

Report No. 48

# CHLORINATED SOLVENTS

by LLOYD M. ELKIN

contributions by Roberta A. Bell

February 1969

A private report by the

PROCESS ECONOMICS PROGRAM



STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

## CONTENTS

1	INTRODUCTION . . . . .	1
2	SUMMARY . . . . .	3
3	INDUSTRY STATUS . . . . .	21
4	CHEMISTRY . . . . .	29
	Chlorination of Acetylene . . . . .	29
	Catalytic Dehydrochlorination of Tetrachloroethane . . . . .	30
	Chlorination of 1,2-Dichloroethane (Vapor Phase) . . . . .	31
	Oxychlorination of 1,2-Dichloroethane . . . . .	32
	Chlorination of Trichloroethylene . . . . .	34
	Dehydrochlorination of Pentachloroethane with Lime . . . . .	34
	Chlorination of Propane-Propylene Mixtures . . . . .	35
	Chlorination of 1,2-Dichloroethane (Liquid Phase) . . . . .	36
	Dehydrochlorination of 1,1,2-Trichloroethane . . . . .	37
	Addition of HCl to Vinylidene Chloride . . . . .	37
	Chlorination of Ethane . . . . .	38
5	TRICHLOROETHYLENE FROM ACETYLENE . . . . .	39
	Review of Processes . . . . .	39
	Process Description . . . . .	44
	Process Discussion . . . . .	55
	Capital Costs . . . . .	55
	Production Costs . . . . .	56
6	TRICHLOROETHYLENE AND PERCHLOROETHYLENE BY CHLORINATION OF DICHLOROETHANE . . . . .	65
	Review of Processes . . . . .	65
	Process Description . . . . .	72
	Process Discussion . . . . .	86
	Capital Costs . . . . .	87
	Production Costs . . . . .	88
7	TRICHLOROETHYLENE AND PERCHLOROETHYLENE BY OXYCHLORINATION OF DICHLOROETHANE . . . . .	99
	Review of Processes . . . . .	99
	Process Description . . . . .	109
	Process Discussion . . . . .	124
	Capital Costs . . . . .	125
	Production Costs . . . . .	128

CONTENTS

8	PERCHLOROETHYLENE FROM TRICHLOROETHYLENE . . . . .	137
	Review of Processes . . . . .	137
	Process Description . . . . .	138
	Process Discussion . . . . .	146
	Capital Costs . . . . .	146
	Production Costs . . . . .	147
9	PERCHLOROETHYLENE (AND CARBON TETRACHLORIDE) FROM (C1 TO) C3 HYDROCARBONS (OR CHLOROHYDROCARBONS) . . . . .	157
	Review of Processes . . . . .	157
	Process Description . . . . .	166
	Process Discussion . . . . .	178
	Capital Costs . . . . .	185
	Production Costs . . . . .	185
10	METHYL CHLOROFORM FROM DICHLOROETHANE . . . . .	195
	Review of Processes . . . . .	195
	Process Description . . . . .	213
	Process Discussion . . . . .	228
	Capital Costs . . . . .	230
	Production Costs . . . . .	230
11	METHYL CHLOROFORM FROM ETHANE . . . . .	237
	Review of Processes . . . . .	237
	Process Description . . . . .	237
	Process Discussion . . . . .	248
	Capital Costs . . . . .	248
	Production Costs . . . . .	254
12	OTHER PROCESSES . . . . .	259
13	PURIFICATION AND MISCELLANEOUS OPERATIONS . . . . .	273
	Purification . . . . .	273
	Miscellaneous Operations . . . . .	276
14	STABILIZERS . . . . .	279

## CONTENTS

APPENDIX A	DESIGN AND COST BASIS . . . . .	307
APPENDIX B	PHYSICAL DATA . . . . .	313
APPENDIX C	PRODUCT SPECIFICATIONS . . . . .	319
APPENDIX D	HANDLING AND SAFETY . . . . .	321
CITED REFERENCES	. . . . .	323
SUPPLEMENTARY REFERENCES	. . . . .	355

## ILLUSTRATIONS

5.1	Trichloroethylene from Acetylene . . . . .	49
5.2	Trichloroethylene from Acetylene Effect of Operating Level and Plant Capacity on Production Cost . . . . .	63
6.1	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane Yield Structure as a Function of Feed Mol Ratio . . . . .	71
6.2	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane . . . . .	77
6.3	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane--Trichloroethylene Production Effect of Operating Level and Plant Capacity on Production Cost . . . . .	97
6.4	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane--Perchloroethylene Production Effect of Operating Level and Plant Capacity on Production Cost . . . . .	98
7.1	Trichloroethylene and Perchloroethylene by Oxychlorination of Dichloroethane . . . . .	115
7.2	Trichloroethylene and Perchloroethylene by Oxychlorination of Dichloroethane Effect of Operating Level and Plant Capacity on Production Cost . . . . .	135
8.1	Perchloroethylene from Trichloroethylene . . . . .	141
8.2	Perchloroethylene from Trichloroethylene Effect of Operating Level and Plant Capacity on Production Cost . . . . .	155
9.1	Perchloroethylene (and Carbon Tetrachloride) from (C1 to) C3 Hydrocarbons (or Chlorohydrocarbons) . . . . .	171
9.2	Relationship Between Equilibrium Constant and Temperature .	180
9.3	Relationship Between Equilibrium Constant and Temperature .	181
9.4	Perchloroethylene (and Carbon Tetrachloride) from (C1 to) C3 Hydrocarbons (or Chlorohydrocarbons) Effect of Operating Level and Plant Capacity on Production Cost . . . . .	193

ILLUSTRATIONS

10.1	Methyl Chloroform from Dichloroethane . . . . .	219
10.2	Methyl Chloroform from Dichloroethane Effect of Operating Level and Plant Capacity on Production Cost . . . . .	235
11.1	Methyl Chloroform from Ethane . . . . .	241
11.2	Methyl Chloroform from Ethane Effect of Operating Level and Plant Capacity on Production Cost . . . . .	257

## TABLES

2.1	Summary of Capital and Production Costs . . . . .	7
2.2	Comparison of Processes with Fixed Capital Amortized in a Two-year Period . . . . .	9
2.3	Summary of Evaluated Processes . . . . .	11
3.1	Plant Capacity United States . . . . .	24
3.2	Plant Capacity The Americas Outside the United States . . . . .	25
3.3	Plant Capacity Europe . . . . .	26
3.4	Plant Capacity Asia, Australia, Middle East, and South Africa . . . . .	27
3.5	Plant Capacity Iron Curtain Countries . . . . .	28
5.1	Trichloroethylene from Acetylene, Tetrachloroethane Production Summary of Patents . . . . .	41
5.2	Trichloroethylene from Acetylene, Dehydrochlorination of Tetrachloroethane Summary of Patents . . . . .	42
5.3	Trichloroethylene from Acetylene Major Process Equipment List . . . . .	49
5.4	Trichloroethylene from Acetylene Stream Flows . . . . .	53
5.5	Trichloroethylene from Acetylene Utilities Summary . . . . .	54
5.6	Trichloroethylene from Acetylene Battery Limits and Utilities Investment . . . . .	57
5.7	Trichloroethylene from Acetylene Total Capital Investment . . . . .	59
5.8	Trichloroethylene from Acetylene Production Costs . . . . .	61
6.1	Trichloroethylene and Perchloroethylene by Chlorination of 1,2-Dichloroethane Summary of Patents . . . . .	67

TABLES

6.2	Trichloroethylene and Perchloroethylene by Chlorination of Ethylene Summary of Patents . . . . .	69
6.3	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane Major Process Equipment List . . . . .	77
6.4	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane--Trichloroethylene Production Stream Flows . . . . .	81
6.5	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane--Perchloroethylene Production Stream Flows . . . . .	83
6.6	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane Utilities Summary . . . . .	85
6.7	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane Battery Limits and Utilities Investment . . . . .	89
6.8	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane Total Capital Investment . . . . .	91
6.9	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane--Trichloroethylene Production Production Costs . . . . .	93
6.10	Trichloroethylene and Perchloroethylene by Chlorination of Dichloroethane--Perchloroethylene Production Production Costs . . . . .	95
7.1	Trichloroethylene and Perchloroethylene by Oxychlorination of 1,2-Dichloroethane Summary of Patents . . . . .	101
7.2	Trichloroethylene and Perchloroethylene by Oxychlorination of Ethylene Summary of Patents . . . . .	105
7.3	Trichloroethylene and Perchloroethylene by Oxychlorination of Dichloroethane Major Process Equipment List . . . . .	115



## TABLES

7.4	Trichloroethylene and Perchloroethylene by Oxychlorination of Dichloroethane Stream Flows . . . . .	119
7.5	Trichloroethylene and Perchloroethylene by Oxychlorination of Dichloroethane Utilities Summary . . . . .	123
7.6	Trichloroethylene and Perchloroethylene by Oxychlorination of Dichloroethane Battery Limits and Utilities Investment . . . . .	126
7.7	Trichloroethylene and Perchloroethylene by Oxychlorination of Dichloroethane Total Capital Investment . . . . .	127
7.8	Trichloroethylene and Perchloroethylene by Oxychlorination of Dichloroethane Production Costs, Trichloroethylene . . . . .	131
7.9	Trichloroethylene and Perchloroethylene by Oxychlorination of Dichloroethane Production Costs, Perchloroethylene . . . . .	133
8.1	Perchloroethylene from Trichloroethylene Major Process Equipment List . . . . .	141
8.2	Perchloroethylene from Trichloroethylene Stream Flows . . . . .	143
8.3	Perchloroethylene from Trichloroethylene Utilities Summary . . . . .	145
8.4	Perchloroethylene from Trichloroethylene Battery Limits and Utilities Investment . . . . .	149
8.5	Perchloroethylene from Trichloroethylene Total Capital Investment . . . . .	151
8.6	Perchloroethylene from Trichloroethylene Production Costs . . . . .	153
9.1	Perchloroethylene (and Carbon Tetrachloride) from (C1 to) C3 Hydrocarbons (or Chlorohydrocarbons) Summary of Patents . . . . .	159
9.2	Perchloroethylene (and Carbon Tetrachloride) from (C1 to) C3 Hydrocarbons (or Chlorohydrocarbons) Major Process Equipment List . . . . .	171

TABLES

9.3	Perchloroethylene (and Carbon Tetrachloride) from (C1 to) C3 Hydrocarbons (or Chlorohydrocarbons) Stream Flows . . . . .	175
9.4	Perchloroethylene (and Carbon Tetrachloride) from (C1 to) C3 Hydrocarbons (or Chlorohydrocarbons) Utilities Summary . . . . .	177
9.5	Perchloroethylene (and Carbon Tetrachloride) from (C1 to) C3 Hydrocarbons (or Chlorohydrocarbons) Battery Limits and Utilities Investment . . . . .	187
9.6	Perchloroethylene (and Carbon Tetrachloride) from (C1 to) C3 Hydrocarbons (or Chlorohydrocarbons) Total Capital Investment . . . . .	189
9.7	Perchloroethylene (and Carbon Tetrachloride) from (C1 to) C3 Hydrocarbons (or Chlorohydrocarbons) Production Costs . . . . .	191
10.1	Methyl Chloroform from Dichloroethane Summary of Patents . . . . .	197
10.2	Methyl Chloroform from Dichloroethane Major Process Equipment List . . . . .	219
10.3	Methyl Chloroform from Dichloroethane Stream Flows . . . . .	223
10.4	Methyl Chloroform from Dichloroethane Utilities Summary . . . . .	227
10.5	Methyl Chloroform from Dichloroethane Battery Limits and Utilities Investment . . . . .	231
10.6	Methyl Chloroform from Dichloroethane Total Capital Investment . . . . .	232
10.7	Methyl Chloroform from Dichloroethane Production Costs . . . . .	233
11.1	Methyl Chloroform from Ethane Major Process Equipment List . . . . .	241
11.2	Methyl Chloroform from Ethane Stream Flows . . . . .	245
11.3	Methyl Chloroform from Ethane Utilities Summary . . . . .	247

## TABLES

11.4	Methyl Chloroform from Ethane Battery Limits and Utilities Investment . . . . .	251
11.5	Methyl Chloroform from Ethane Total Capital Investment . . . . .	253
11.6	Methyl Chloroform from Ethane Production Costs . . . . .	255
12.1	Other Routes to Tetrachloroethane Summary of Patents . . . . .	261
12.2	Other Routes to Trichloroethylene Summary of Patents . . . . .	262
12.3	Trichloroethylene and Perchloroethylene from Acetylene Summary of Patents . . . . .	263
12.4	Trichloroethylene and Perchloroethylene from Tetrachloroethane and Oxygen Summary of Patents . . . . .	265
12.5	Trichloroethylene and Perchloroethylene from Tetrachloroethane and Chlorine Summary of Patents . . . . .	267
12.6	Trichloroethylene and Perchloroethylene from Other Raw Materials Summary of Patents . . . . .	269
12.7	Perchloroethylene and Carbon Tetrachloride from Acetylene Summary of Patents . . . . .	271
14.1	Stabilizers for Trichloroethylene, Perchloroethylene, and Methyl Chloroform Summary of Patents . . . . .	281
B.1	Some Physical Properties of Chlorohydrocarbons . . . . .	315