I.1 Emulsion Crumb Process

As shown in the general flow diagram depicted in Figure I.1, fresh styrene and butadiene are piped separately to the manufacturing plant from the storage area and, if necessary, the butadiene stream is passed through a caustic soda (NaOH) scrubber to remove any inhibitors that have been added to prevent premature polymerization during shipment and storage. The inhibitors are removed in a 20 percent caustic soda solution, which is subjected to continual makeup and blowdown (with subsequent purging). Before entering the polymerization reactor train, fresh monomer streams are mixed with the recycle styrene and butadiene streams from the monomer recovery areas of the process.

Soap solution, activator, catalyst, and modifier are added to the monomer mixture prior to entering the polymerization reactor train. The soap solution, which is generally a mixture of a rosin acid soap and a fatty acid soap, is used to maintain the monomers in an aqueous emulsion state. The activator is usually a hydroperoxide or a peroxysulfate which initiates the polymerization reaction by supplying free radicals. The catalyst assists in generating the free radicals more rapidly and at lower temperatures than is possible with thermal decomposition of the activator alone. The modifier is an additive used to adjust the chain length and molecular weight distribution of the rubber product during polymerization.

Polymerization of styrene and butadiene proceeds stepwise through a train of reactors on a continuous basis, with a residence time in each reactor of approximately 1 hour. The reaction is normally carried out at a temperature of $4^{o}C$ ($40^{o}F$) and produces excess heat which is removed by cooling coils implanted in each reactor. Use of the reactor train system contributes significantly to the manufacturing facility's high degree of flexibility in producing different grades of crumb rubber. The overall polymerization reaction is ordinarily carried out to a

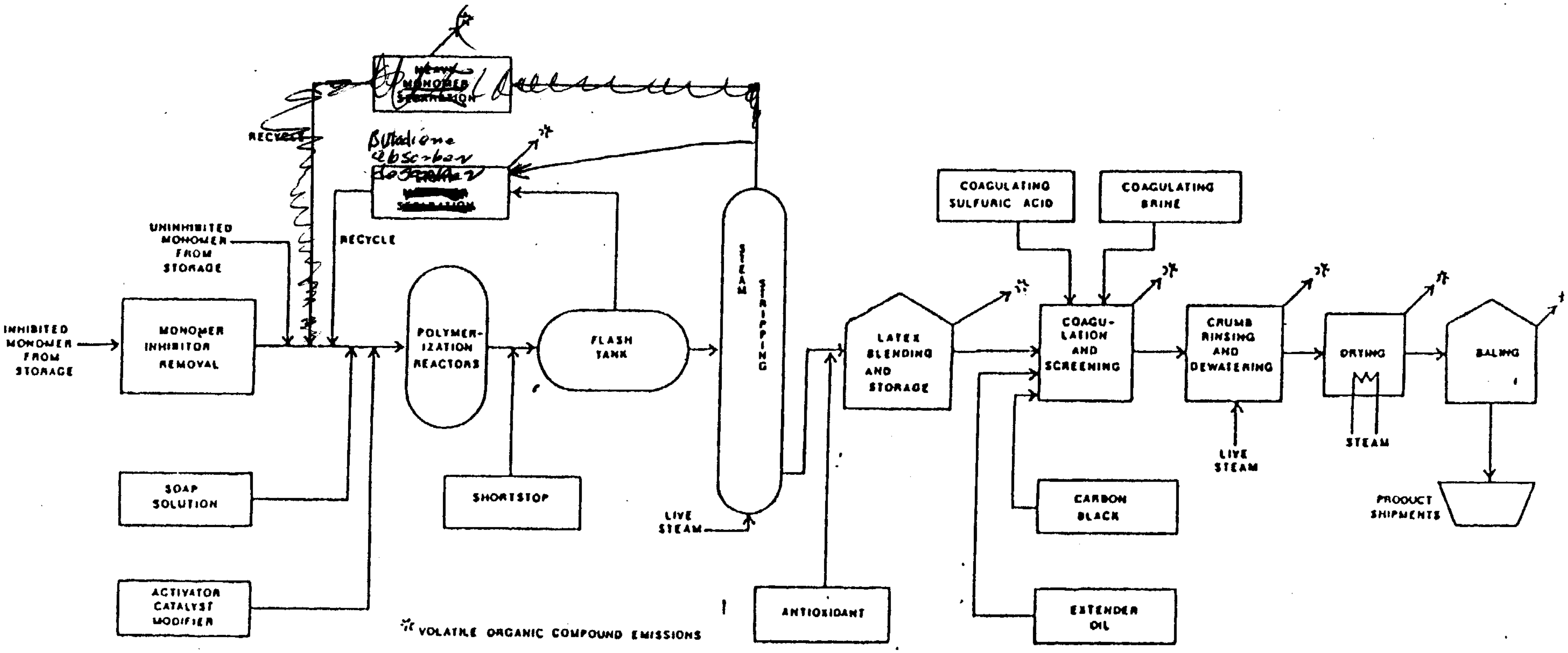

Figure I-1. Schematic flow diagram for crumb production by emulsion polymerization.

60 percent conversion of monomers to polymer, because the reaction rate falls off considerably beyond this point and product quality begins to deteriorate. The reaction product forms in the emulsion phase of the reaction mixture, yielding a milky-white emulsion called latex.

Shortstop solution, consisting mainly of sodium dimethyldithiocarbamate $((CH_3)_2NCS_2Na)$ or hydroquinone $(C_6H_6O_2)$, is added to the latex leaving the reactors to stop the polymerization process at the desired conversion. The "stopped" latex is held in blowdown tanks (which function as flow-regulating holding tanks) prior to recovery operations for the unreacted monomers.

Because recovery of the unreacted monomers and their subsequent purification are essential to economical operation, unreacted butadiene and styrene are recovered during the emulsion crumb polymerization process. The latex is introduced to flash tanks (using pressure flashing or vacuum flashing, either separately or in combination) where the overhead butadiene vapor stream is compressed, passed through a condenser, and finally processed in a kerosene absorber before it is vented to the atmosphere. The absorbed butadiene is recovered using either steam stripping, a pressure reduction, or a temperature increase, and is combined with the recovered butadiene from the condensers before being mixed with fresh butadiene for reactor feed. The latex stream from the butadiene recovery area is then sent to the styrene recovery process. Styrene removal from latex usually takes place in perforated-plate steam stripping columns. These operate at less than atmospheric pressure using steam injection at approximately 60^{o}C (140^{o}F). The steam and styrene vapor are condensed in a water-cooled condenser and sent to a decanter, where the water phase and styrene phase are separated. The styrene phase is sent to recycle storage tanks to be blended later with fresh styrene for reactor feed. The water from the decanter is discharged to the wastewater treatment system. Noncondensibles are directed through the butadiene compressors and are eventually scrubbed by the kerosene absorber before being vented to the atmosphere.

An antioxidant is added to the stripped latex in a blend tank to protect the polymer from attack by oxygen and ozone. The latex is then stabilized, and, as a result, different batches can be mixed.

The latex is pumped from the blend tanks to coagulation vessels where dilute sulfuric acid (H_2SO_4 with 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. Carbon black and extender oil can be added just prior to this step to produce a more specialized crumb product. The coagulation vessels are open to the atmosphere.

After leaving the coagulation process the crumb and brine acid slurry is separated into its solid and liquid phases using screens. The crumb product is processed in rotary presses that squeeze out most of the water entrained in the crumb. The liquid (brine acid) streams from the screening area and the rotary presses are recycled to the coagulation area for reuse.

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

I.2 Emissions Data

Data from Section 114 letters and one EPA test are available for emulsion crumb processes. Section 114 responses from the following plants were used in the development of emissions factors:

A. Texas-U.S. Chemical Company
B. Copolymer Rubber & Chemical Corporation
C. B. F. Goodrich Chemical Company
D. Phillips Petroleum Company
E. General Tire and Rubber Company
F. American Synthetic Rubber Company

I.3 Emissions Factors

The emission factors developed for the styrene-butadiene copolymers ~~CTG are used in this document~~. These factors were developed by grouping the process into three separate emission points (monomer recovery, blend/coagulation ta...s, and dryers). Uncontrolled ..nissions per unit of production from the Section 114 responses were averaged for each emission point and the resulting factors appear in Table I.1.

~~Emissions from the monomer recovery vent can be controlled with a thermal oxidation system. Thermal oxidation systems are capable of reducing VOC emissions by 98 percent. VOC vapors from the coagulation and blend tanks may be routed to the incinerator by a capture system designed in accordance with good engineering practice. Assuming a 90 percent capture efficiency and a 98 percent incineration efficiency, VOC emissions from coagulation and blend tanks could be reduced by 88 percent. No controls are available for dryers. The above level of control was chosen as "Reasonably Available Control Technology (RACT)" for the control techniques guideline (CTG) document. Emission factors for a plant controlled to the level specified as RACT also appear in Table I.1.~~

I.4 Calculation of Crumb Plant Emissions

1. Monomer recovery - absorber vent (35 Mg/yr, 15 SCFM, 65,000 ppm)

Three values of g VOC/kg net polymer were averaged. Emissions reported by three companies in lbs VOC/hr or lbs VOC/day were converted to lbs VOC/yr. These were divided by the annual production rate of net polymer. Net polymer consists of only styrene and butadiene and excludes any of the additives (extender oils, carbon black, etc.) that may be in the final product. Net polymer production rate was determined by multiplying the usage rate of each monomer by the percentage of the monomer that appears in the final product and summing these two values for styrene and butadiene. Most companies have declared the data used in these calculations confidential; thus, the actual data cannot be presented here. An example using hypothetical data is presented below to illustrate the methodology.

Example. Plant A used 20,000,000 gal of butadiene (5.19 lb/gal) and 5,000,000 gal of styrene (7.52 lb/day). 98% of the butadiene and 96% of the styrene appeared in the final polymer.

$$\text{Bd: } 20{,}000{,}000 \text{ gal} \times 5.19 \frac{\text{lb}}{\text{gal}} \times .98 = 101.7 \times 10^6 \text{ lb Bd}$$

$$\text{Sty: } 5{,}000{,}000 \text{ gal} \times 7.52 \frac{\text{lb}}{\text{gal}} \times .96 = 36.1 \times 10^6 \text{ lb Sty}$$

$$137.8 \times 10^6 \text{ lb}$$

Net polymer produced

Table I.1. VOC EMISSION FACTORS FOR EMULSION CRUMB PROCESS

	Emission point	Emission factor (grams of VOC emitted per kg of net copolymer)	
		Controlled	Uncontrolled
1.	Monomer recovery vent Uncontrolled Absorber Vent	.0 .~~0052~~ .32 lb/Ton	5.2 lb/Ton ~~0.26~~[a]
2.	Coagulation/blend tanks	.05	0.42[b]
3.	Dryers	2.51	2.51[a, b]
4.	Total process	2.52	3.19

[a] Emissions determined by stack test.

[b] Emissions determined by engineering estimate.

The plant reported emissions of 50 [illegible] VOC/day from the monomer recovery vent, or 18,250 lbs VOC/yr. The emission factor was calculated to be:

$$\frac{18{,}250 \text{ lbs VOC/yr}}{137.8 \times 10^{6} \text{ lb net polymer/yr}} = 1.32 \times 10^{-4} \frac{\text{lbs VOC}}{\text{lb net polymer}}$$

$$= .132 \text{ g VOC/kg net polymer.}$$

The values calculated from 114 data were: 0.08, 0.31, and 0.40 g VOC/kg net copolymer. The resulting average is 0.2525 g/kg, yielding 34.34 Mg VOC from a model plant with production of 136,000 Mg/yr.

Data from a single EPA emission test showed 6.7% VOC in a stream averaging 13.3 SCFM. Data from two 114 responses show 6.1% VOC in a stream of 13 SCFM and 6.8% VOC in 6 cfm (g/kg were not definable for these plants because the flows cannot be assumed constant and the production rates at the time were not reported). Data from the plants with emission factors of 0.08, 0.31, and 0.40 g VOC/kg net copolymer (above) show flowrates of 3.6 SCFM, 2.6 SCFM, and 4.04 SCFM, respectively. The flowrates and concentration were adjusted to equal 35 Mg in 8,760 hrs. The result is 6.49% (≈65,000 ppm) at 15 SCFM.

Data from one 114 letter were not used because they showed much lower emissions than the stack test data for that plant. One company reported only fugitive sources from monomer recovery, and another reported an unknown rate of VOC from the butadiene recovery vent.

2. Coagulation and blend tanks (57 Mg/yr, 1200 scfm, 700 ppm)

Data on coagulation and/or blend tanks were reported by only three companies on the 114 responses. Emissions reported on a lbs/day basis were converted to g VOC/kg net polymer using the methodology described above. One company reported 0.38 g/kg from both types of tanks, another reported 0.72 g/kg from coagulation tanks only, and the third reported 0.16 g/kg from blend tanks only. An average of these three yields 0.42 g/kg or 57.12 Mg/yr for 136,000 Mg/yr production.

The stack test showed 0.99 g/kg for the black rubber line, and 5.81 g/kg from the white rubber line. These tests were run on the roof vents using a pseudo-stack. Beside the fact that no explanation is available for the difference between the two lines, these tests would also measure dryer fugitives. They were therefore not considered in the average. The three figures included were arrived at by material balance.

Flowrates and concentrations:

57 Mg/yr from 2 coagulation tanks = 28.5 Mg from each
62,700 lbs/yr tank = 0.12 lbs VOC/min-tank = 0.0011 lb mole styrene for 4 ft diameter tanks: assume lip-type collector with capture of 50 cfm/square foot of tank
$50\ (\pi)\ (r^2)$ = 628 cfm @ 120°F = 572 scfm (68°F)
assume 600 scfm = 1.67 lb moles air/min
.0011 lb moles/1.67 = 686 ppm styrene, or approximately 700 ppm

Net: 2 streams, each 600 scfm, 700 ppm styrene; or
1 stream 1,200 scfm, 700 ppm sytrene

3. Dryers (341 Mg/yr; 60,000 SCFM; 80 ppm)

Dryer emissions reported by four plants were converted to 4.94 g/kg, 1.32 g/kg, 0.51, and 3.26 g/kg using the methodology described above. The first, third, and fourth responses are based on stack tests. The average of these four values yields 2.51 g/kg. The stack tests showed 2.45 g/kg from the black line (4 vents/dryer) and 4.31 g/kg from the white line (one vent). The white line was operating at a very low rate. Adding in the 2.45 does not change the average. Adding in both as one plant's value raises the average emission factor to 3.36. Due to uncertanties in the test, as well as the small effect of including it, only the four 114 letter values were used, yielding an average of 2.51 g/kg, or 341 Mg for the model plant producing 136,000 Mg/yr.

Flowrates from the stack test were scaled to the 136,000 Mg/yr model, yielding a vent flowrate of 61,000 scfm. For a flow of 60,000 scfm, concentration = 80 ppm VOC.

II.1 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 the crumb products, but the plants are typically much smaller. Latex production basically follows the same processing steps as emulsion crumb polymerization (shown schematically in Figure II.1) with the exception of the final product processing steps.

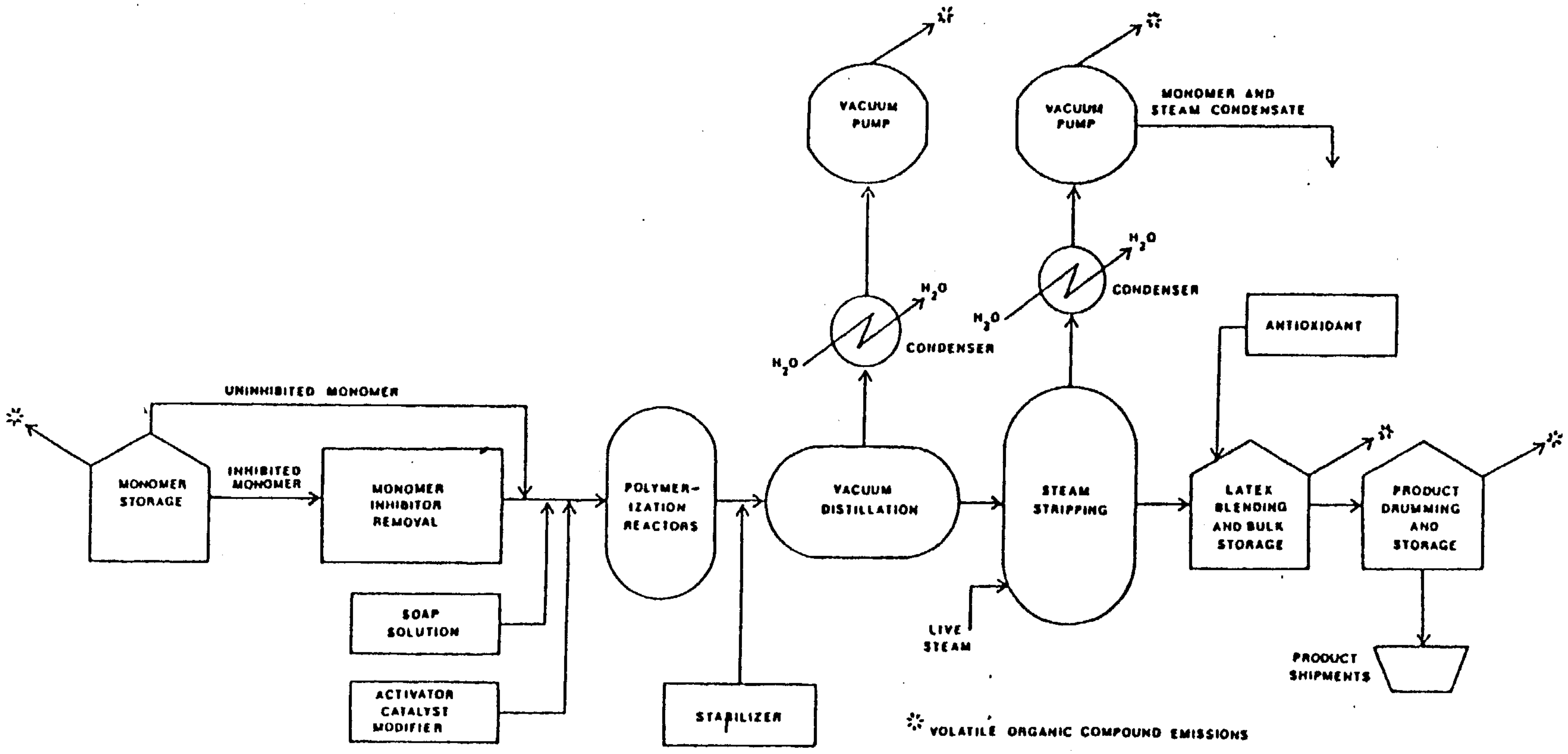

Figure II.1. Schematic flow diagram for latex production by emulsion polymerization.

As in emulsion crumb polymerization, the monomers are piped to the processing plant from the storage area. At the manufacturing facility, monomer inhibitors are scrubbed out using a caustic soda solution, if necessary. Soap solution, activator, and modifiers are then added to the monomers to produce a feed emulsion that is fed to the reactors. The reaction produces excess heat which is removed by cooling coils implanted in the reactor vessel. The polymerization reaction is taken essentially to completion (about 98 to 99 percent conversion), and, as a result, the recovery of unreacted monomers is uneconomical. Process economics are directed towards maximum conversion on a once-through basis.

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 polymerization reaction is normally carried out at 49°C (120°F), although some manufacturers (approximately 15 percent) use the "cold" polymerization process, which operates at 4°C (40°F). The degree of conversion of monomers to copolymer for the cold process is less than for the hot process, so recovery operations similar to those of a crumb plant are used in cold process latex plants. Also, crumb plants may produce latex as an end product using the same equipment that produces crumb by simply bypassing the coagulation and drying equipment.

Completion of the polymerization process requires from 6 to 24 hours. The latex is sent to a blowdown tank where, under an absolute pressure of 6.5 kPa (≈28 in. of mercury vacuum) and steam agitation, any unreacted butadiene and some unreacted styrene are removed from the latex. The overhead stream from the blowdown tank is sent to a water-cooled condenser where any condensibles are removed from the vapor stream and sent to a wastewater treatment facility. Noncondensibles from the condenser are discharged to the atmosphere.

After discharge from the blowdown tank the latex is stored in process tanks where additives are introduced based upon product specifications. Starting from this point in the manufacturing process to the final product storage for shipment, latex is processed on a continuous basis.

Subsequently, the latex is screened using shaker screens to remove any large, agglomerated solids present in 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 unreacted styrene content. Any steam and styrene vapor from these stripping steps is taken overhead and sent to a water-cooled condenser. Any noncondensibles leaving the condenser are vented to the atmosphere. The liquid stream from the condenser is discharged to the wastewater treatment system.

The stripped latex is then passed through a series of screen filters to remove unwanted large solids and is stored in blending tanks where antioxidants are mixed with the latex. Finally, latex is pumped from the blending tanks to be packaged into drums or bulk loaded into railcars or tank trucks.

II.2 Emissions Data

Emission data obtained by stack tests are available on two emulsion latex plants. The emissions data have been reviewed by three industry representatives and have been confirmed by them as being representative of their plants.

The process has been grouped into three separate emission points. These are: 1) monomer recovery-butadiene, 2) monomer recovery-styrene, and 3) blend tanks. Table II.1 presents the uncontrolled and controlled emission factors for each emission point.

VOC emissions from an emulsion latex plant may be controlled by incinerating the vapors from the styrene and butadiene removal vents and installing a vapor capture system in the latex blend tank that will route the vapors to the incinerator. Incineration of the vapors exiting the styrene and butadiene removal vents can be 98 percent efficient. Assuming a 90 percent capture efficiency and a 98 percent incineration efficiency, this control system will reduce VOC emissions from blend tanks by 88 percent. The above level of control was selected as RACT for emulsion latex plants in the CTG.

Table II.1. VOC EMISSION FACTORS FOR EMULSION LATEX PROCESSES

	Emission point	Emission factor (grams of VOC emitted per kg of net copolymer) Controlled	Uncontrolled
1.	Monomer removal - styrene	0.17	8.3
2.	Monomer removal - butadiene	.003	0.15
3.	Blend tank	.01	0.1
4.	Total process	0.183	8.55

II.3 Calculation of Latex Plant Emissions

Two values for emissions from monomer stripping are available from 114 responses: 7.76 g/kg from a plant with 53% styrene/47% butadiene, 6.55 g/kg from a plant with 43% styrene/57% butadiene.

The second value (6.55) cannot be split into butadiene and styrene removal streams. The first value (7.76) was split into 7.72 g/kg from butadiene stripping, 0.14 g/kg from styrene stripping.

Based on these numbers, a letter was sent to 9 plants showing a plant with 40% styrene, 60% butadiene and emission factors of 8.52 g/kg butadiene stripping/0.15 g/kg styrene stripping; 0.11 g/kg blend; total = 8.78 g/kg. Blend tank emissions were estimated from a test report.

One plant responded by providing the following:

1.78 g/kg bd stripping; 1.48 g/kg styrene; 0.12 g/kg blend
Total = 3.38 g/kg for a plant of approximately 50% styrene/ 50% butadiene (assumed)

Three companies answered that the 8.78 g/kg was representative.

The two plants originally reporting on 114's also reported that 1.5% of butadiene purchased went into air; one of these plants reported that 0.1% of styrene purchased went into air, 0.9% into effluent. Neglecting fugitive emissions, the following expression can be used to estimate emissions from a latex plant with no recovery operations:

(1) Total VOC emissions = (100-% conv) (10) (wt. frac. butadiene) + (wt. frac. styrene) (2/3) (100-% conv) g/kg

This assumes a water-cooled condenser removes 90% of the stripped styrene and discharges it as effluent, and no control on butadiene stripping.

There are three major types of SBR: 23% styrene - rubber form made by crumb plants (usually "cold" process); 46% styrene - carboxylated carpet backing (usually "hot" process); 60% styrene - paints, paper filler (usually "hot" process).

For example, since most latex is made by the hot process, a model plant producing a product of 46% styrene yields the following: at 98.5% conversion, equation (1) yields 8.56 g/kg. Allowing 0.15 and 0.11 for styrene stripping and blending, respectively, as most plants acknowledged, leaves 8.30 g/kg from butadiene stripping. (Prorating 0.15 and 0.11 down by ratio of 8.78/8.56 makes no difference to second decimal place.)

These emission factors yield the following:

Production	Butadiene Stripping	Styrene Stripping	Blend Tanks
27,000 Mg	224 kg/yr	4 kg/yr	3 kg/yr
3,750 Mg	31 kg/yr	0.6 kg/yr	0.4 kg/yr

III. SBR Emission Factor Calculation Summary

Table I.1 (Emulsion Crumb Plants) AP-42 Table 5.20-1

1. Monomer Recovery Vent

Uncontrolled emissions: $$\frac{0.08\ g/kg + 0.31\ g/kg + 0.40\ g/kg}{3} = 0.26\ g/kg$$

Controlled: assuming 98% control efficiency, = 0.26 (0.02) = .0052 g/kg

2. Blending/Coagulation

Uncontrolled = $$\frac{0.38 + 0.72 + 0.16}{3} = 0.42\ g/kg$$

Controlled: assuming 88% control efficiency, = 0.42 (0.12) = .05 g/kg

3. Dryers

Uncontrolled: $$\frac{4.94 + 1.32 + 0.51 + 3.26}{4} = 2.51\ g/kg$$

(No controls are available)

Table II.1 (Emulsion Latex Plants) AP-42 Table 5.20.~~2~~-1

Emulsion latex emission factors were calculated as explained in the background document text.

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