Montreal Protocol

Process Agents Task Force

Case Study #6

Use of CTC in Dicofol production

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CS-6 Use of CTC in Dicofol production

C-6.1 Introduction

Dicofol is an organo chlorine broad spectrum non systemic acaricide with little insecticidal activity. It is currently being used on many fruits, vegetable, ornamental and field crops for the control of various species of mites. In India it is mainly used for tea crop and kitchen gardens. The recommended applications on wide range of crops varies between 0.56 - 4.5 kaI/ha. Acute oral LD for rats is 668-842 mg/kg and 1870 mg/kg for rabbits.

1-1,Bis (4-chlorophenyl) 2,2,2-trichloroethanol is the chemical name for Dicofol. Pure Dicofol is a colourless solid with a melting point 78.5 - 79.5 C.

The technical grade is brown viscous liquid (82% pure) and has density 1.45. It is primarily a mixture of 1-1, Bis (4-chlorophenyl) - 2,2,2 - trichloro ethanol and 1-1 (4-chlorophenyl, 2- chlorophenyl) - 2,2,2 - trichloro ethanol in the ratio of 4 : 1

Technical Dicofol is practically insoluble in water but soluble in most aliphatic and aromatic solvents. The product is compatible with all but highly alkaline pesticides. Its wettable powder (wp) formulations are sensitive to solvents and surfactants and these may affect acaricidal activity and phytotoxicity.

The various formulations of Dicofol are:

a) 35% wettable powder (wp)
b) 18.5% and 42% emulsifiable concentrates (EC)
c) and as 41% flowable

Of the above formulations, generally 18.5% (EC) is widely used in India

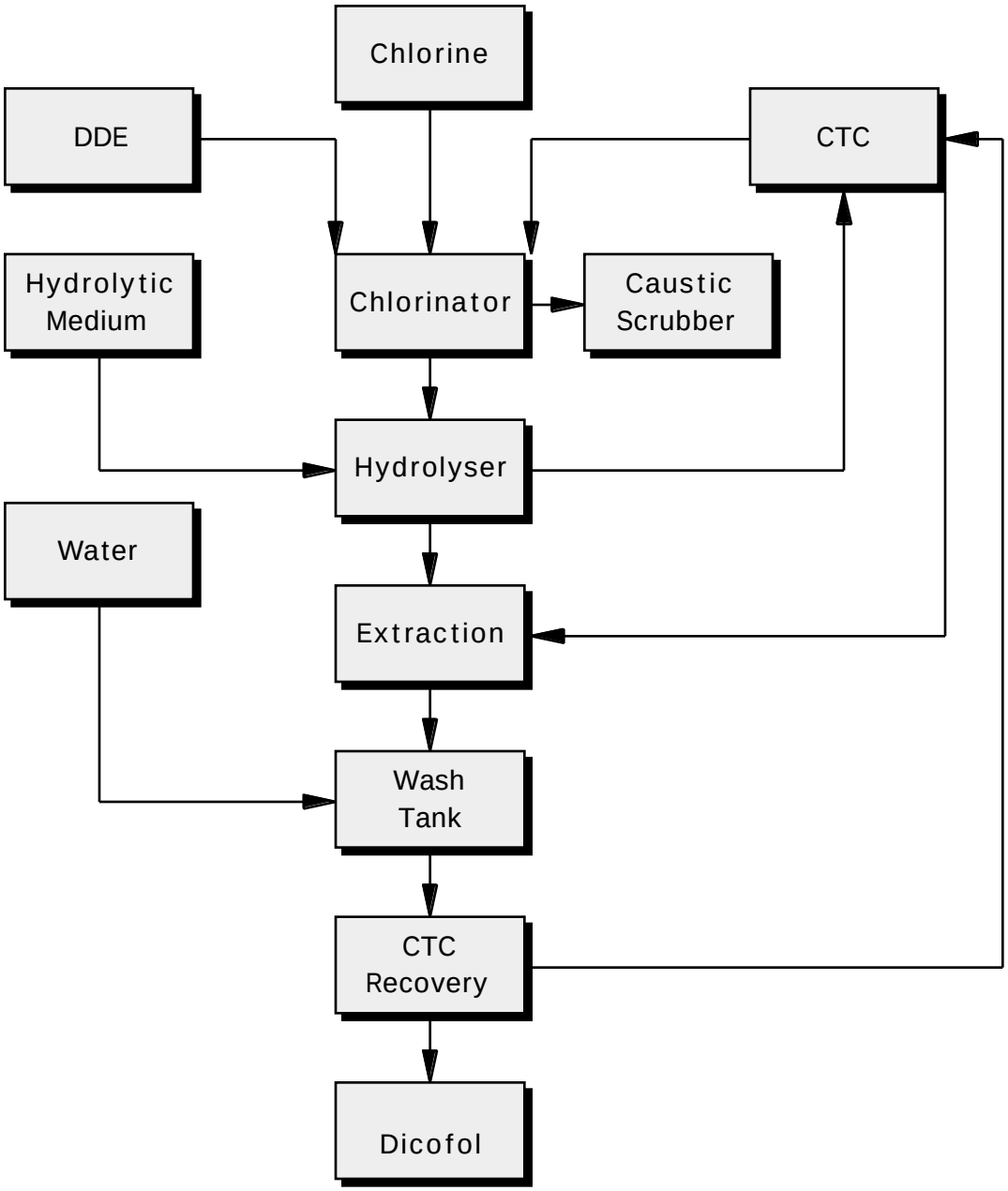
C-6.2 Manufacturing process

The current capacity of the plant in India is 150 tonnes/annum. The product is manufactured by converting tech-DDT, which is mainly a mixture of 1,1 Bis (4-chlorophelyl) - 2,2,2 trichloro ethane and 1,1 (4-chlorophenyl, 2 chlorophenyl), 2,2,2 trichloro ethane to tech-DDE which is also a mixture of 1,1 Bis (4-chlorophenyl) 2,2 - dichloro ethene and 1,1 - (4-chlorophenyl; 2 - chlorophenyl) 2,2 dichloro ethene.

After the conversion of tech-DDT to tech-DDE, carbon tetrachoride (CTC) (4.5 kg for 1 kgh of DDE) is added. The CTC solution containing DDE is then taken to special chlorinators and then chlorinated with chlorine till the intermediate tetrachloro, 1-chloro, 1,1 Bis (4-chlorophenyl), 2,2,2 trichloro ethane and 1-chloro, 1,1 (4-chlorophenyl, 2-

chlorophenyl) - 2,2,2-trichloro ethane are formed. The chlorinating solvent CTC is then removed and is recycled.

The product is then hydrolysed by an acidic hydrolytic medium. After the complete conversion of tetrachloro to tech Dicofol, CTC is added to the reaction mixture to extract tech Dicofol from the reaction mixture. The CTC layer which contains Dicofol is separated and then taken to wash tank and washed till product is neutral. CTC is then removed from the product by simple distillation, followed by vacuum distillation to get tech Dicofol.



C-6.3 Conversion to a non-ODS process agent

This process presently produces 150 tonnes/year of Dicofol and uses 960 tonnes of CTC in the production cycle. Due to increasing demands and good potential of the product the company envisages a 20% annual production increase. Although most of the CTC used during chlorination and as a Dicofol extractor after tetrachloro DDT hydrolysis is recycled, 48 tonnes is emitted annually, including residual trace amounts in the product . These emissions will likely increase as production increases.

There is a limited choice of solvents, as only Chlorinated aliphatic solvents can be used as a replacement process agent. Work at the laboratory level has already been initiated to replace CTC using 1,2 dichloro ethane (DCE). The initial results are quite optimistic and it is hoped that this process agent will be a suitable replacement for CTC in this process. However, laboratory experiments so far indicate that if dichloro ethane (DCE) is used as a replacement for CTC, some process modifications will be required to meet the needs of the present and future production schedules, which would have a bearing upon productivity and cost economics of the product.

In order to carry out this change from CTC to DCE more studies in pilot plant at 5 kg level are to be undertaken. Moreover, before marketing technical Dicofol, as per C.I.B. guidelines, phytotoxicity studies of the product must be carried out on the alternatively produced product.

Although there is not much change in the solvent ratio in the change from CTC to DCE at the chlorination stage, it has been observed that the chlorination time is 15 to 20% longer, as chlorine has more residence time in CTC compared to DCE. Hence to maintain the present production schedule a complete chlorination unit consisting of a 3 Kl, all glass lined, jacketed vessel, along with two seavengers of the same capacity and kind having proper condenser and other requisite accessories will have to be installed.

The extraction of technical Dicofol after hydrolysis of tetra chloro DDT with CTC is easier as CTC is heavier (density 1.6), compared to DCE (density 1.24) and thus CTC containing the Dicofol remains in the lower layer. However when DCE is used there is no separation of the layer for DCE, either at the top or at the bottom, and much more DCE an water is required to get DCE containing technical Dicofol in the lower layer. Due to the larger volume of DCE and water, the size of the vessel has to be increased substantially. Simultaneously, the present wash tank for washing technical Dicofol in DCE also has to be replaced with a larger one. Therefore to maintain the present production level of technical Dicofol, a 5 Kl MSGL hydrolyser and another 5 Kl MSGL wash tank with necessary accessories must be installed.

C-6.4 Material balance

Item Description	Quantity	Tonnes
Annual Dicofol (tech) production	t/a	150
Annual CTC recycle	t/a	960
CTC recycle per production	t/t	3.2
Annual CTC make-up	t/t	48
CTC consumed per production	t/t	0.16
Annual CTC transformed or destroyed	t/a	0.00
CTC transformed or destroyed	%	0.00
Annual CTC used as CPA	t/a	960
Annual CTC emission	t/a	48
to atmosphere	t/a	47.52
to water	t/a	0.00
to product	t/a	0.48
CTC emission per production	t/t	0.16
to atmosphere	t/t	0.1584
to water	t/t	0.00
to product	t/t	0.0016
CTC emission per recycle	t/t	0.05