SNAP CODE: **040508**

SOURCE ACTIVITY TITLE: **PROCESSES IN ORGANIC CHEMICAL INDUSTRIES (BULK PRODUCTION)**
Polyvinylchloride

NOSE CODE: **105.09.82**

NFR CODE: **2 B 5**

1 ACTIVITIES INCLUDED

Polyvinylchloride is made by polymerizing vinylchloride. This can be done in several ways: mass, emulsion or suspension polymerization. All processes use free-radical initiator.

2 CONTRIBUTION TO TOTAL EMISSIONS

The NMVOC emission of polyvinylchloride plants contributes on average <0.01% to the total NMVOC emission in a country.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Polyvinylchloride	040508	-	-	0.1	-	-	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

3 GENERAL

3.1 Description

The different processes are:

- Mass polymerization; a batch process.
  This is a two stage process. In the first stage, the liquid vinylchloride monomer with an initiator is prepolymerized for 1 - 1.5 hours until 7 - 10% monomer conversion is reached. The grains resulting from this stage function as skeleton seeds for growing in the second stage.
  In the second stage, a mixture of the effluent from the first reactor, extra monomer and initiator are fed to an autoclave. The reaction is stopped as the pressure drops and no free liquid monomer is available; the free liquid monomer is needed for heat removal by a condensor. The unreacted monomer, adsorbed in the polymer grains, is removed by vacuum and recovered by vapor compression and condensation in a recycle condensor. The reaction temperature is 50 - 70 °C.

- Suspension polymerization; a batch process.
  Vinylchloride monomer is dispersed in water by agitation. Polymerization starts by adding monomer-soluble initiators and addition of suspension stabilizers and suspending agents minimizes coalescence of the grains. The reaction temperature is used for the control of the M_w and varies between 45 - 75 °C. Reactor pressure is between 800 - 1200 kPa. Reaction is carried out till 85% conversion is reached.

  After polymerization most unreacted monomer is recovered in a dump tank. The remaining monomer is stripped from the polymer with steam. The waste water is separated in a centrifugator. The PVC resin is dried with hot air and stored.

- Emulsion polymerization; batch, semi-continuous or continuous.
  Vinylchloride monomer is emulsified in water by means of surface-active agents. The monomer is thus present as droplets and a small fraction is dissolved in micelles. Water-soluble initiator is added and polymerization starts in the micelles. Monomer is added to the latex particles (=micelles) by diffusion from the emulsion droplets through the aqueous fase.

  Batch: all components in reactor; polymerization is stopped when the yield is reached.

  Semi-continuous: emulgator is continuously added during the polymerization.

  Continuous: water, initiator, monomer and emulgator are added at the top of the reactor. The PVC latex is removed at the bottom of the reactor. The latex is degassified and dried; the resulting solid PVC is stored.

3.2 Definitions

3.3 Techniques

See section 3.1.

3.4 Emissions

The major emissions to air are: vinylchloride and methane. Methane is emitted due to combustion and vinylchloride due to leakage and storage loss.

For the Netherlands, the VOC emission due to polyvinylchloride production is 55 ton/y. This emission is related to a production of 387 kton/y and a capacity of 409 kton/y (data for 1992). The VOC emission can be subdivided as follows:

Emission source	[1]
Leakage losses from appendages, pumps, etc.	94.4%
Flaring, disruptions	0 %
Losses due to storage and handling	5.5%
Combustion emissions	0.1%
Other process emissions	0 %

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

The simpler methodology would involve the use of an overall emission factor for the PVC production to estimate total emissions. The amount of emitted VOC is thus directly related to the PVC 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, like 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 multiplying each equipment emission factor by the number of pieces of that 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

Table 6.1.: Polyvinylchloride capacity in some countries

Country or Region	kton/y	source	year
Latin America	1410	EurChemNews 13/4/92	1991
Indonesia	164	EurChemNews 1/6/92	1990?

Table 6.2.: Polyvinylchloride production in some countries and regions for 1990

Country or Region	kton/y	source
France	1028	Chem&EngNews 29/6/92
Germany, West	1323	Chem&EngNews 29/6/92
Italy	618	Chem&EngNews 29/6/92
U.K.	349	Chem&EngNews 29/6/92
Japan	2049	Chem&EngNews 29/6/92
Korea, South	541	Chem&EngNews 29/6/92
Taiwan	921	Chem&EngNews 29/6/92
U.S.S.R.	606	Chem&EngNews 13/4/92
Poland	199[1]	EurChemNews 9/12/91

1) Production in 1989

7 POINT SOURCE CRITERIA

PVC production plants can be considered as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1.: Emission factors for Polyvinylchloride production :

Source	factor (kg/ton)	Quality Code
TNO Emission Registration 1992 [1]	0.14	C
TNO Emission Registration 1987 [2]	3 (emulsion)	C
TNO Emission Registration 1987 [2]	1.5 (suspension)	C
EPA [3]	8.5	E

9 SPECIES PROFILES

Tables 9.1 and 9.2 list the VOC profile respectively for the different sources and the overall profile.

Table 9.1.: The composition of the VOC emissions for the different sources is [1]:

	methane	ethylene	vinylchloride	benzene	other HC's
Leakage loss	0%	0%	100%	0%	0%
Flaring and disruptions	-	-	-	-	-
Storage and handling loss	0%	0%	100%	0%	0%
Combustion	60%	10%	0%	1%	29%
Other process emissions	-	-	-	-	-

Table 9.2.: The overall VOC emission profile for polyvinylchloride plants

	TNO ER [1]	EPA [4]
Methane	0.1%	-
Ethylene	0%	-
Vinylchloride	99.9%	100%
Benzene	0%	-
Other HC's	0%	-

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 23, 3rd edition (1983)
- 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 1992
2 TNO Emission Registration 1987
3 EPA AP-42
4 EPA Airchief 1991

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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20 POINT OF ENQUIRY

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