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ENVIRONMENTAL IMPACT ANALYSIS OF THE MANUFACTURE OF 2,2-DIMETHYL-3-(2,2-DICHLOROVINYL)-CYCLOPROPANECARBOXYLIC ACID ETHYLESTER (DDCA - ETHYLESTER)

1. BACKGROUND

Pyrethroids, the synthetic analogues of pyrethrins, have become an important group of insecticides after the introduction of the first light stable product Permethrin (NRDC 143), to the agrochemical market. Pyrethroids ranked second after the organophosphates in worldwide sales of insecticides in 1987. The R&D efforts of leading pesticide manufacturers have resulted in innovative chemical extensions of the core structure, and permethrin, cypermethrin (NRDC 149), deltamethrin (NRDC 161) and fenvalerate are becoming commodity chemicals.

The general structural formula of some pyrethroids is illustrated below:

	X	Y	Z
Permethrin	-Cl	-H	-H
Cypermethrin	-Cl	-CN	-H
Cyfluthrin	-Cl	-CN	-F
Deltamethrin	-Br	-CN	-H

The last step of pyrethroids manufacture, esterification of the acid with the alcohol, is a relatively simple conversion and the competitiveness of the products depends mainly on the cheap availability of acid and alcohol components. Large pyrethroid manufacturers produce these intermediates themselves but some fine chemical companies are specialized in the manufacture of one or both intermediates and sell their production on the open international market.

The 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropanecarboxylic acid (DDCA) is the key intermediate in the production of permethrin, cypermethrin and cyfluthrin.

2. INFORMATION SOURCE

Firm specific data from a commercial scale manufacturer.

3. PROCESS INFORMATION

Since time was an important factor in the marketing strategy of the company, production was started from purchased intermediates: glycinester and dichlorodiene-1,3. At the same time, efforts were made to increase the backward integration of the chemical process and the currently used feedstocks are chloral, isobutylene, and monochloroacetic acid.

Several processes have been described for the synthesis of cyclopropanecarboxylic acids.

The so-called diazoester route of synthesis was selected for process development because the company had experience in handling the disadvantages of the method, namely:

- diazotation and the subsequent addition are dangerous (explosion risk) conversions;
- diazoesters are toxic in general (severe skin irritation, carcinogen effect)
- the yield of the addition reaction is very low due to many side reactions (primarily diethylmaleinate and diethylfumarate are formed).

3.1 Schematic illustration of the synthesis

3.2 Definition of educts, intermediates and products

The common names, chemical formulae and molecular weights of reactants and auxiliary chemicals are listed in appendix 1.

3.3 Chemical reactions of the synthesis

(a) $C_2HCl_3O + C_4H_8 = C_6H_9Cl_3O$

147.39 56.11 203.50

(b) $C_6H_9Cl_3O + C_4H_6O_3 = C_8H_{11}Cl_3O_2 + C_2H_4O_2$

203.50 102.09 245.53 60.05

(c) $2C_8H_{11}Cl_3O_2 + 2Zn = 2C_6H_8Cl_2 + ZnCl_2 + C_4H_6O_4Zn$

491.06 130.76 302.08 136.29 183.46

(d) $C_6H_8Cl_2 = C_6H_8Cl_2$

151.04 151.04

(e) $C_4H_9NO_2HCl + NaNO_2 = C_4H_6H_2O_2 + NaCl + 2H_2O$

139.58 69.00 114.10 58.44 36.03

(f) $C_4H_6N_2O_2 + C_6H_8Cl_2 = C_{10}H_{14}Cl_2O_2 + N_2$

114.10 151.04 237.13 28.01

(g) Combined equation of the synthesis

$2C_2HCl_3O + 2C_4H_8 + 2C_4H_6O_3 + 2Zn + 2C_4H_9NO_2HCl + 2NaNO_2 =$

294.78 112.22 204.18 130.76 279.16 138

$= 2C_{10}H_{14}Cl_2O_2 + 2C_2H_4O_2 + ZnCl_2 + C_4H_6O_4Zn + 2NaCl + 4H_2O + 2N_2$

474.26 120.10 136.29 183.46 116.88 72.06 56.02

3.4 Other reactions considered in the analysis

(h) $ZnCl_2 + C.H_6O_4Zn + 2Na_2CO_3 = 2NaCl + 2ZnCO_3 + 2C_2H_3NaO_2$

136.29 183.46 212.00 116.90 250.78 164.08

(i) $5ZnCO_3 + 3H_2O = 3Zn(OH)_2.2ZnCO_3 + 3CO_2$

626.95 54.05 548.96 132.03

(j) $C_4H_6O_3 + H_2O = C_2H_4O_2$

102.09 18.02 120.10

(k) $C_2H_4O_2 + KOH = C_2H_3KO + H_2O$

60.05 56.11 98.14 18.02

(l) $H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O$

98.07 112.22 174.25 36.04

(m) $HCl + KOH = KCl + H_2O$

36.46 56.11 74.55 18.02

(n) $2NaNO_2 + H_2SO_4 = Na_2SO_4 + 2HNO_2$

138.00 98.08 142.06 94.02

(o) $HNO_2 + NaHCO_3 = NaNO_2 + H_2O + CO_2$

47.01 84.01 69.00 18.02 44.01

(p) $2C_4H_6N_2O_2 = C_8H_{12}O_4 + 2N_2$

228.20 172.18 56.02

(q) $C_8H_{12}O_4 = 2NaOH = C_4H_2Na_2O_4 + 2C_2H_6O_6$

172.18 80.00 162.04 92.14

3.5 Chemical conversion efficiencies

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

Table 1. Overall nominal conversion factors of reactants to DDCA-ethylester

Material input	F
Chloral	0.622
Isobutylene	0.237
1,1,1-trichloro-4-methyl-pentene 4-ol (TMP)	0.858
Acetic anhydride	0.431
Dichlorodiene 1,3	0.637
Glycine-ethylester hydrochloride	0.587
Sodium nitrite	0.291
Diazoacetic acid ethylester	0.481

The yields of the studied process are listed in table 2.

Table 2. DDCA-ethylester yields on feedstocks and intermediates (percentage)

Chloral	28.3
Isobutylene	29.9
TMP	35.1
Dichlorodiene 1,3	58.8
Glycinester hydrochloride	50.0
Diazoacetic acid ethylester	54.1

3.6 Brief description of process

Isobutylene gas is introduced, under cooling, into chloral containing the catalyst to yield 1,1,1-trichloro-4-methylpentene-4-ol-2 (TMP).

TMP is subsequently esterified with acetic anhydride and the obtained 1,1,1-trichloro-4-methylpentene-4-ol-2 (TMP-acetate) is reduced by zinc powder to give 1,1-dichloro-4-methylpentadiene-1,4 (dichlorodiene-1,4). The by-products, zinc chloride and zinc sulfate, are precipitated from their aqueous solutions by the addition of sodium carbonate. The basic zinc carbonate precipitate can be sold for industrial processing.

Dichlorodiene-1,4 is isomerized in the presence of p-toluenesulfonic acid as the catalyst and the obtained dichlorodiene-1,3 is purified by distillation.

The manufacture of the second key intermediate starts with the diazotation of glycinethylester hydrochloride, in the presence of dichloroethane, in aqueous sulfuric acid solution, at a pH between 5 and 8, using sodium nitrite as the reactant. The dichloroethane solution of diazoaceticacid ethylate is separated as a distinct phase which is purified by washing with the aqueous solution of sodium bicarbonate.

The coupling of diazoester and dichlorodiene takes place in a dichloroethane solution, at a temperature between 100° and 120°C, in the presence of an organic copper-compound as the catalyst. By-products are removed by aqueous-alkaline washing, and the 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylic acid ethylate is obtained by distillation.

4. ENVIRONMENT IMPACT ASSESSMENT

Round 12,000 kg of materials are used for the production of 1,000 kg of permethrin acid ethylester. The total material requirement is analyzed from various points of view.

4.1 Material flow

The material flow schemas and informative material balances are shown in appendices 2 and 3, respectively.

4.2 Material requirements

4.2.1 Material consumption by nature of inputs

	kg		
Reactants			
Chloral	2,198		
Isobutylene	792		
Acetic anhydride	1,842		
Zinc	1,332		
Sodium nitrite	669		
Glycineethylester hydrochloride	1,177	8,010	67.8%
Reaction promoters			
Ferric chloride	4		
Polyethyleneglycol	2		
p-Toluenelsulfonic acid	63		
Cupric stearate	4		
Sulfuric acid	41	114	1.0%
Solvents			
Methanol	2,576		
Dichloroethane	530	3,106	26.3%
pH adjusters			
Hydrochloric acid	3		
Sulfuric acid	4		
Potassium hydroxide	345		
Sodium hydroxide	190		
Sodium bicarbonate	35	577	4.9%
Total:		11,807	100.0%

Round 12,000 kg of materials are used for the production of 1,000 kg of DDCA-ethylester.

4.2.2 Material consumption by process stage (in kg)

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

Step 1 - 1,1,1-trichloro-4-methylpentene-4-ol (TMP)

	kg		
Chloral	2,198		
Isobutylene	792		
Ferric chloride	4		
Polyethyleneglycol	2		
Hydrochloric acid	1	2,997	25.4%

Step 2 - Dichlorodiene-1,3

Acetic anhydride	1,842		
Zinc	1,332		
Hydrochloric acid	2		
Sulfuric acid	4		
p-Toluenesulfonic acid	63		
Potassium hydroxide	345		
Methanol	2,576	6,164	52.2%

Step 3 - DDCA-ethylester

Glycine ethylester hydrochloride	1,177		
Sodium nitrite	669		
Cupric stearate	4		
Sulfuric acid	41		
Sodium hydroxide	190		
Sodium bicarbonate	35		
Dichloroethane	530	2,646	22.4%
Total:		11,807	100.0%

Round 52 per cent of the total material requirement is consumed during the synthesis of dichlorodiene-1,2 from TMP, because the yield is relatively low, solvent consumption is high in spite of recycling, and both the esterification with acetic anhydride and the reductive elimination with zinc powder require large quantities of reactants.

Reactants account for about two thirds of total material consumption. The 22 per cent share of organic solvents attracts also attention.

Material consumption could therefore be reduced primarily by the improvement of the yields, optimization of reactant concentrations and recycling the excesses into the process; significant savints can be achieved also through the reduction of solvent losses.

4.4.2 Material consumption by process stage

The following quantities of materials are used in the subsequent steps of the synthesis:

1.	1,1,1-Trichloro-4-methylpentene-4-01-2(TMP)	2,997 kg	25.2%
2.	Dichlorodiene-1,3	6,273 kg	52.6%
3,	Permethrin acid ethylester	2,646 kg	22.2%
	Total:	11,916 kg	100.0%

4.3 Waste streams and treatments

The following wastes are generated during the manufacture of 1,000 kg of DDCA-ethylester:

Step 1

	kg		
Material inputs, non-defined by products and wastes	544		
Ferric chloride	4		
Poliethylene glycol	2		
Hydrochloric acid	1	551	5.2%

Step 2

Material inputs, intermediates, non-defined by-products and wastes	731		
Zinc chloride	819		
Zinc acetate	2,634		
Potassium acetate	590		
Potassium sulfate, chloride	11		
Acetic acid	82		
p-Toluene sulfonic acid	63		
Hydrogene	17		
Methanol	2,576	523	71.5%

Step 3

Material inputs, intermediates, non-defined by-products and wastes	877		
Cupric stearate	4		
Sodium hydroxide	ι73		
Sodium chloride	419		
Sodium sulfate	60		
Sodium nitrite	173		
Nitrogen	201		
Carbon dioxide	18		
Dichloroethane	530	2,455	23.3%
Total:		10,529	100.0%

Summary

Material inputs, intermediates, non-defined by-products and wastes	2,152	20.4%
Acetic acid	82	0.8%
p-Toluene sulfonic acid	63	0.6%
Methanol	2,576	24.5%
Dichloroethane	530	5.0%
Cupric stearate	4	
Poliethyleneglycol	2	
Hydrochloric acid	1	0.1%
Ferric chloride	4	
Zinc chloride	819	7.8%
Zinc acetate	2,634	25.0%
Potassium acetate	590	5.6%
Pc assium chloride, sulfate	11	0.1%
Sodium hydroxyde	173	1.6%
Sodium chloride	419	4.0%
Sodium nitrite	173	1.6%
Sodium sulfate	60	0.6%
Carbon dioxide	18	0.2%
Hydrogen	17	0.2%
Nitrogen	201	1.9%
Total:	10.529	100.0%

Inorganic salts with a high proportion of zinc to salts, account for 46 per cent of total waste. The share of organic solvents and other organic waste is 30 and 20 per cent, respectively.

4.3.1 Liquid effluent

Zinc chloride and acetate, together with potassium salts, are by-products of the reductive elimination conversion. The zinc salts are precipitated with sodium carbonate and removed by filtration for use in the manufacture of zinc oxide. The filtrate is treated and discharged into the public sewage system. The aqueous phases of solvent extractions and a small part of organic matter (sodium maleinate and sodium fumarate) are also treated and discharged into the public sewage system.

4.3.2 Air pollutants

The significant air pollution comes from the solvent loss which can be reduced by improving the recovery efficiency and by recycling the solvents in a closed system.

Other gases generated during the process (nitrogen, hydrogen and carbon dioxide) are not significant pollutants.

4.3.3 Solid wastes

Solid wastes from the reactors contain a high percentage of chlorinated organic compounds which should be incinerated in a special equipment wherein the produced hydrochloric acid is chemically neutralized.

4.4 Industrial safety

Nearly all materials used in the process are potentially harmful or toxic to human health. Chloral, sodium, hydroxide, potassium hydroxide, sulfuric acid and hydrochloric acid are dangerous materials.

As regards fire and explosion risks, isobutylene is very dangerous, whereas methanol and dichloroethane are dangerous.

Acetic anhydride and sulfuric acid react vehementaly with water.

The diazoacetic acid ethylester intermediate is poisonous and extremely reactive.

4.4.2 Chemical conversions

The chemical conversions involved in the synthesis of permethrin acid ethylester are: catalytic addition, esterification with acetic anhydride, reductive elimination with zinc, isomerization with p-toluenesulfonic acid promoter, diazotation and catalytic coupling of the diazoester and dichlorodiene-1,3.

The last two conversions are dangerous to carry out (explosion risk). Diazoacetic acid ethylester, formed during diazotation, is a toxic material. Esterification is a generally used, simple conversion. The remaining three conversions do not require special conditions but their techno-economic efficiency depends on experience with such type of reactions.

The current diazotation and coupling process is continuous, automated and carried out in a completely closed system.

Diazotation is controlled through the regulated dosage of the acid to maintain the pH at an optimum value. The produced diazoester is continuously removed by extraction with an organic solvent. Heavy metal ions are removed by washing with a sodium bicarbonate solution containing complexing agents. The high purity of the diazoester favourably affects the yield of the subsequent addition reaction.

A homogeneous phase catalyst is used in the addition reaction of the diene and diazoester. This prevents or greatly reduces the development of an induction period which is the danger factor of explosion. The elimination of heavy metals from the diazoester solution contributes also to the reduction of explosion risk.

Both the yield and product quality are favourably affected by the high (six-to-seven-fold) excess of diene reactant in the addition step; this excess can be guaranteed with a low material consumption, by recycling the diene into the continuous process.

Dangerous and toxic materials are present in small quantities in solution, and in a closed system, which contributes to the high industrial safety of the process.

The specific target was to elaborate a commercial scale synthesis for the manufacture of DDCA-ester which meets both the techno-economic criteria, and industrial safety and environment protection requirements.

SUMMARY EVALUATION

Dimethyl-dichlorovinyl-cyclopropanecarboxylic acid (DDCA) and its ethyl ester are key intermediates in the synthesis of permethrin, cypermethrin and cyflutrin.

These pyretrhoids represent the third generation of insecticides. They are much more active than the first-aid second-generation insecticides; as a result, their unit consumption per hectare of cultivated agricultural land is also lower. This is important, because less waste is generated during production and pollution of the external environment is reduced. Another advantage is their relatively low toxicity to human health and quick chemical decomposition both in the soil and in the treated plants.

Diazottion and the subsequent coupling reactions are dangerous conversions, partly because the diazoacetic acid is poisonous, partly because explosion might occur in both chemical reactions. These risks have been reduced to a minimum by carrying out the synthesis with a continous process in a closed system under automatic control and by using a homogenous catalyst and a complex-forming agent to remove metal impurities. Thus, the dangerous materials are present in the system only in small amounts and for a short period of time.

The specific material input-output ratio is 1:12, which is very high even if the high degree of backward integration is taken into account. The feedstocks are simple commodity organic chemicals: chloral, isobutylene and glycine ethylester. 68 per cent of the input materials is reactant and 26 per cent is solvent. Hence, process development targets should aim at improving the yields of individual conversions and at reducing solvent losses.

Zinc salts represent 33 per cent of the total waste. Their recovery in the form of basic zinc carbonate and use in the manufacture of zinc oxide is a good example of the secondry utilization of raw materials.

Organic wastes - mainly chlorinated compounds - are primarily found in the final distillation residue. These must be incinerated in special equipment and/or by a special method, so that the produced hydrogen chloride does not contaminate the air.

It is worth mentioning that the economic objectives of process development coincide with the environment protection objectives; this conclusion can be generalized to the major part of commodity fine chemicals.

Appendix 1 to annex .. of the

ENVIRONMENT IMPACT ANALYSIS OF THE MANUFACTURE OF
2,2-DIMETHYL-3-(2,2-DICHLOROVINYL)-CYCLOPROPANECARBOXYLIC ACID ETHYLESTER

Reactants, products and auxiliary materials
in DDCA manufacture

Compound	Chemical formula	Molecular weight
Acetic acid	$C_2H_4O_2$	60.05
Acetic anhydride	$C_4H_6O_3$	102.09
Carbon dioxide	CO_2	44.01
Chloral	C_2HCl_3O	147.39
Diazoacetic acid ethylester	$C_4H_6N_2O_2$	114.10
1,1-Dichloro-4-methyl-pentadiene	$C_6H_8Cl_2$	151.04
2,2-Dimethyl-3-(2.2-dichlorovinyl) cyclopropanecarboxylic acid ethylester	$C_{10}H_{14}Cl_2O_2$	237.13
Diethylmaleinate	$C_8H_{12}O_4$	172.18
Ethanol	C_2H_6O	45.06
Glycinethylester	$C_4H_9NO_2$	103.12
Glycinethylester hydrochloride	$C_4H_9NO_2.HCl$	139.58
Hydrochloric acid	HCl	36.46
Isobutylene	C_4H_8	56.11
Nitric acid	HNO_3	47.0
Potassium acetate	C_2H_3KO	98.14
Potassium chloride	KCl	74.55
Potassium hydroxide	KOH	56.11
Potassium sulfate	K_2SO_4	174.25
Sodium acetate	$C_2H_3NaO_2$	82.04
Sodium bicarbonate	$NaHCO_3$	84.00
Sodium carbonate	Na_2CO_3	106.00

Compound	Chemical formula	Molecular weight
Sodium chloride	$NaCl$	58.44
Sodium hydroxide	$NaOH$	40.00
Sodium maleinate	$C_4H_2Na_2O_4$	162.04
Sodium nitrite	$NaNO_2$	69.00
Sodium sulfate	Na_2SO_4	142.06
Sulfuric acid	H_2SO_4	98.08
p-Toluenesulfonic acid	$C_7H_8O_3S$	172.20
1,1,1-Trichloro-4-methyl-pentene-4-ol-2 (TMP)	$C_6H_9Cl_3O$	203.50
1,1,1-Trichloro-4-methyl-pentene-4-ol-2-acetic acid ester (TMP-acetate)	$C_8H_{11}Cl_3O_2$	245.53
Zinc	Zn	65.38
Zinc acetate	$C_4H_6O_4Zn$	183.46
Zinc carbonate	$ZnCO_3$	125.38
Zinc carbonate, basic	$3Zn(OH)_2.2ZnCO_3$	548.96
Zinc chloride	$ZnCl_2$	136.29

Appendix 2 to annex .. of the

ENVIRONMENT IMPACT ANALYSIS OF THE MANUFACTURE OF DDCA

Appendix 3 to annex .. of the

ENVIRONMENT IMPACT ANALYSIS OF THE MANUFACTURE OF DDCA

Material balances
for the manufacture of 1,000 kg of DDCA
(in kilogrammes)

Step 1

Chloral	2,198	118
Isobutylene	792	
Ferric chloride	4	4
Polyethyleneglycol	2	2
Hydrochloric acid	1	1
TMP		2,872
Total:	2,997	2,997

Waste	2,997	
	-2,446	551

Step 2

TMP	2,446	
Acetic anhydride	1,842	
Zinc	1,332	
Hydrochloric acid	2	
Sulfuric acid	4	
p-Toluenesulfonic acid	63	63
Potassium hydroxide	345	
Methanol	2,576	2,576
Zinc chloride		819
Zinc acetate		2,634
Potassi m sulfate, chloride		11
Water	109	111
Potassium acetate		590
Hydrogen		17
Dichlorodiene-1,3		1,815
Acetic acid		82
Total:	8,719	8,718

Waste	8,718	
	-1,084	
	- 111	7,523

Step 3

Dichlorodiene-1,3	1,084	
Glycine-ethylester hydrochloride	1,177	
Sodium nitrite	669	
Cupric stearate	4	4
Sulfuric acid	41	
Sodium hydroxide	190	173
Sodium bicarbonate	35	
Dichloroethane	530	530
Sodium chloride		419
Sodium sulfate		60
Sodium nitrite		173
Nitrogen		201
Water		275
Carbon dioxide		18
Glycinethylester hydrochloride		175
Permethrin acid ethylester		1,702
Total:	3,730	3,730

Waste	3,730	
	-1,000	
	-275	2,455

Summary