

6.10 Synthetic Rubber

6.10.1 Emulsion Styrene-Butadiene Copolymers

6.10.1.1 General -

Two types of polymerization reaction are used to produce styrene-butadiene copolymers, the emulsion type and the solution type. This section addresses volatile organic compound (VOC) emissions from the manufacture of copolymers of styrene and butadiene made by emulsion polymerization processes. The emulsion products can be sold in either a granular solid form, known as crumb, or in a liquid form, known as latex.

Copolymers of styrene and butadiene can be made with properties ranging from those of a rubbery material to those of a very resilient plastic. Copolymers containing less than 45 weight percent styrene are known as styrene-butadiene rubber (SBR). As the styrene content is increased over 45 weight percent, the product becomes increasingly more plastic.

6.10.1.2 Emulsion Crumb Process -

As shown in Figure 6.10-1, fresh styrene and butadiene are piped separately to the manufacturing plant from the storage area. Polymerization of styrene and butadiene proceeds continuously through a train of reactors, with a residence time in each reactor of approximately 1 hour. The reaction product formed in the emulsion phase of the reaction mixture is a milky white emulsion called latex. The overall polymerization reaction ordinarily is not carried out beyond a 60 percent conversion of monomers to polymer, because the reaction rate falls off considerably beyond this point and product quality begins to deteriorate.

Because recovery of the unreacted monomers and their subsequent purification are essential to economical operation, unreacted butadiene and styrene from the emulsion crumb polymerization process normally are recovered. The latex emulsion is introduced to flash tanks where, using vacuum flashing, the unreacted butadiene is removed. The butadiene is then compressed, condensed, and pumped back to the tank farm storage area for subsequent reuse. The condenser tail gases and noncondensables pass through a butadiene adsorber/desorber unit, where more butadiene is recovered. Some noncondensables and VOC vapors pass to the atmosphere or, at some plants, to a flare system. The latex stream from the butadiene recovery area is then sent to the styrene recovery process, usually taking place in perforated plate steam stripping columns. From the styrene stripper, the latex is stored in blend tanks.

From this point in the manufacturing process, latex is processed continuously. The latex is pumped from the blend tanks to coagulation vessels, where dilute sulfuric acid (H_2SO_4 of pH 4 to 4.5) and sodium chloride solution are added. The acid and brine mixture causes the emulsion to break, releasing the styrene-butadiene copolymer as crumb product. The coagulation vessels are open to the atmosphere.

Leaving the coagulation process, the crumb and brine acid slurry is separated by screens into solid and liquid. The crumb product is processed in rotary presses that squeeze out most of the entrained water. The liquid (brine/acid) from the screening area and the rotary presses is cycled to the coagulation area for reuse.

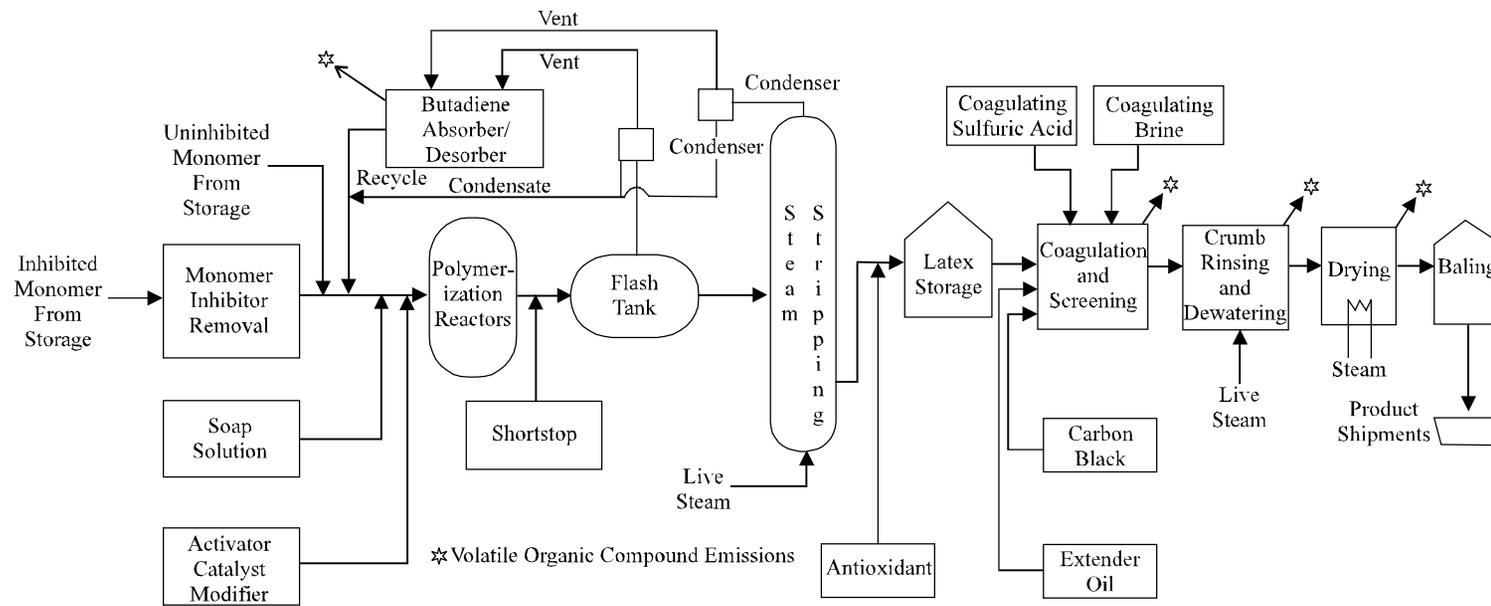


Figure 6.10-1. Typical process for crumb production by emulsion polymerization.

The partially dried crumb is then processed in a continuous belt dryer that blows hot air at approximately 93°C (200°F) across the crumb to complete the drying of the product. Some plants have installed single-pass dryers, where space permits, but most plants still use the triple-pass dryers, which were installed as original equipment in the 1940s. The dried product is baled and weighed before shipment.

6.10.1.3 Emulsion Latex Process -

Emulsion polymerization can also be used to produce latex products. These latex products have a wider range of properties and uses than do the crumb products, but the plants are usually much smaller. Latex production, shown in Figure 6.10-2, follows the same basic processing steps as emulsion crumb polymerization, with the exception of final product processing.

As in emulsion crumb polymerization, the monomers are piped to the processing plant from the storage area. The polymerization reaction is taken to near completion (98 to 99 percent conversion), and the recovery of unreacted monomers is therefore uneconomical. Process economy is directed towards maximum conversion of the monomers in one process trip.

Because most emulsion latex polymerization is done in a batch process, the number of reactors used for latex production is usually smaller than for crumb production. The latex is sent to a blowdown tank where, under vacuum, any unreacted butadiene and some unreacted styrene are removed from the latex. If the unreacted styrene content of the latex has not been reduced sufficiently to meet product specifications in the blowdown step, the latex is introduced to a series of steam stripping steps to reduce the content further. Any steam and styrene vapor from these stripping steps is taken overhead and is sent to a water-cooled condenser. Any uncondensables leaving the condenser are vented to the atmosphere.

After discharge from the blowdown tank or the styrene stripper, the latex is stored in process tanks. Stripped latex is passed through a series of screen filters to remove unwanted solids and is stored in blending tanks, where antioxidants are added and mixed. Finally, latex is pumped from the blending tanks to be packaged into drums or to be bulk loaded into railcars or tank trucks.

6.10.2 Emissions And Controls

Emission factors for emulsion styrene-butadiene copolymer production processes are presented in Table 6.10-1.

In the emulsion crumb process, uncontrolled noncondensed tail gases (VOCs) pass through a butadiene absorber control device, which is 90 percent efficient, to the atmosphere or, in some plants, to a flare stack.

No controls are presently employed for the blend tank and/or coagulation tank areas, on either crumb or latex facilities. Emissions from dryers in the crumb process and the monomer removal part of the latex process do not employ control devices.

Individual plant emissions may vary from the average values listed in Table 6.10-1 with facility age, size, and plant modification factors.

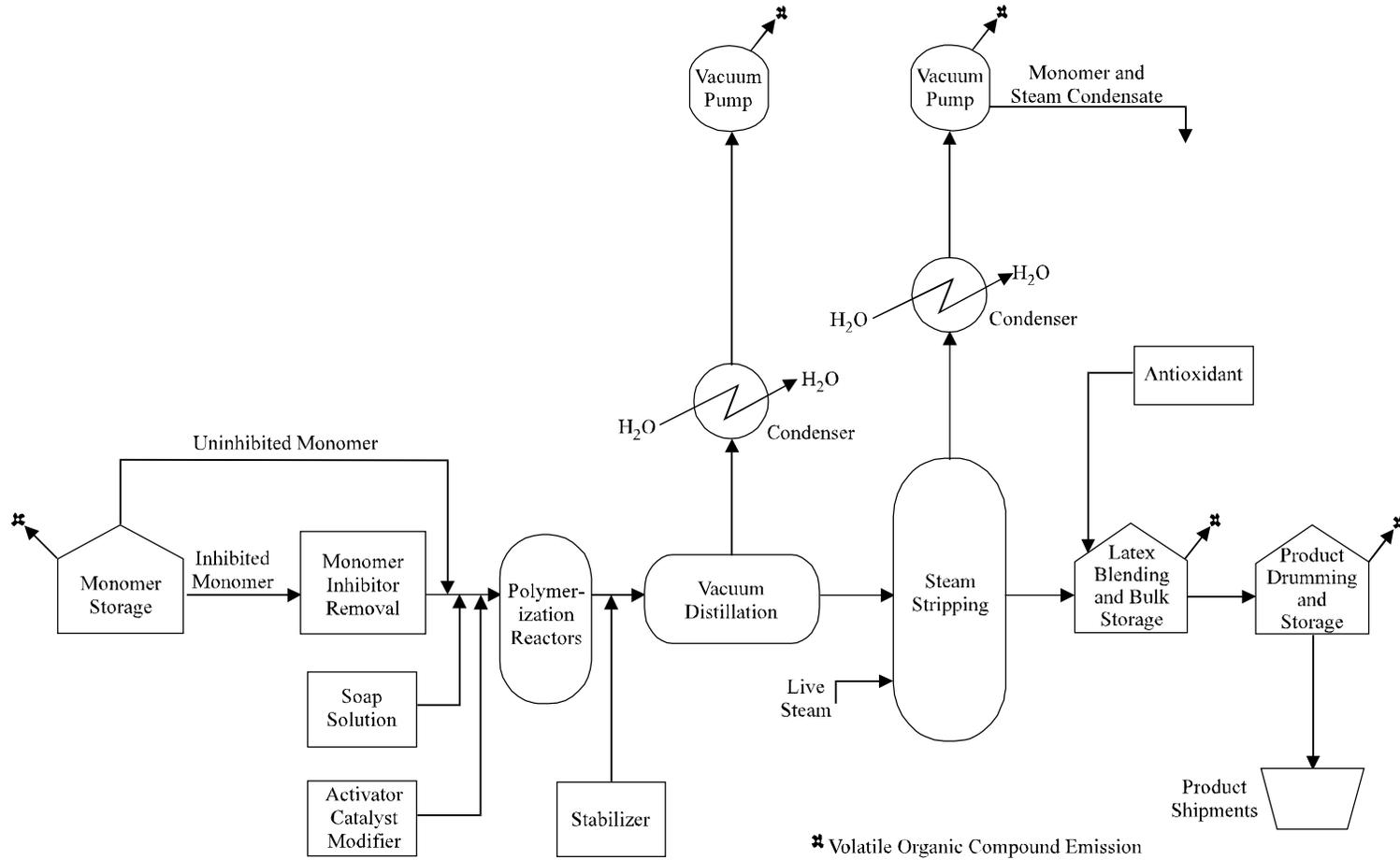


Figure 6.10-2. Typical process for latex production by emulsion polymerization.

Table 6.10-1 (Metric And English Units). EMISSION FACTORS FOR EMULSION STYRENE-BUTADIENE COPOLYMER PRODUCTION^a

EMISSION FACTOR RATING: B

Process	Volatile Organic Emissions ^b	
	g/kg	lb/ton
Emulsion Crumb		
Monomer recovery, uncontrolled ^c	2.6	5.2
Absorber vent	0.26	0.52
Blend/coagulation tank, uncontrolled ^d	0.42	0.84
Dryers ^e	2.51	5.02
Emulsion Latex		
Monomer removal condenser vent ^f	8.45	16.9
Blend tanks, uncontrolled ^f	0.1	0.2

^a Nonmethane VOC, mainly styrene and butadiene. For emulsion crumb and emulsion latex processes only. Factors for related equipment and operations (storage, fugitives, boilers, etc.) are presented in other sections of AP-42.

^b Expressed as units per unit of copolymer produced.

^c Average of 3 industry-supplied stack tests.

^d Average of 1 industry stack test and 2 industry-supplied emission estimates.

^e No controls available. Average of 3 industry-supplied stack tests and 1 industry estimate.

^f EPA estimates from industry supplied data, confirmed by industry.

References For Section 6.10

1. *Control Techniques Guideline* (Draft), EPA Contract No. 68-02-3168, GCA, Inc., Chapel Hill, NC, April 1981.
2. *Emulsion Styrene-Butadiene Copolymers: Background Document*, EPA Contract No. 68-02-3063, TRW Inc., Research Triangle Park, NC, May 1981.
3. Confidential written communication from C. Fabian, U. S. Environmental Protection Agency, Research Triangle Park, NC, to Styrene-Butadiene Rubber File (76/15B), July 16, 1981.