex do not wash any rubber crumb and thus use less process water than plants producing dry SBR. Latex plants use process water principally in the soap solution pumped to the reactor and therefore discharge little or no process water to waste. Most plants that do not produce latex do not use any process water consumptively. The amount of process water consumptively used by latex plants ranges from 0.065 to 0.421 gallon of water per pound of finished rubber.

The makeup water to boiler feed ranges from 0.087 to 1.21 gallons per pound of finished rubber. A large part of this makeup water is used to replace the steam injected into the blowdown tank and the steam contaminated in the styrene stripping. In both uses the steam is condensed and becomes part of the 0.035 to 1.21 gallons of the steam condensate discharged to waste for each pound of finished rubber produced. The steam injected into the blowdown tanks commonly is lost in the coagulation and drying processes. The recommended steam rate into the styrene stripping tower illustrated in figure 38 is 5.5 pounds of steam per pound of styrene in the column. At a monomer conversion rate of 72 percent, this requires 0.118 gallons of boiler-feed water per pound of rubber in the column (Johnson and Otto, 1949). Lower conversion rates require more steam and thus more boiler-feed makeup.

Plants producing only latex use more makeup water, per pound of dry SBR, for boiler feed than plants producing dry SBR. Plants producing rubbers extended with oil and carbon black use less makeup water for boiler feed, per pound of finished rubber, than plants producing latex and nonextended SBR. The lower values of makeup water per pound of extended SBR may be caused by the increased weight of extender oil and carbon black in the extended rubbers.

In addition to the water used directly in the manufacture of styrene-butadiene rubber, water is used for company cafeterias, washing floors, other services, and sanitary purposes. The amount of water used for these services is summarized in table 13. Waters used for sanitary and service purposes are not recirculated in any plant.

TREATMENT OF WASTE WATERS

SBR plants, at capacity production, discharge about 25.5 million gallons of water each day—principally to surface waters. Most of the effluent waters are given little or no treatment. The treatment given to effluent containing latex, rubber crumb, or other settleable solids generally consists of pumping the effluent to a settling basin, where the heavy solids are allowed to settle out and the floatable materials are retained by a separator at the basin discharge. At some plants chemicals may be added to aid flocculation.

The sanitary wastes are processed in Imhoff tanks or discharged to sanitary sewers to be processed further elsewhere.

AGGREGATE QUANTITY OF WATER REQUIRED TO PRODUCE STYRENE-BUTADIENE RUBBERS

The published values of the quality of water required to produce SBR and its required amounts of styrene and butadiene are summarized in table 14.

The aggregate amounts of makeup water withdrawn to produce SBR-type synthetic rubbers depend upon the amounts of water withdrawn to make the raw materials, styrene and butadiene, and the amounts of water used in the direct manufacture of the synthetic rubbers. The near-minimum amounts of makeup water used to make 1 pound of SBR composed of about 75 percent butadiene and 25 percent styrene is illustrated in figure 40. This schematic drawing shows the amounts of (a) makeup water, (b) effluent, and (c) water consumptively used in the manufacture of the required amounts of styrene and butadiene and in the direct manufacture of SBR. It is assumed that no once-through cooling water is used; in the manufacture of styrene or butadiene, once-through cooling water could require more than 40 times the amount of makeup water shown. It is also assumed that no SBR latex is made; the manufacture of SBR latex would decrease the amount of effluent and would increase the consumptive use of water.

TABLE 14.—*Published quantities of makeup water required to produce styrene-butadiene rubber in the United States*

Location	Water required		Source reference
	Gallons per pound	Gallons per ton	
Institute, W. Va-----	281	631, 000	Olive and Shreve (1947).
Entire industry (U.S.)--	13. 8-330	31, 000-740, 000	United Nations (1958).



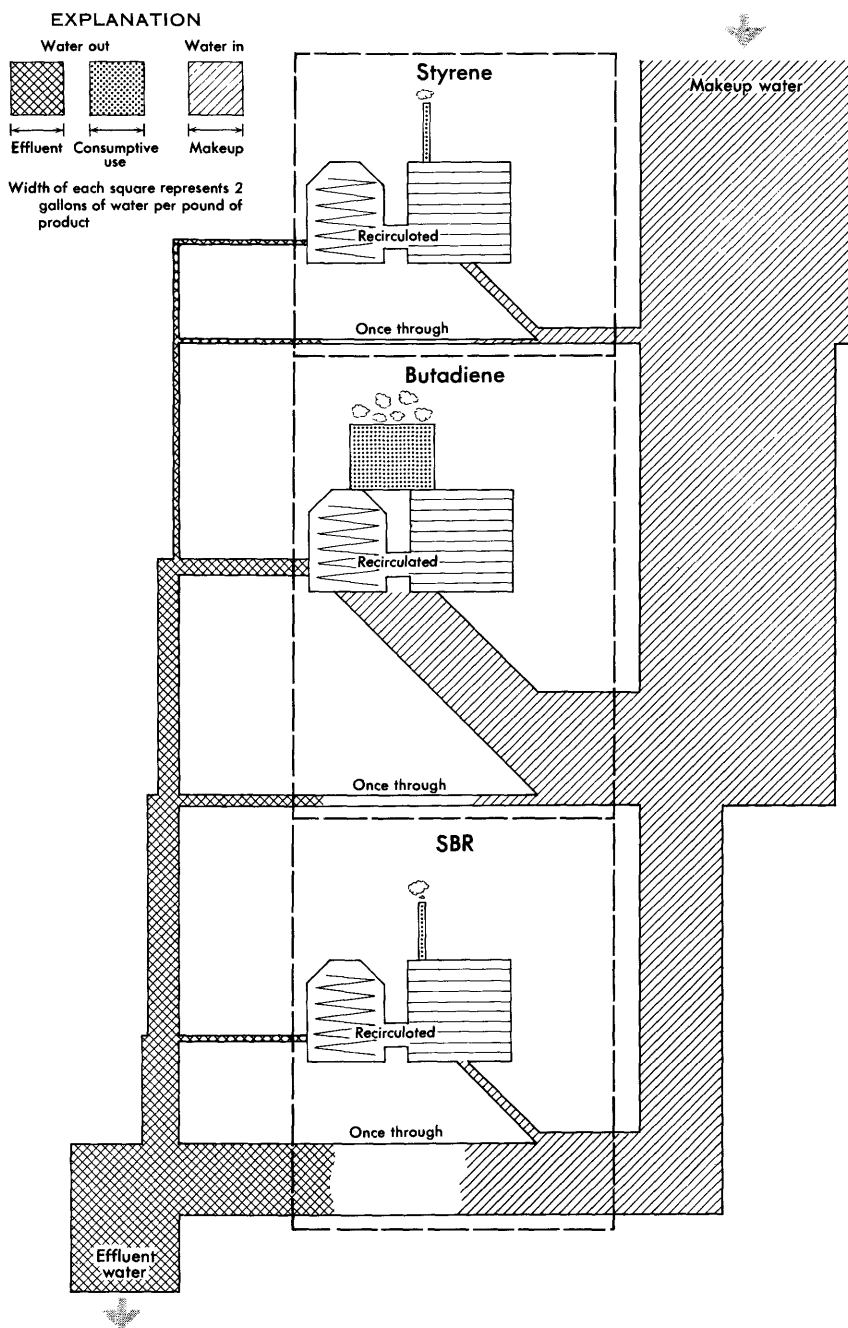


FIGURE 40.—Near-minimum amounts of makeup water used to produce styrene-butadiene rubber (SBR).

The amounts of styrene and butadiene used to produce 1 pound of SBR-type synthetic rubber depends upon the type of the synthetic rubber. A pound of SBR extended with carbon black and extender oil requires less styrene and butadiene than 1 pound of SBR. As a result, the amount of makeup water used to produce the styrene and butadiene used in 1 pound of SBR extended with carbon black and extender oil is less than the amount of makeup water needed to produce the styrene and butadiene needed for 1 pound of nonextended SBR.

The amounts of makeup water used in producing styrene and butadiene and the amount used in the direct manufacture of the SBR-type synthetic rubbers depends upon the process used and the availability of water supply. The amount of makeup water withdrawn to produce 1 pound of styrene ranges from 2.2 to 123 gallons; that withdrawn to produce 1 pound of butadiene ranges from 5.4 to 221 gallons; and that withdrawn in the direct manufacture of SBR-type synthetic rubbers ranges from 0.883 to 10.2 gallons.

The minimum and maximum amounts of makeup water required to produce 1 pound and 1 long ton (2,240 pounds) of SBR latex, SBR, oil-extended SBR, and SBR extended with carbon black and extender oil are summarized in table 15. The minimum (and maximum) quantities of makeup water were calculated by adding the minimum (and maximum) quantities of makeup water used to make the required amounts of styrene and butadiene in 1 pound of each type of synthetic rubber to the minimum (and maximum) quantities of water used in the direct manufacture of 1 pound of each type of synthetic rubber.

TABLE 15.—*Minimum and maximum quantities of makeup water required to produce styrene-butadiene rubbers (SBR)*

Product	Makeup water required			
	Gallons of water per pound of finished rubber		Gallons of water per long ton of finished rubber	
	Minimum	Maximum	Minimum	Maximum
SBR latex.....	5. 1	187	11, 400	418, 000
SBR.....	8. 4	187	18, 800	420, 000
Oil-extended SBR.....	6. 2	164	13, 900	368, 000
SBR extended with oil and carbon black..	6. 2	145	13, 900	324, 000

## USE OF WATER IN THE MANUFACTURE OF SPECIAL-PURPOSE SYNTHETIC RUBBERS

During the last complete defense mobilization, in 1941-45, thiokol, neoprene, butyl, and nitrile rubbers were considered essential to the war effort. The shortage of certain kinds of these special rubbers was a detriment to the war plans. The use of water in these specialty-rubber plants was determined and is presented in order to give a more complete picture of the utilization of water in the synthetic-rubber industry. A brief description of water use in the manufacture of these special rubbers follows.

### HOW WATER IS USED

#### NITRILE RUBBER

Nitrile rubber, which is sold under the trade names of Perbunan, Hycar, Chemigum, and Butaprene, is commonly made by polymerizing butadiene and acrylonitrile, catalytically, in a soapy water solution. The preparation of nitrile rubber is similar to the preparation of SBR. (One plant is manufacturing nitrile rubber in equipment designed to produce SBR.)

About 22-24 gallons of distilled or deionized water, containing chemicals which control polymerization, are charged with each 75 pounds of butadiene and 25 pounds of acrylonitrile into a glass-lined or stainless-steel reactor. The exothermic polymerization reaction is generally controlled at temperatures less than 80°F by circulating cooling water in coils around the reactor. After the polymerization is terminated, the unreacted butadiene and acrylonitrile are recovered by procedures described in the section on the recovery of butadiene and styrene from SBR latex.

The controlled addition of brine to the nitrile rubber latex coagulates and flocculates the rubber particles to a rubber crumb. The rubber crumb is then separated from the slurry on a rotating vacuum filter and reslurried with water to remove soap and water-soluble salts. The washed crumb is refiltered, dried, and packaged for shipment.

In the manufacture of nitrile rubber, a large part of the makeup water is used to control the temperature of the reactor and to condense and cool recovered butadiene and acrylonitrile. At plants making nitrile rubber crumb, large amounts of water are used for washing the crumb; at plants manufacturing only nitrile latex, smaller amounts of process water are required—principally to charge the reactor. The steam in the stripping column comes in contact with the latex and is not returned directly to the boilerhouse.

### BUTYL RUBBER

Butyl rubber is made by mixing, at low temperatures, 98 percent isobutylene with 2 percent isoprene that contains methyl chloride, an inert diluent that controls polymerization. The manufacture of butyl rubber is illustrated schematically in figure 41. The isoprene and isobutylene are recovered from petroleum refinery products by absorption and distillation. Isobutylene and isoprene are cooled and sent to reactors regulated to  $-140^{\circ}\text{F}$ , where they react, in the presence of a catalyst, to form fine particles of butyl rubber. The rubber polymer, along with unreacted hydrocarbons, is sent from the reactor into a large volume of vigorously agitated hot water in a flash tank. The hydrocarbons are vaporized from this tank and collected, compressed, dried, refined, and recycled to the reactor.

The slurry of butyl from the flash tank is pumped to a vibrating screen or a rotating vacuum filter, where the rubber crumb is separated from the water, which is recycled to the flash drum (see fig. 41). The rubber product is passed through a dryer to remove most of the remaining water; it is then extruded, milled, cut into squares, and packaged for shipment.

In the manufacture of butyl rubber, cooling water is used in condensers on distillation towers and to cool the refrigerant used to regulate the reactor temperature. Process water is used for scrubbing hydrocarbons. Steam is used to vaporize the hydrocarbons in the flash tank, to dry the rubber, and as a source of heat for distillation columns.

### NEOPRENE

Neoprene is produced by polymerizing an aqueous emulsion of chloroprene. The basic steps in the manufacture of neoprene are shown schematically in figure 41. Acetylene is converted catalytically in a reactor to monovinyl-acetylene, which is separated from other reactor products by low-temperature condensation and by fractional distillation. The purified monovinyl-acetylene is reacted with hydrogen chloride, in the presence of a catalyst, to form liquid chloroprene. The crude chloroprene is purified by condensation and distillation to remove unreacted monovinyl-acetylene and hydrogen chloride.

Purified chloroprene is emulsified in  $100^{\circ}\text{F}$  water containing chemicals that regulate polymerization; about 20 gallons of water are needed for each 100 pounds of chloroprene charged to the reactor (Whitby, 1954). The chloroprene emulsion is polymerized to a latex of butyl rubber in a polymerization tank. The latex from several polymerization tanks is blended and pumped onto a freeze roll maintained at about  $10^{\circ}\text{F}$ . Here the latex, which is composed of about 35 percent solids and 65 percent water, is frozen. A thin continuous film of

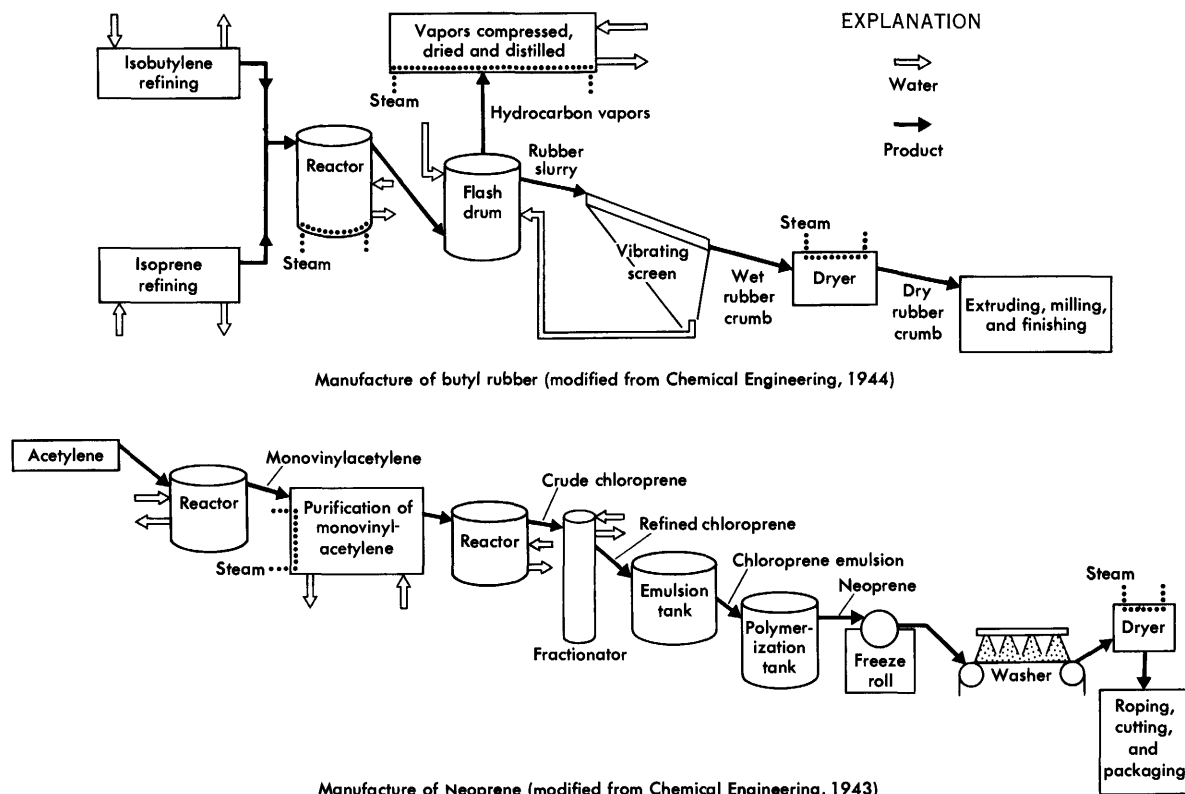


FIGURE 41.—Flowsheet illustrating the use of water in the manufacture of neoprene and butyl rubber.

polymer forms, which is stripped from the freeze roll. The frozen film of polymer is sprayed with warm water, which replaces "the aqueous phase in the film with pure water" (Youker, 1947). The washed film of rubber is then passed through squeeze rolls and dried in a steam-heated air drier. The dried film is formed into a rope, about an inch in diameter, which is cut and packaged for shipment.

In the manufacture of neoprene rubber, cooling water is used to cool reactors, and refrigerants and to cool reflux condensers on the distillation towers. Process water is used to scrub intermediates, to make aqueous emulsions, and to wash the neoprene film. Steam is used in reboilers of the distillation towers and in the air drier.

### THIOL

Thiol is a synthetic rubber made by the condensation of an alkyl dihalide (commonly ethylene dichloride) and sodium polysulfide; the latter is made by mixing sulfur in an aqueous solution of sodium hydroxide. The exothermic condensation reaction between ethylene dichloride and sodium polysulfide is regulated to about 160°F by circulating cooling water in a jacket around the reactor. The product of polymerization is allowed to settle and is then washed with water. Part of the washed latex is shipped; part is coagulated into a crumb, filtered, dried, and milled for shipment; and part is mixed with a sulfur compound to form a liquid rubber which is washed with water and distilled.

Cooling water is used to cool reactors and to cool the reflux condensers of distillation towers. Process water is used for making the sodium polysulfide solution and for washing the latex, the crumb, and the liquid rubber. Steam is used in the distillation tower reboilers and in drying the rubber crumb.

## FINDINGS OF THE SURVEY

### SOURCES

At capacity production, about 93.8 million gallons of makeup water is withdrawn daily by the plants visited in this survey that manufacture special-purpose synthetic rubbers. Of this amount, 13.9 million gallons a day is obtained from company-owned wells, and 79.9 million gallons a day of surface water is pumped by companies from streams and is purchased from municipal supplies and State water authorities. No saline, ocean, or sewage-water supplies are used in the manufacture of these special rubbers. The sources of makeup-water supply for cooling, process, boiler-feed, and sanitary and service waters used in the specialty-rubber plants are summarized in table 16.

The majority of the plants visited obtain ample water for present and future production requirements. Several plants obtain adequate water from present sources but will require more water for anticipated increases in production. Several plants are exploring additional sources of water supply because of diminishing ground-water yields. One plant indicated that the present ground-water source is not adequate for present production. Of the 11 plants, 7 now obtain water from more than 1 source of supply. Several of the plants purchase steam.

TABLE 16.—*Sources of makeup water used in the manufacture of special-purpose synthetic rubbers*

Source	Number of plants being served by indicated sources				
	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water
Well water: Self-supplied.....	6	5	6	4	8
Surface water:					
Self-supplied.....	2	3	-----	1	2
Water authority.....	1	-----	1	1	1
Municipal water supply.....	1	-----	2	2	2

#### CHEMICAL QUALITY

The chemical constituents of untreated makeup waters used in plants manufacturing special-purpose synthetic rubbers are summarized in table 17. The table contains the minimum, lower quartile, median, upper quartile, and maximum values of each constituent of water used for makeup. Because many plants use the same sources of water for many purposes, the chemical analyses of all makeup waters were used. Chemical analyses of makeup water of purchased steam were not available. The significance of the more important chemical constituents in water were discussed on page 232.

As indicated in table 17, waters used as makeup to plants manufacturing special-purpose synthetic rubbers range from soft (less than 60 ppm) to hard (618 ppm). The majority of the plants used waters having a hardness less than 60 ppm, and 75 percent of the plants used waters having a hardness of 132 ppm or less. The establishments manufacturing a special rubber whose latex is coagulated by calcium or magnesium try to use process-water makeup with low hardness.

Most of the makeup waters contain less than 500 ppm of dissolved solids. At one location, the high concentration of iron in the ground water causes problems and restricts the use of the water. Although the waters used for makeup for cooling, process, boiler-feed, and sani-

tary and service purposes were similar in chemical quality, the waters used for makeup for process and boiler feed contain slightly less dissolved solids and have lower hardnesses than waters used for cooling and sanitary and service purposes.

TABLE 17.—*Chemical properties of untreated water used in the manufacture of special-purpose synthetic rubbers*

Chemical analyses were furnished by plants manufacturing special-purpose rubbers and by the U.S. Geol. Survey]

Constituent or property	Number of samples	Parts per million				
		Minimum	Lower quartile	Median	Upper quartile	Maximum
Silica (SiO <sub>2</sub> )-----	10	5. 7	13	15	23	46
Iron (Fe)-----	6	. 01	. 05	. 14	. 40	. 57
Calcium (Ca)-----	11	. 6	3. 2	14	30	170
Magnesium (Mg)-----	11	. 1	. 5	2. 8	5. 3	45
Sodium (Na) and potassium (K)-----	7	3. 9	21	45	72	121
Bicarbonate (HCO <sub>3</sub> )-----	18	22	107	153	274	560
Carbonate (CO <sub>3</sub> )-----	18	0	0	0	0	18
Sulfate (SO <sub>4</sub> )-----	14	4. 0	5. 3	12	43	280
Chloride (Cl)-----	18	4. 8	7. 0	28	55	378
Dissolved solids: Residue on evaporation at 180°C-----	13	80	183	218	312	1, 039
Hardness as CaCO <sub>3</sub> -----	18	2	31	58	132	618
Noncarbonate hardness as CaCO <sub>3</sub> -----	18	0	0	6	33	350
pH-----	18	6. 9	7. 1	7. 6	8. 2	9. 0

#### TREATMENT OF MAKEUP WATER

The treatments given to makeup waters withdrawn for cooling, process, boilerfeed, and sanitary and service purposes are summarized in table 18. This table does not include any treatment given to the makeup water prior to its entry into the plant. Of the 11 plants visited, 8 used once-through cooling water. Of the 4 plants that did not treat the once-through cooling water, 3 used ground waters with a hardness of less than 20 ppm; the other purchased water with a hardness of less than 60 ppm that had been clarified and chlorinated.

Of the 11 plants, 7 used recirculated cooling water; the treatment given to the makeup for recirculated cooling depending upon the quality of the water and the recirculation rate. Three plants, using naturally soft ground water, did not treat this makeup water. Of the 9 plants using process water, 6 plants did not treat the makeup water for process use. Three plants, manufacturing a latex that can be coagulated by calcium and magnesium, use a water supply having a hardness of less than 20 ppm, demineralize the process water, or use recovered steam condensate.



The makeup for boiler feed, at most plants, was treated to reduce the hardness, but a few plants used naturally soft ground water for boiler-feed makeup that does not require softening. Two plants purchased steam; the treatment of this makeup water is unknown. Many of the sanitary and service waters withdrawn from ground waters required no treatment; the most common treatments of the other water supplies were chlorination and softening.

TABLE 18.—*Treatment of makeup water at specialty-rubber plants*

[Does not include prior treatment of purchased water]

Treatment	Number of plants using indicated treatment				
	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water
None.....	4	3	6	-----	6
Clarification (sedimentation, coagulation, settling, and filtering).....	2	1	-----	1	2
Disinfection: Chlorine.....	4	2	-----	2	3
Prevention of corrosion and scale:					
Chromate and phosphate.....	2	3	-----	1	1
pH adjustment.....		2	-----	1	-----
Softening:					
Lime-soda.....	1	-----	-----	1	1
Ion exchange.....	-----	-----	3	2	1
Phosphate.....	-----	-----	-----	5	-----

#### QUANTITY OF WATER WITHDRAWN AND CONSUMED

The author did not find published information on the quantity of makeup water required by the specialty-rubber industry. The amounts of makeup water used for once-through cooling, recirculated cooling, process, boiler-feed, and sanitary and service in the plants visited in this survey are summarized in table 19. Most special-purpose synthetic rubbers are produced by exothermic polymerization reactions that are controlled by cooling waters. More than 90 percent of all water withdrawn by this industry is used for cooling. Special-purpose synthetic rubbers that are produced at low temperatures require considerably more cooling water than rubbers that are produced at temperatures greater than 70°F.

Once-through cooling water is used in the manufacture of nitrile, thiokol, and neoprene rubbers, thus accounting for about 77 percent of all makeup water withdrawn by this industry. Neoprene uses more once-through cooling water than do the thiokol rubbers, which use more than do the nitrile rubbers. The minimum amount of once-through cooling water required for nitrile rubber was 3.43 gallons per pound of finished rubber, for thiokol was 5.85 gallons per pound, and for neoprene was 60.3 gallons per pound.

TABLE 19.—Quantity of makeup water used in the manufacture of special-purpose synthetic rubbers

Water use	Once-through cooling water	Recirculated cooling water	Process water	Boiler-feed water	Sanitary and service water	All uses
Number of plants.....	8	7	10	11	11	11
Gallons per pound						
Minimum.....	3. 08	0. 156	0. 522	0. 356	0. 053	8. 45
Lower quartile.....	4. 64	1. 57	1. 27	. 578	. 313	17. 4
Median.....	20. 8	3. 43	4. 78	. 775	. 813	19. 8
Upper quartile.....	65. 0	5. 43	9. 45	1. 03	1. 81	62. 1
Maximum.....	97. 6	14. 1	14. 6	5. 56	13. 2	104
Million gallons per day						
Total for industry.....	77. 4	7. 5	3. 9	2. 2	2. 7	93. 8

Recirculated cooling water is used in the manufacture of butyl, neoprene, thiokol, and nitrile rubbers. Cooling water is circulated about 47 times on the average and as much as 170 times at one plant. The amount of water consumed in recirculating cooling water through cooling towers ranges from 1.37 to 6.1 gallons per pound of finished rubber. Butyl and neoprene use more recirculated cooling-water makeup than nitrile rubber; the minimum amount of makeup water for butyl rubber is 1.57 gallons per pound. The range of makeup water to the cooling towers for the specialty-rubber industry was from 0.156 to 14.1 gallons per pound of finished rubber.

The amount of makeup water for process use ranged from 0.52 to 14.6 gallons per pound. The minimum water requirements for butyl were negligible, for neoprene were 0.52 gallon per pound, for nitrile rubber were 0.548 gallon per pound, and for thiokol were 4.78 gallons per pound. The minimum amount of process water consumptively used in the manufacture of thiokol, neoprene, and butyl rubbers was negligible. The amount of process water consumptively used in the manufacture of nitrile rubber ranged from 0.05 to 7.1 gallons per pound of finished rubber.

The amount of makeup water for boiler feed for special-purpose synthetic rubbers ranged from 0.356 to 5.56 gallons per pound of finished rubber. The minimum amount of makeup water for boiler feed used by thiokol rubber was 0.055 gallon of water per pound of finished rubber, and by nitrile rubber was 0.15 gallon per pound. Most producers of special-purpose synthetic rubbers return less steam condensate than the amount of boiler-feed makeup water, and these

plants reported negligible consumptive use of boiler-feed water. Water used for sanitary and other services is used once and discharged to waste. The amount of makeup water for these purposes ranged from 0.053 to 13.2 gallons per pound of finished rubber.

#### TREATMENT OF WASTE WATERS

At capacity production, producers of special-purpose synthetic rubbers discharge more than 85 million gallons of water into surface streams each day. The largest part of this waste water comes from cooling and is given no treatment before discharge. Most plants operate settling basins or retention ponds to remove rubber particles and other settleable solids from waste water. Where necessary, most plants employ oil separators to retain the floatable materials. Generally the sanitary wastes are processed in Imhoff tanks or discharged to septic tanks and sanitary sewers.

#### FUTURE WATER REQUIREMENTS OF THE SYNTHETIC-RUBBER INDUSTRY

The styrene, butadiene, SBR, and specialty-rubber industries are young, and the production of these industries in the last 20 years has increased tremendously. The production of SBR is influenced by the imports of natural rubber, which have been decreasing, and by the production of special-purpose rubbers, which has been increasing. The production of SBR in 1959 was 32 percent higher than in 1958 (Chemical and Engineering News, 1960a). The U.S. Bureau of the Census (oral communication) anticipates that the SBR industry will expand production during the next 5 years at a rate of 50,000 tons per year. Unless production methods are changed radically, the production of 1.4 million long tons of SBR in 1964 will require a minimum of 43.8 million gallons of water daily, and perhaps as much as 1,602 million gallons. Radical changes, such as the "superfast polymerizations" predicted by Whitby (1954), would change the water-use requirements. These methods require at least twice as much deionized process water and also alter the cooling-water demands.

Since the birth of the SBR industry, the production of butadiene has been related closely to the demands of the synthetic-rubber industry. In 1956, the synthetic-rubber industry took 92 percent (85 percent by SBR) of the butadiene produced. To offset its dependence upon the SBR, the butadiene industry is striving for more markets in liquid polymers, intermediates, and *cis*-polybutadiene rubbers (Chemical and Engineering News, 1957b). Based on estimates of Petro-Tex (1958), the production of butadiene in 1964 will require 378 million gallons of water daily. No anticipated changes in pro-

duction methods would greatly change the water-use requirements. No production of butadiene from alcohol is anticipated except in the event of a national emergency.

In recent years, with the introduction of polystyrene plastics, styrene production has been becoming independent of SBR production; and in 1965 only about 29 percent of the styrene produced will be used in the production of SBR (Chemical and Engineering News, 1959). Production of styrene has been expanding and, according to Chemical and Engineering News (1960c), will increase another 40 percent by 1962. The anticipated production of styrene in 1964 (Chemical and Engineering News, 1959), will require about 180 million gallons of water daily. No anticipated changes in production methods would greatly alter the water-use requirements.

The production of special-purpose synthetic rubbers has been increasing radically. The following are the increases in 1959 over 1958: butyl, 42.5 percent; neoprene, 34 percent; nitrile rubber, 53.0 percent (Chemical and Engineering News, 1960a). Because of the radical changes in production and the introduction of the new rubbers like polyisoprene and polybutadiene, no estimates have been made of the future water-use requirements.

### SUMMARY

Most of the plants manufacturing styrene, butadiene, SBR, and special-purpose synthetic rubbers have adequate supplies of water for capacity production. Some plants would not have adequate water if their production were greatly expanded or if their water supply were decreased. Most plants use more than one source of supply, and some plants are exploring for additional water supplies. The sources of water supply are summarized in table 20. The salty waters from ocean, bay, and estuaries are used only for once-through cooling. The municipal sewage waters, after treatment, are used principally for makeup for boiler feed and recirculated cooling.

Most makeup waters from streams, lakes, and wells contain less than 1,000 ppm of dissolved solids, and most makeup waters used in the direct manufacture of SBR contain less than 500 ppm of dissolved solids. Salty water from the ocean, bays, and estuaries contain as much as 35,000 ppm of dissolved solids. The median hardness of the makeup waters used in the manufacture of butadiene, SBR, and special-purpose synthetic rubber was less than 80 ppm; the median hardness for makeup waters used in the styrene industry was less than 120 ppm. The maximum hardness of untreated makeup waters used for the production of butadiene was 342 ppm; for styrene, 404 ppm; for SBR, 495 ppm; and for special-purpose synthetic rubbers, 618 ppm.

TABLE 20.—*Sources of water used in the manufacture of styrene, butadiene, SBR, and special-purpose synthetic rubbers, in percent*

Source	Styrene	Butadiene	SBR	Special rubbers
Ground water .....	2	6	55	15
Surface water .....	56	3	45	85
Salty water .....	42	90	-----	-----
Municipal sewage .....	<1	<1	<1	-----

Most once-through cooling waters are given a minimum of treatment; the surface waters are commonly clarified and some surface and ground waters are chlorinated. The makeup waters to the cooling towers are commonly treated with chromates and phosphates to prevent corrosion, or are softened to prevent scale formation. For the most part, the process waters used in the manufacture of styrene and butadiene are not treated. The process waters used in the manufacture of SBR and special-purpose synthetic rubbers are softened to prevent coagulation of latex. Most makeup water for boiler feed is softened and deaerated to prevent scale formation and corrosion.

The makeup water requirements, at capacity production, of the industries manufacturing styrene, butadiene, SBR, and special-purpose synthetic rubbers are summarized in table 21. The total of 123 mgd withdrawn in 1959 for manufacturing SBR and special-purpose synthetic rubbers is about 36 percent greater than the 90.4 mgd withdrawn in 1954 reported by the Bureau of the Census (1957).

TABLE 21.—*Summary of makeup water requirements of industries manufacturing styrene, butadiene, SBR, and special-purpose synthetic rubbers during 1959*

Industry	Total makeup for industry (mgd)	Percent used for cooling	Percent used for process
Styrene .....	158	98	-----
Butadiene .....	429	96	-----
SBR .....	29	17	62
Special-purpose synthetic rubber .....	94	90	-----

The makeup water requirements vary according to the product, the process used, and the availability of water. The maximum and minimum amounts of makeup water, in gallons per pound of finished product, used to make the petrochemicals and rubbers are as follows:

Product	Minimum	Maximum
Styrene .....	2. 19	123
Butadiene .....	5. 38	221
SBR .....	. 883	10. 2
Special-purpose synthetic rubber .....	8. 45	104

Plants with no once-through cooling and with high recirculation rates withdrew minimum quantities of makeup water. Where once-through cooling was used and the recirculation rates were low, larger amounts of makeup water were withdrawn. The water in cooling towers was circulated as much as 83 times in the manufacture of butadiene; as much as 160 times in the making of styrene; as much as 170 times in the making of special-purpose synthetic rubber; and as much as 240 times in the SBR industry. Most plants reused the boiler-feed condensate less than 5 times.

The aggregate amount of makeup water used to produce a pound of SBR is the sum of water used to manufacture the styrene and butadiene in a pound of SBR and the amount of water used in the direct manufacture of SBR. The aggregate amount of makeup water used to produce 1 pound of SBR is calculated to range from 5.1 to 186.8 gallons per pound of finished rubber, which is 11,400 to 418,400 gallons per long ton of finished rubber.

At capacity production, the styrene industry consumptively uses about 3.1 million gallons of water a day; the butadiene industry, about 18.7 mgd; direct manufacture of SBR, about 3.2 mgd; and the specialty-rubber industry, about 8.6 mgd.

A large part of the waste water discharged by these industries is from once-through cooling and is commonly given no waste treatment. Generally, oils are removed from waste water by gravity separation or by steam distillation; settleable solids are commonly retained in settling basins; where necessary, effluent waters are neutralized and diluted by waste cooling waters.

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