SNAP CODES: **040512**
040513
040514

SOURCE ACTIVITY TITLES: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Styrene Butadiene
Styrene Butadiene Latex
Styrene Butadiene Rubber

NOSE CODE: **105.09.85**
105.09.86
105.09.87

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

The process described or the polymerisation reaction to produce styrene-butadiene copolymers, is the emulsion polymerisation.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of all styrene butadiene (SB) plants contributes on average 0.02% to the total NMVOC emission in the to Corinair 90 reporting countries.

(These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006)).[1]

3 GENERAL

3.1 Description

The copolymerization of styrene and butadiene can be done in several ways. In this guidebook two ways are distinguished: styrene butadiene latex and styrene butadiene rubber.

<u>SB latex</u>

- SB latex is made by emulsion polymerization. The reaction is started with free-radical initiators. The emulsion consists for 5 - 10 wt.% of non-rubber, more than half being emulsifiers (others components: initiators, modifiers, inorganic salts, free alkali and short stops). A polymer string consists of random blocks of styrene and butadiene.
- Another way of producing SB latex is emulsification of SB rubber: SB rubber particles are dissolved in water with dispersing and wetting agents.

[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

<u>SB rubber</u>
The production of SB rubber can be done in several ways:

- anionic polymerization.
  The reaction can be started with reaction of the initiator with either styrene or butadiene.
  - When the reaction starts with styrene, the propagation can be with styrene or butadiene.
    Reaction conditions:
    - in an inert hydrocarbon solvent under a nitrogen blanket (no water or oxygen may be present).
    - temperature: 5 °C ('cold'); conversion 60 - 80%.
    - temperature: 50 - 65 °C ('hot'); conversion >90%.
  - When the reaction starts with butadiene, all butadiene will first react and then the styrene to form a block copolymer of the type SB and/or SBS.
    The length of the polymer can be varied by varying the amount of initiator.
    Statistical (random) copolymerization is possible by adding 'donators' like ether or tertiary amines.
- polymerization with redox-system.
  The redox-system: oxidizing compounds (peroxides), reducing compounds and heavy metalions, like Fe^{2+}.

  Operation temperature is 5 °C; the low(er) temperature contributes to the regular structure of the polymer (the polymer has more styrene blocks in the 'backbone', more *tert*-1,4-butadiene is incorporated, the branches are shorter and the percentage of gel in the polymer is lower.

3.2 Definitions

Latex: a colloidal aqueous emulsion of an elastomer.
Synthetic latex: latex with in situ polymerised elastomer.
Artificial latex : latex from reclaimed rubber polymers.

3.3 Techniques

See section 3.1.

3.4 Emissions

The VOC emission from SB rubber production can be subdivided as follows:

Cause of the emission	**[1]**
leakage losses from appendages, pumps, etc.	99.9%
flaring, disruptions	0.0%
losses due to storage and handling	0.0%
combustion emissions	0.0%
other process emissions	0.1%

3.5 Controls

The losses due to leakage can be limited by use better abatement methods.

4 SIMPLER METHODOLOGY

Use of an overall emission factor for the SB production (latex or rubber) emissions. The amount of emitted VOC is then directly related to the SB production.

5 DETAILED METHODOLOGY

A more detailed methodology is used by the United States EPA.

Instead of one emission factor for the whole plant, emission factors for each piece of equipment, such as valves, flanges, etc., can be used. Each type of equipment has its own emission factor. The total emission factor for the plant can be calculated by first multiplying each equipment emission factor by the number of pieces of that type of equipment, than adding up the emission for each type of equipment. So, for this method it is necessary to know how many pieces of each type of equipment are present in the plant.

6 RELEVANT ACTIVITY STATISTICS

The Rubber Statistical Bulletin provides relevant data on SB polymer production.

7 POINT SOURCE CRITERIA

SB plants can be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1: Emission factors for SB polymer

Source	Emission factor (kg/ton)	Quality Code
Netherlands Emission Inventory 1987 [1]	5 - 10	E
US Environmental Protection Agency AP-42 [2]	5.8 - 8.6	E
US Environmental Protection Agency Airchief 1993 [3]	2.9 - 7.8	E

The World bank handbook (5) gives for an SBR plant a factor of 3 to 10 kg/ton product.
The Handbook of Emission factors (6) gives factors for butadiene an emission factor of 0.1 to 0.5 kg/ton and for styrene 0.1 to 2.0 kg/ton.

**Table 8.2 Emission factors for Emulsion polymerisation of SB polymer. (4)
US Airchief gives for 1995 the following table (quality class B):**

Process step	Emission styrene and butadiene gr/kg product
Monomer recovery uncontrolled	2.6
Absorber vent	0.26
Blend coagulation tank uncontrolled	0.42
Dryers	2.51

Table 8.3: Emission factors for SB latex

Source	factor (kg/ton)	Quality Code
Netherlands Emission inventory 1987 [1]	10	E
US Environmental Protection agency AP-42 [2]	8.55	E
US Environmental Protection Agency Airchief 1993 [3]	7.8	E

Table 8.4 Emission factors for Emulsion polymerisation of SB latex according to US Airchief 1995. (quality class B) (4)

Process step	
Monomer removal condenser vent	8.45 gr/kg
Blend tanks uncontrolled	0.1 gr/kg

Table 8.5: Emission factors for SB rubber

Source	factor (kg/ton)	Quality Code
Netherlands Emission Inventory 1992 [1]	3.7	C
Netherlands Emission Inventory 1987 [2]	5	C
US Environmental Protection Agency AP-42 [3]	5.8	E
US Environmental Protection Agency Airchief 1993 [4]	2.9	E

9 SPECIES PROFILES

Table 9.1 lists the overall VOC profile for SB latex.

Table 9.1: The overall VOC emission profile for SB latex plants

Compound	NL Emission Inventory(1)
Styrene	75 %
1,3-butadiene	25 %

Tables 9.2 and 9.3 list the VOC profile respectively for the different sources and the overall profile for SB rubber.

Table 9.2: The composition of the VOC emissions for the different sources is [1]:

	ethylene	acrylonitrile	styrene	Toluene	other HC's
Leakage loss	0.1%	0.0%	86.8%	0.1%	13.0%
flaring and disruptions	-	-	-	-	-
storage and handling loss	-	-	-	-	-
Combustion	-	-	-	-	-
other process emissions	0%	0%	0%	0%	100%

Table 9.3: The overall VOC emission profile for plants

	NL Emission Inventory [1]	NL Emission Inventory [2]
Styrene	87	95 %
1,3-butadiene	incl. in HC's	5 %
other HC's	13	-

10 UNCERTAINTY ESTIMATES

Depending on the fit of the overall emission factors

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Not relevant

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not relevant,

13 TEMPORAL DISAGGREGATION CRITERIA

The plants are operated in continuous flow, thus no variation in emissions diurnally or seasonally is expected to occur.

14 ADDITIONAL COMMENTS

No additional comments

15 SUPPLEMENTARY DOCUMENTS

- Kirk-Othmer, Encyclopedia of chemical technology, Volume 20, 3rd edition (1984) & Volume 9, 4th edition (1994).
- Winnacker-Küchler, Chemische Technologie, Organische Technologie II, Band 6 4. Auflage (1982) (in German).

16 VERIFICATION PROCEDURES

Verification of the emissions can be done by comparing with measurements in the individual plant or by setting up a mass balance over the entire plant.

17 REFERENCES

1 Emission Inventory in the Netherlands 1987
2 US Environmental Protection agency AP-42, 1985
3 US Environmental Protection Agency Airchief 1993
4 US Environmental Protection Agency Airchief 1995
5 World Bank Group Pollution Prevention and Abatement Handbook (1998)
6 Handbook of Emission Factors Part 2 Industrial sources. Ministry of Housing Spatial Planning and the Environment M.E.Reinders (editor) (1983)

18 BIBLIOGRAPHY

Detailed process descriptions to be found on Internet

19 RELEASE VERSION, DATE AND SOURCE

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20. POINT OF ENQUIRY

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