

SUBMISSION TO

THE COMMITTEE OF ENQUIRY INTO POSSIBLE HEALTH  
EFFECTS OF MANUFACTURE OF AGRICULTURAL CHEMICALS  
IN NEW PLYMOUTH

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ventilation air principal chimney, and provision for representative sampling of the vent line.

#### Process Incidents

The only incident known to me which resulted in, or could have resulted in, abnormal emissions to atmosphere is the radial failure of No. 2 autoclave rupture disc on 15 April 1986. This is well documented in the DSIR Report by Drs Ross Nicol and Donald Smith. My commentary about the event, and my requirements on the Company to be implemented prior to re-commencing TCP production are appended to that report. A copy is also attached to this submission as Appendix 6 and Appendix 7.

#### Preparation of High Purity Sodium Trichlorophenate

A batch of sodium TCP was purified to pharmaceutical grade in Building 03 early 1986. Sodium TCP, ex TCP process was treated to reduce impurities by a system of washing, caustic extraction, filtration and centrifuging etc. The phenolic odour of sodium TCP was evident in the process vicinity but no complaints were recorded. If the Company wish to proceed with preparation of high purity TCP on a regular basis then a section 31 application will be required and the process will be evaluated.

#### PHENOXY PROCESSES

The Phenoxy Plant produces a range of technical herbicides of the 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, and monochlorophenoxyacetic acid families. In each case the appropriate chlorinated phenol is reacted with monochloroacetic acid to form the chlorinated phenoxyacetic acid sodium salt. The processes are undertaken in Building 48, with some stages undertaken in Phenoxy Preparation in Building 03. (Monochloroacetic acid is prepared here by splitting the bags, mixing MCA with water and pumping the slurry to Building 48.)

#### \* Manufacture of 2,4,5-T

The maximum production of this herbicide is between 800 and 900 tonnes per annum. Sodium TCP is reacted with sodium monochloroacetate with water in a heated autoclave at ambient pressure.

\* Sodium trichlorophenoxyacetate is separated by filtering or centrifuging. It is washed to remove salt and unreacted TCP.  
The sodium trichlorophenoxyacetate can then be acidified with mineral acid to produce the free acid, which is practically insoluble in water. The 2,4,5-T acid is then esterified by heating the acid with an appropriate alcohol such as butanol to produce the ester. No TCDD is formed during these reactions.

#### \* Manufacture of 2,4-D

\* Reaction of 2,4-dichlorophenol (imported) with chloroacetic acid in aqueous sodium hydroxide. The acid is either separated as such, esterified, or reacted to an amine salt. Maximum production would be of the order of 500 tonne/annum. No TCDD generated during this process. Centrifuging of 2,4-D acid undertaken in Building 03.

### Manufacture of MCPA and MCPB

Parachloro-ortho-cresol (PCOC) is reacted with sodium monochloroacetate to form the sodium salt of methyl-chlorophenoxyacetic acid (MCPA). About 250 tonnes may be produced per annum. PCOC is reacted with gamma buterolactone to form the sodium salt of methyl-chlorophenoxy butyric acid (MCPB). About 130 tonnes may be produced per annum.

No TCDD is formed during these processes.

### Phenoxy Plant Waste Treatment System

\* The phenoxy processes have liquid effluent containing sodium chloride, sodium sulphate, product, chlorophenols, solvents etc which is treated in the Phenoxy Plant Waste Treatment System. Approximately 50m<sup>3</sup>/day of liquid effluent is produced at maximum production. In addition, the treatment plant caters for waste water from the TCP process which contains sodium chloride, solvents, TCA, sodium TCP, and some TCDD. A variety of treatment methods are used, including xylene washing and resin adsorption. The waste water is pH adjusted before discharge to the sewer. The processes are fully described on pages 32-34 inclusive of IWD's submission to the Environmental Council.

In June 1982 the Pesticides Regulations were amended to limit the maximum concentration of TCDD in 2,4,5-T to 0.01 ppm (10 ppb). To meet this requirement with an adequate margin, and to ensure that TCDD in waste water discharges is reduced as far as practicable, the Company installed a xylene distillation unit in the Phenoxy Plant Waste Treatment Process. About 10,000 litres at normal production of distillation residues (xylene with some esters and trichloroanisole containing about 0.3 ppm TCDD) are generated annually and is stockpiled until sufficient quantities are available to operate the liquid waste incinerator. These distillation residues (containing about 3 grammes of TCDD per annum at normal production rates) is the only TCDD-containing stream to waste as such being generated in the TCP-Phenoxy Plant processes.

Water discharged to the sewer contains less than 50 ppt of TCDD.

### Vents to Atmosphere

Vents to atmosphere from the Phenoxy Plant and associated processes are from the Phenoxy Plant building ventilation system, from the Phenoxy process ventilation, from the waste treatment plant, and from the process pressure relief blowdown vessel.

(a) Building ventilation air. Fugitive emissions of chlorophenols, methanol, butanol, xylene, and octanol, are treated by carbon adsorption before discharge from a 23 metre high chimney (vent No. - 48-1). Approximately 18m<sup>3</sup>/second (ambient temperature) of ventilation air is discharged from this vent. The introduction of the Phenoxy Plant ventilation air control in 1977 has virtually eliminated the phenoxy background odours previously noted in the Paritutu Road area.

(b) Process ventilation air. This ventilation system extracts similar compounds to that listed (a) above but their concentrations are somewhat higher. Process ventilation air is treated by

1986 \*

TABLE 9 : THEORETICAL MAXIMUM SHORT TERM GROUND LEVEL CONCENTRATIONS FOR METHYLENE CHLORIDE DOWN-WIND OF VENT 04-2 (DISCHARGE OF 69 GM/SEC FROM 11 METRE HIGH VENT)

Atmospheric Stability Category	Description	Max. GLC (mg/m <sup>3</sup> )	Distance from Vent (metres)	Equivalent 24-hr GLC (mg/m <sup>3</sup> )
A	Highly unstable	8	100	3
B	Moderately unstable	14	100	5
C	Slightly unstable	16	100	6
D	Neutral	13	200	5
E	Slightly stable	10	300	4
F	Moderately stable (Inversion)	50	100	18

NOTE:

- (i) GASDIS Dispersion Model (2)
- (ii) Wind velocity at discharge height 5m/second.
- (iii) Discharge of 69 g/second corresponds to 125 kg over 30 minutes. If evaporation of the methylene chloride carrier extends over a longer period then the maximum ground level concentrations will reduce.
- (iv) The short term GLCs are converted to 24-hour equivalents by using GASDIS averaging factor 0.36.

\* TRIAZINES PLANT

The Triazine Plant is situated in Building 15 and produces two products - Atrazine and Simazine. Both products are in powder form and are used for weed control particularly in crops. They are produced by reacting cyanuric chloride with amines in an agitated reactor. The slurry produced is centrifuged to separate the water from the product and the wet cake is dried and milled to produce a fine powder which is packed in multi-wall paper bags. The amines concerned are ethylamine to produce Simazine, and a mixture of ethylamine and isopropylamine to produce atrazine. Note: some of the triazine cake is dried in Building 03, the remainder is used as-is.

A summary of relevant properties of compounds associated with the triazines plant is appended in Table 10.

Table 9. Average levels of TCDD (ng/g) in 2,4,5-T produced in New Zealand\*

Year	TCDD
1971	950
1972	430
1973	47
1974	31
1975	24
1976	22
1977	31
1978	32
1979	13
1980	14
1981	7.3
1982	8.5
1983	5.3
1984	5.9
1985	4.7

\*From Smith and France (1985)

translocation of these compounds are necessary for herbicidal activity, and all herbicides in this class must be applied to the foliage of actively growing plants. Chlorophenoxy herbicides are used primarily for selective control of broadleaf weeds in cereal grains, pastures and turf and for removing unwanted brushy species in rangeland, forests and noncropland. Rates of application range from as low as 0.25 kg/ha in grain crops to as high as 16 kg/ha for spot treatment of individual trees in rights-of-way. Very dilute solutions of 2,4-D and other derivatives have also been used as growth regulators in fruit orchards. Chlorophenoxy herbicides are applied alone or as mixtures with other herbicides, in solutions, dispersions, or emulsions in water and/or oil, using equipment that produces large droplets to avoid spray drift (Hayes, 1982; Leung, 1986).

Registrations in the USA for 2,4-D and 2,4,5-T in the 1940s included many food crops, and use of these pesticides in the USA was up to nearly 17 million kg annually by 1960. By the mid-1960s, chlorophenoxy herbicides were the most important single class of herbicides. In 1966-1969, they were used for weed control on over 62 million acres (25 million ha) of US agricultural land, and annual US usage of all chlorophenoxy herbicides was nearly 20 million kg (Hazardous Materials Advisory Committee, 1974). It was also during the 1960s that 2,4-D and 2,4,5-T, principally as Agent Orange, were heavily used in South Viet Nam and Cambodia for defoliation of forests by the US Armed Forces. From 1961 to 1971, mixtures of 2,4-D and 2,4,5-T in butyl esters and 2,4-D and picloram tri-isopropylammonium salts were applied at rates of up to 28.6 kg/ha to an estimated 2 million hectares of Vietnamese forests (almost 20% of the forested land area of South Viet Nam). It has been estimated that a total of 25 million kg of 2,4-D and 21 million kg of 2,4,5-T were applied during this time (Weisling, 1971).

US production and use of 2,4,5-T and 2,4-D decreased markedly in 1969 and the early 1970s due to governmental restrictions on their use (Hazardous Materials Advisory Committee, 1974; Grant, 1979). In 1974, an estimated 437 000 kg of 2,4,5-T were used in the USA, the majority of which was applied to rangeland and pasture (US Environmental Protection Agency, 1979a).

Although MCPA has never attained the level of consumption of 2,4-D or 2,4,5-T, it has found specialized use for weed control in cereal grain production. US consumption of MCPA was 2.1-2.9 million kg in 1980 (Hofforf, 1982), most (70-71%) was used on wheat and rice.

Metoprop is used similarly as a post-emergence herbicide for control of cleavers and chickweed in cereal grains (Worthing, 1983).

Silvex has been recommended for control of aquatic weeds, weeds in pasture, sugar cane and rice, and especially for brush. The triethanolamine salt has been used to reduce preharvest dropping of apples (Hayes, 1982; Meisner, 1983). In California, for example, only approximately 360 kg were used in 1983 on pasture, rangeland and landscaped areas (California Department of Agriculture, 1984). All US registrations for silvex were cancelled in 1983 (US Environmental Protection Agency, 1983).

Dichloroprop has been used and is still recommended for removal of brush on rangeland and rights-of-way, and for control of aquatic weeds (Aron, 1983). Approximately 3150 kg of dichloroprop were used in California for these applications in 1983 (California Department of Agriculture, 1984).

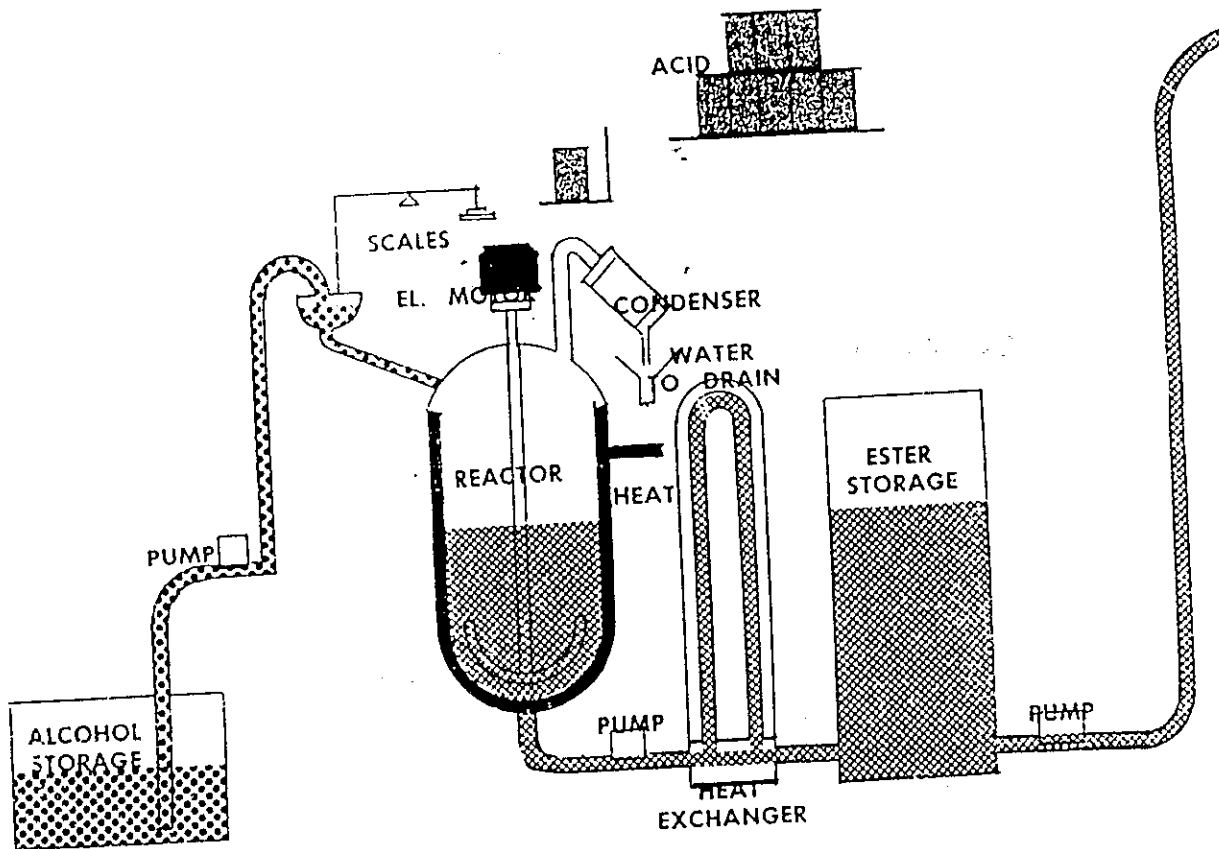
#### 1.4 Regulatory status and guidelines

By 1974, the US Environmental Protection Agency had cancelled all registrations for chlorophenoxy herbicides, except those pertaining to uses other than on foods and on rice paddies, pastures and rangelands (Aron, 1974). In 1983, all registrations for 2,4,5-T were cancelled, and this chemical can therefore no longer be used legally for any purpose in the USA (US Environmental Protection Agency, 1983). Registrations have also been cancelled in, e.g., Sweden, the Netherlands, the USSR and Australia (Aron, 1983). 2,4,5-T was banned in Italy in 1970 (Vignati *et al.*, 1986) and in the Federal Republic of Germany in 1985.

Occupational exposure limits for 2,4-D in 14 countries and for 2,4,5-T in nine countries have been reported and are presented in Table 10. Regulations pertaining to the pesticide use of chlorophenoxy herbicides are not reviewed or reported comprehensively in this monograph.

#### 1.5 Occupational exposure

Exposure to chlorophenoxy herbicides may occur through inhalation, skin contact or ingestion. In most cases, the predominant route of occupational exposure has been by the absorption of spills or aerosol droplets through the skin (Leung *et al.*, 1982). International Programme on Chemical Safety, 1984). Measurements are usually reported in terms of



CERVANTES had a line for it. "Everyone," he made Don Quixote say, "is the son of his own works." Even a modern factory, planned with the prime thought that many of its future customers are the occupants of today's bassinets and play pens, is built on foundations of solid experience, and will forever be influenced by its yesterdays and todays. While its builders and operators are tempted and entitled to look far ahead, they must be prudent enough to turn out a payable and a saleable article for the current market and contemporary needs. It is the functioning link between scientific discovery and the buyer-user on the land.

So, the new premises of Ivon Watkins, Ltd., were laid out with the object of manufacturing products in the most economical way and of the highest quality. Follow the pictorial flow sheet, and you will see that, as on a well-run farm, there is a place for everything, coming and going. Except for certain liquids, mainly alcohols, raw materials are held in their own store, 15 feet above the packing floor, thus making use of gravity to charge the reactors and blenders.

## ESTER FORMATION

The flow diagram depicts the production of a weed-killer in the form of an emulsifiable concentrate. A weedkiller acid is mixed with an alcohol in one of the reactors and is subject to a carefully controlled heat treatment until the alcohol has reacted with the acid to form a compound known as an ester. In the course of this reaction water is also produced and this is

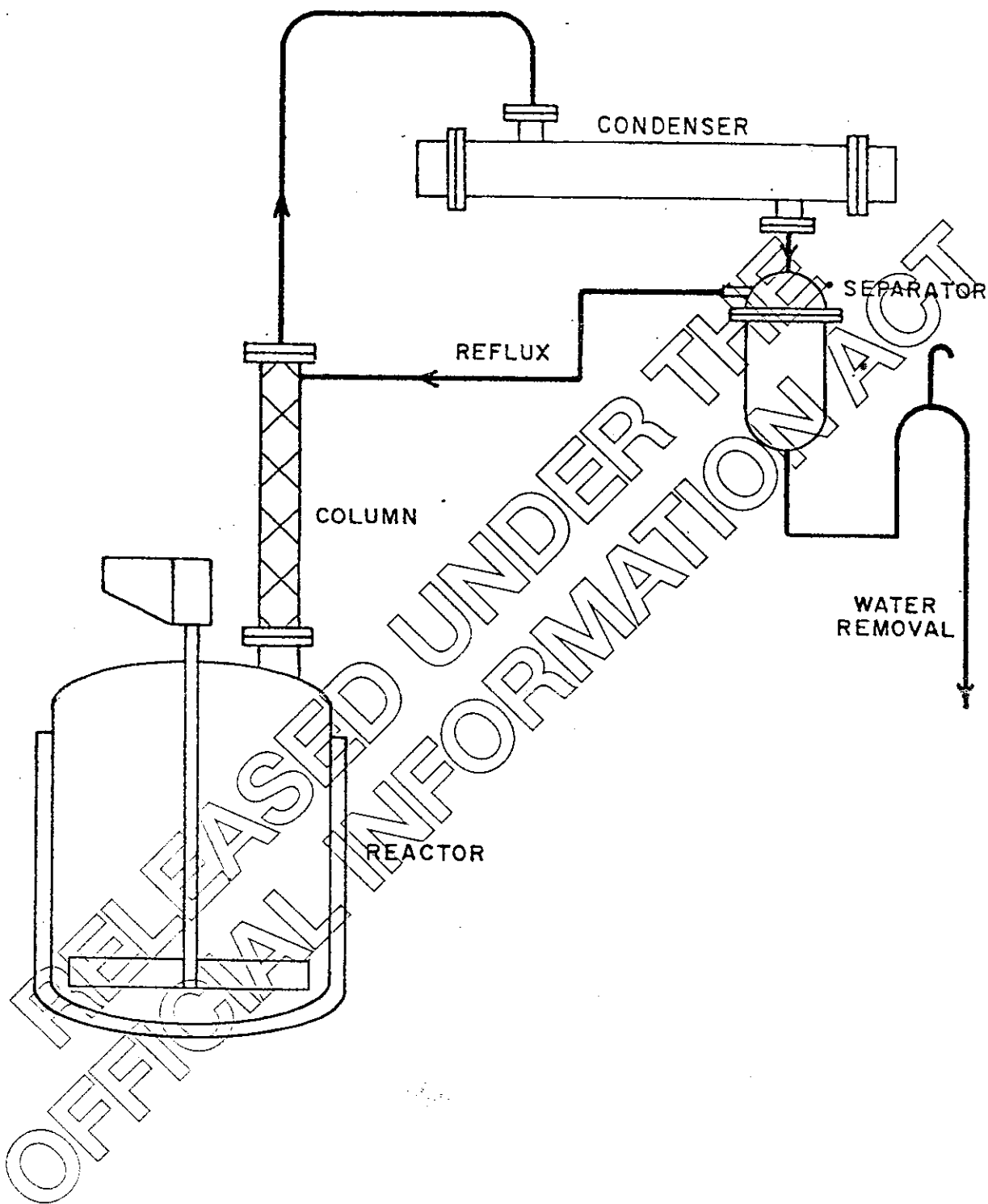
distilled off, leaving the ester, a heavy oily liquid somewhat like light lubricating oil, in the reactor. When the laboratory has advised the factory that the reaction is complete the hot ester is passed through a heat exchanger to cool, and is then stored in one of a series of ester storage tanks.

## THE BLENDER'S PURPOSE

The ester is the active ingredient of the finally formulated product, but, because it is quite insoluble in water and in a form not capable of application to plants, it is necessary in a second stage of manufacture to modify it so that it is easy to apply.

This is carried out by carefully weighing a series of ingredients, including the ester, into a mixing vessel known as a blender. Apart from the ester, the main ingredients are a solvent and an emulsifier. The solvent has to be a liquid which will dissolve not only the ester but also the emulsifier. When the necessary ingredients have been placed in the blender and thoroughly mixed by means of the stirrer, samples are taken by the laboratory for analysis to ensure that the product manufactured meets the necessary specifications. When passed as satisfactory, the blended product is pumped to storage tanks above the packing unit.

From these storage tanks the product is filled into the containers and packed off ready for distribution. When packed the weedkiller is transferred to the finished goods store ready for despatch throughout New Zealand.



• FIGURE 1  
PLANT LAYOUT

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