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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

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ENVIRONMENT IMPACT ANALYSIS OF THE MANUFACTURE OF BENOMYL

1. INFORMATION SOURCES

Process I: commercial scale manufacturer.

Process II: pilot plant level R&D of the same manufacturer.

2. PROCESS INFORMATION

2.1 Schematic illustration of the syntheses

2.2 Definition of educts, intermediates and products

The chemical formulae and molecular weights of compounds used in the synthesis of Benomyl are listed in appendix 1.

2.3 Chemical reactions

(a) $2CaNCN + 2H_2O + 2ClCOOCH_3 = 2NCNHCOOCH_3 + CaCl_2 + Ca(OH)_2$

160.22 + 36.03 + 189.00 200.16 110.99 74.10

(b) $NCNHCOOCH_3 + C_6H_4(NH_2)_2 + HCl = C_9H_9N_3O_2 + NH_4Cl$

100.08 108.14 36.46 191.19 53.49

(c) $C_9H_9N_3O_2 + H_3C(CH_2)_3NCO = C_{14}H_{18}N_4O_3$

191.19 99.13 290.32

(d) $HCOOC_2H_5 + H_3C(CH_2)_3NH_2 = H_3C(CH_2)_3NHCHO + C_2H_5OH$

74.08 73.14 101.15 46.07

(e) $H_3C(CH_2)_3NHCHO + SO_2Cl_2 = H_3C(CH_2)_3NHCClO + SO_2 + HCl$

101.15 134.98 135.59 64.07 36.46

(f) $2C_9H_9N_3O_2 + 2H_3C(CH_2)_3NHCClO + CaCO_3 = 2C_{14}H_{18}N_4O_3 + CaCl_2 + H_2O + CO_2$

382.38 271.18 100.09 580.64 110.99 18.02 44.01

Combined equation of the synthesis

(g) **Process I**

$2CaNCN + 2ClCOOCH_3 + 2H_2O + 2HCl + 2C_6H_4(NH_2)_2 + 2H_3C(CH_2)_3NCO =$

160.22 189.00 36.03 72.92 216.28 198.26

$= 2C_{14}H_{18}N_4O_3 + CaCl_2 + Ca(OH)_2 + 2NH_4Cl$

580.64 110.99 74.10 106.98

(h) **Process II**

$2CaNCN + 2ClCOOCH_3 + 2H_2O + 2HCl + 2C_6H_4(NH_2)_2 + HCOOC_2H_5 +$

160.22 189.00 36.03 72.92 216.28 148.16

$+ H_3C(CH_2)_3NH_2 + 2SO_2Cl_2 + CaCC_3 = 2C_{14}H_{18}N_4O_3 + 2CaCl_2 + Ca(OH)_2 +$

146.28 269.96 100.09 580.64 221.98 74.10

$+ 2NH_4Cl + 2C_2H_5OH + 2SO_2 + 2HCl + H_2O + CO_2$

106.98 92.14 128.14 72.92 18.02 44.01

2.4 Other reactions used in the analysis

(i) $SO_2 + 2NaOH = Na_2SO_3 + H_2O$

64.07 80.00 126.06 18.02

(j) $SO_2Cl_2 + 4NaOH = 2NaCl + Na_2SO_4 + 2H_2O$

134.96 160.00 116.88 142.06 36.02

(k) $HCl + NaOH = NaCl + H_2O$

36.46 40.00 58.44 18.02

(l) $N\equiv C-NH-COOCH_3 + 3H_2O + 2HCl = 2NH_4Cl + 2CO_2 + CH_3OH$

100.08 54.05 72.92 106.98 88.02 32.04

2.5 Chemical conversion coefficients

The molar chemical input conversion factors, F, and the material input coefficients, f, are given in table 1.

Table 1. Material requirements for benomyl synthesis (quantity/1000 kg of output)

Material input	F	f1	f2
Calcium cyanamide	276	628	644
Methylchlorocarbonate	326	454	465
o-Phenylenediamine	372	407	417
Carbendazim	659	686	705
Butylisocyanate	341	355	-
Ethyl formate	255	-	393
Butylamine	252	-	353
Butylformamide	348	-	483
Sulfuryl chloride	465	-	760
Butylcarbamyl chloride	467	-	644
Calcium carbonate	172	-	185

Table 2. Yields in benomyl synthesis (percentage)

Material input	Process I	Process II
Calcium cyanamide	43.9	42.9
Methylchlorocarbonate	71.8	70.1
o-Phenylenediamine	91.6	89.2
Butylisocyanate	96.1	-
Butylamine	-	71.4
Ethyl formate	-	64.9
Sulfuryl chloride	-	61.2
Butylformamide	-	72.0
Butylcarbamyl chloride	-	72.5
Carbendazim	96.1	93.5

2.6 Brief description of processes

Calcium cyanamide is dispersed in water and reacted with methyl chlorocarbonate at a temperature of 40 to 45°C. The mixture is filtered, o-phenylenediamine is added to the filtrate, the temperature is elevated to 90°C and the pH is adjusted between 4.0 and 4.5 to facilitate the formation of the benzimidazole ring.

The reaction mixture is cooled, solids are allowed to settle down, the supernatant liquid is pumped off and acetone is added to the aqueous suspension. Carbendazim is reacted either with butylisocyanate or with butylcarbamyl chloride at a temperature of about 20°C to yield benomyl. The mixture is cooled down to 0°C, benomyl is separated by filtration and dried.

Butylcarbamyl chloride is produced in two steps at room temperature. In step 1, the by-product ethanol is distilled off in vacuum. Hydrogen chloride and sulfur dioxide gases are by-produced in step 2 which are scrubbed in water and an aqueous alkali solution, respectively. Hydrochloric acid can be used in carbendazim synthesis whereas sodium sulfite solution can be sold for other industrial purposes.

3. ENVIRONMENT IMPACT ASSESSMENT

Round 2,500 kg of materials are used for the production of 1,000 kg of benomyl using o-phenylenediamine as the feedstock (process I). The same figure is 4,020 kg, if the intermediate butylcarbamoyl chloride is synthetized from butylamine.

3.1 Material flow and informative material balance

A flow diagram is illustrated and related material balance calculations are summarized in appendices 2 and 3, respectively.

3.2 Material requirements

3.2.1 Material consumption by nature of inputs

Reactants	Process I		Process II	
Calcium cyanamide	628 kg		644 kg	
Methylchlorocarbonate	454 kg		465 kg	
o-Phenylenediamine	407 kg		417 kg	
Butylisocyanate	355 kg			
Butylamine			353 kg	
Ethyl formate			393 kg	
Sulfuryl chloride			760 kg	
	1,844 kg	73.9%	3,032 kg	75.5%
Reaction promoters				
Hydrochloric acid	213 kg		219 kg	
Calcium carbonate			185 kg	
	213 kg	8.5%	404 kg	10.1%
Solvents				
Acetone	440 kg	17.6%	415 kg	11.2%
Auxiliary materials				
Sodium hydroxide	______	_____	129 kg	3.2%
Total	2,497 kg	100.0%	4,016 kg	100.0%

Reactants account for about three quarters of total material consumption. The shares of reaction promoters and solvents are about 10 per cent each.

3.2.2 Material consumption by process stage

The material requirement is analyzed according to the distinct steps in the chemical synthesis.

Product	Process I		Process II	
Carbendazim				
Calcium cyanamide	628 kg		644 kg	
Methylchlorocarbonate	454 kg		465 kg	
o-Phenylenediamine	407 kg		417 kg	
Hydrochloric acid	213 kg		219 kg	
	1,702 kg	68.2%	1,745 kg	43.5%
Butylcarbamyl chloride				
Butylamine			353 kg	
Ethyl formate			393 kg	
Sulfuryl chloride			760 kg	
Sodium hydroxide			129 kg	
			1,635 kg	40.7%
Benomyl				
Acetone	440 kg		451 kg	
Butylisocyanate	355 kg			
Calciumcarbonate			185 kg	
	795 kg	31.8%	636 kg	15.8%
Total:	2,497 kg	100.0%	4,016 kg	100.0%

The main difference between the two alternatives comes from buying butylisocyanate (process I) and in-plant synthesis of butylcarbamyl chloride. The yield of carbamylation is also lower with butylcarbamyl chloride than with butylisocyanate.

3.3 Waste streams and treatments

The following waste streams are generated during the manufacture of 1,000 kg of benomyl:

Product	Process I			Process II		
Carbendazim						
Material inputs, intermediates, non-defined by-products and wastes	31 kg			32 kg		
Methanol	33 kg			34 kg		
Calcium cyanamide excess	243 kg			249 kg		
Calcium chloride	269 kg			273 kg		
Calcium hydroxide	177 kg			183 kg		
Ammonium chloride	312 kg			321 kg		
Carbon dioxide	92 kg	1,157 kg	70.5%	94 kg	1,186	38.3%

Butylcarbamoyl chloride						
Material inputs, intermediates, by-products				45 kg		
Ethanol				223 kg		
Sulfur dioxide				309 kg		
Hydrochloric acid				176 kg		
Sodium sulfate				115 kg		
Sodium chloride				94 kg	962 kg	31.0%
Benomyl						
Material inputs, non-defined by-products, benomyl	44 kg			215 kg		
Acetone	440 kg	484 kg	29.5%	451 kg		
Calcium chloride				205 kg		
Carbon dioxide				81 kg	952 kg	30.7%
Total:		1,641 kg	100.0%		3,100 kg	100.0%

3.3.1 Liquid effluent

There are two waste waters in process I. The mother liquor pumped off after the sedimentation of carbendazim contains ammonium chloride, calcium chloride and methanol. The distillation residue of acetone recovery from the benomyl mother liquor contains also ammonium chloride and calcium chloride, furthermore, unreacted organic chemicals, intermediates, non-defined by-products and finished product. About 84 per cent of the waste is inorganic salts. The share of liquid effluent in the total waste is 42 per cent.

Ethanol can be recovered as a saleable by-product in process II. The carbendazim mother liquor is the same as in process I. The benomyl mother liquor is similar in nature: sodium sulfate, sodium chloride and non-defined by-products prevail in it. A third waste water is the mother liquor of butylcarbamoyl chloride left after the decomposition of excess sulfuryl chloride. About 76 per cent of the waste is inorganic salts. The share of liquid effluent in total waste is 43 per cent.

3.3.2 Air pollutants

In process I, a minor quantity of carbon dioxide is produced which does not pollute the environment. The acetone loss during benomyl drying and solvent recovery operation contaminates the air. Acetone emission can be reduced mainly by recovering the solvent from the drying outlet air stream.

Waste gases, including solvent vapours, account for about 30 per cent of the total waste. Their quantity is higher in process II because sulfur dioxide and hydrogen chloride are generated during chlorination with sulfuryl chloride. Sulfur dioxide is absorbed in an alkali solution, whereas hydrogen chloride in water. The obtained sodium sulfite solution is used in other processes and hydrochloric acid is recycled into carbendazim manufacture.

3.3.3 Solid wastes

Lime sludge, containing calcium cyanamide, calcium hydroxide and some calcium carbonate, is produced during carbendazim synthesis. The share of solids in the total waste is around 26 and 14 per cent, respectively.

3.4 Industrial safety

3.4.1 Materials

Except calcium carbonate, all other chemicals are toxic, therefore benomyl production should be carried out in a closed system.

3.4.2 Chemical conversions

Acylation, benzimidazole-cyclization, formylation, chlorination and carbamoylation are carried out in multipurpose batch reactors.

4. SUMMARY EVALUATION

Methylchlorocarbonate and butylisocyanate are both produced from phosgene, an extremely toxic chemical. They are toxic themselves and very reactive, therefore their transport is strictly regulated. Butylisocyanate is less toxic and dangerous than methylisocyanate responsible for the Bhopal disaster, nonetheless, several manufacturers have investigated the synthesis of benomyl with butylcarbamyl chloride, produced on the spot from butylamine and ethyl formate, in order to eliminate the use of butylisocyanate.

There is a significant difference between the two processes as regards material consumption and waste generation. In process I, 2,497 kg of chemical inputs are required for the production of 1,000 kg of benomyl and 1,641 kg of waste is generated. The same figures for process II are 4,016 kg and 3,100 kg, respectively. The waste streams by the state of matter are summarized as follows:

	Process I		Process II	
Solid	420 kg	25.6%	432 kg	13.9%
Liquid	689 kg	42.0%	1,557 kg	50.2%
Gas	532 kg	32.4%	1,111 kg	35.8%
Total	1,641 kg	100.0%	3,100 kg	100.0%

708 kg of waste can be recovered in a reusable form in process II. The quantity of hazardous waste is 968 kg with process I and 1,917 kg, of which 1,189 kg can be recycled into industrial production, with process II. Round 23 per cent more toxic waste is generated in process II than in process I. On the other hand, the feedstocks of process II are easily available (in contrast to butylisocyanate) and direct material costs are smaller than with process I, in spite of the lower yields.

Technology is available for the treatment of hazardous and toxic wastes.

Appendix 1 to annex .. of the

ENVIRONMENT IMPACT ANALYSIS OF THE MANUFACTURE OF BENOMYL

Reactants, products and auxiliary materials in benomyl manufacture

Compound	Chemical formula	Molecular weight
Ammonia	NH_3	17.03
Ammonium chloride	NH_4Cl	53.49
Benomyl	$C_{14}H_{18}N_4O_3$	290.32
n-Butylamine	$H_3C(CH_2)_3NH_2$	73.14
Butylcarbamyl chloride	$H_3C(CH_2)_3NHCClO$	135.59
Butyl formamide	$H_3C(CH_2)_3NHCHO$	101.15
Butylisocyanate	$H_3C(CH_2)_3NCO$	99.13
Calcium carbonate	$CaCO_3$	100.09
Calcium chloride	$CaCl_2$	110.99
Calcium cyanamide	CaNCN	80.11
Calcium hydroxide	$Ca(OH)_2$	74.10
Calcium sulfate	$CaSO_4$	136.14
Carbendazim	$C_9H_9N_3O_2$	191.19
Carbon dioxide	CO_2	44.01
Ethanol	C_2H_5OH	46.06
Ethyl formate	$HCOOC_2H_5$	74.08
Hydrogen chloride	HCl	36.46
Methanol	CH_3OH	32.04
Methyl chlorocarbonate	$ClCOOCH_3$	94.50
o-Phenylessediamine	$C_6H_4(NH_2)_2$	108.14
Sodium chloride	NaCl	58.44
Sodium hydroxide	NaOH	40.00
Sodium sulfate	Na_2SO_4	142.06
Sodium sulfite	Na_2SO_3	126.06
Sulfur dioxide	SO_2	64.07
Sulfuryl chloride	SO_2Cl_2	134.96

Appendix 2 to annex .. of the

ENVIRONMENT IMPACT ANALYSIS OF THE MANUFACTURE OF BENOMYL

Material flow sheet

Appendix 3 to annex .. of the

ENVIRONMENT IMPACT ANALYSIS OF THE MANUFACTURE OF BENOMYL

Material balances for the manufacture of 1,000 kg of benomyl

(in kilogrammes)

Process I:

1. Carbendazim (reactions a,b,1)

	Input	Output
Calcium cyanamide	628	243
Methyl chlorocarbonate	454	
Water	143	
o-Phenylenediamine	407	
Hydrogen chloride	213	
Calcium chloride		269
Calcium hydroxide		177
Ammonium chloride		312
Carbendazim		720
Carbon dioxide		92
Methanol		33
Sub-total:	1,845	1,846

2. Benomyl (reaction c)

	Input	Output
Carbendazim	689	
Butylisocyanate	355	
Acetone	440	440
Benomyl		1,044
Sub-total:	1,484	1,484

Summary process I

	Inputs		Waste
	1,845		1,846
	+1,484		+1,484
	3,329		3,330
Carbendazim	-689	Carbendazim	-689
	2,640		2,641
Water	-143	Benomyl	-1,000
Total process I:	2,497		1,641

Process II

1. Carbendazim (reactions a,b,l)

Calcium cyanamide	644	249
Methyl chlorocarbonate	465	
Water	147	
o-Phenylenadiamine	417	
Hydrogen chloride	219	
Calcium chloride		273
Calcium hydroxide		183
Ammonium chloride		321
Carbon dioxide		94
Methanol		34
Carbendazime		737
Sub-total:	1,892	1,891

2. Butylcarbamyl chloride 1,892 kg (reactions c,d,e)

Butylamine	353	
Ethyl formate	393	35
Sulfuryl chloride	760	
Sodium hydroxide	129	
Ethanol		223
Sulfur dioxide		309
Hydrogen chloride		176
Sodium chloride		94
Sodium sulfate		115
Water		29
Butylcarbamyl chloride		654
Sub-total:	1,635	1,635

3. Benomyl (reaction f)

Carbendazim	705	
Butylcarbamyl chloride	644	144
Calcium carbonate	185	
Calcium chloride		205
Water		33
Carbon dioxide		81
Acetone	451	451
Benomyl		1,071
Sub-total:	1,985	1,985

Summary process II

	Inputs		Waste
	1,892		1,891
	+1,635		+1,635
	+1,985		+1,985
	5,512		5,511
Carbendazim	-705	Carbendazim	-705
Butylcarbamyl chloride	-644	Butylcarbamyl chloride	-644
Water	-147	Water	-62
		Benomyl	-1,000
Total process II:	4,016		3,100