**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

#### 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 a country. The contributions of styrene butadiene latex and rubber plants alone are not known.

#### 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.

### SB latex

- 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.

### SB rubber

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 of certain types of seals and application of double seals near pumps.

#### 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 if individual plant data are available.

## 8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

**Table 8.1: Emission factors for SB polymer** 

Source	Emission	Quality Code	
	factor (kg/ton)		
TNO Emission Registration 1987 [1]	5 - 10	E	
EPA AP-42 [2]	5.8 - 8.6	Е	
EPA Airchief 1993 [3]	2.9 - 7.8	Е	

**Table 8.2: Emission factors for SB latex** 

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1987 [1]	10	E
EPA AP-42 [2]	8.55	E
EPA Airchief 1993 [3]	7.8	Е

Table 8.3: Emission factors for SB rubber

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1992 [1]	3.7	C
TNO Emission Registration 1987 [2]	5	С
EPA AP-42 [3]	5.8	Е
EPA Airchief 1993 [4]	2.9	Е

### 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	TNO ER [1]
styrene	75 %
1,3-butadiene	25 %
other HC's	

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

	TNO ER [1]	TNO ER [2]
styrene	87	95 %
1,3-butadiene	incl. in HC's	5 %
other HC's	13	-

#### 10 UNCERTAINTY ESTIMATES

# 11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

#### 12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

#### 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

#### 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 TNO Emission Registration 1987
- 2 US EPA AP-42, 1985
- 3 US EPA Airchief 1993, CD-ROM

#### 18 BIBLIOGRAPHY

## 19 RELEASE VERSION, DATE AND SOURCE

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## 20 POINT OF ENQUIRY

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