

THE MANUFACTURE OF A HIGHLY TOXIC ORGANIC PHOSPHORUS COMPOUND

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SUMMARY

This paper describes how a plant designed for the manufacture of an organic phosphorus compound of comparatively low toxicity was modified to permit the safe manufacture of another far more toxic material.

Introduction

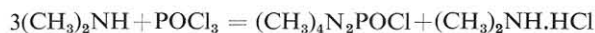
Both compounds made by the plant were the major ingredients of systemic pesticides for the protection of crops from aphids and red spider. A systemic insecticide is one with the property of being taken up into the system of the plant treated with it; the insecticide is transferred to the various parts of the plant so that insects which suck the sap perish.

Field trials carried out upon the second more poisonous compound, *bis*-dimethylamino-fluoro-phosphine oxide, proved its exceptional effectiveness as an insecticide and since an economic process for its manufacture had been developed¹ and a ready sale of the product was assured, there was ample incentive for its early manufacture. Moreover, the plant erected earlier for the small-scale manufacture of the less toxic material required little alteration, from processing considerations, to render it suitable for making the fluoro-phosphine oxide (which for convenience we shall refer hereafter to as compound 'B').

The Process

The process has been described in detail elsewhere.¹ It consists of three main stages, the preparation of *bis*-dimethylamino-chloro-phosphine oxide, the reaction of this material with potassium fluoride to form 'B', and the recovery of dimethylamine from dimethylamine hydrochloride formed in the first of these reactions—an operation essential to the economy of the process.

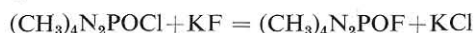
In the first reaction in the series to a solution of phosphorus oxychloride in toluene is added continuously a solution of dimethylamine also in toluene. The following reaction takes place:—



The dimethylamine hydrochloride is insoluble and is separated by filtration from the intermediate product, *bis*-dimethylamino-chloro-phosphine oxide, which in the remainder of this paper we shall refer to as compound 'A'. The filtered dimethylamine hydrochloride is dissolved in water and fed continuously to a concentrated solution of caustic soda. This liberates the dimethylamine which is then absorbed in toluene in readiness for the first reaction of the process. The solution

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of 'A' is reacted with potassium fluoride according to the following reaction:—



This reaction requires the presence of a small quantity of water. When the reaction is complete the solution of 'B' has to be separated from the remaining reaction products which are present in the lower, aqueous layer, as a finely divided slurry. This done the solution is distilled to give a concentrated product ready for formulating into the finished insecticidal preparation, and toluene, which is re-used in the process.

The Hazards

A two-fold hazard really accompanies this process for in addition to the highly toxic 'B', there is a fire hazard through the use of toluene and dimethylamine. This hazard had been looked after satisfactorily in the original plant. Some of the measures taken included the location of feed-pipes to reactors so as to avoid a free fall of flammable liquids, reactors and piping systems were electrically grounded, flame-proof equipment was employed, and so on.

The action of compound 'B' upon human beings is to paralyse the central nervous system. If the exposure or dose is large enough complete paralysis and even death can occur. The effect of 'B' is to reduce the enzyme cholinesterase thereby inhibiting muscular contraction of an affected person. It can be dangerous by contact with the liquid and by inhalation of its vapours.

As to the contact danger, an unpleasant property of 'B' is the rapidity with which it is absorbed through the skin; the absorption of 500 mg would be sufficient to cause death, and the absorption of 200 mg would lead to paralysis. With regard to the danger of inhaling vapours of 'B', it is known that brief exposure to an atmosphere containing $7-13.7 \times 10^{-5}$ lb/ft³ can prove fatal. A concentration of 6.2×10^{-8} lb/ft³ or greater can lead to a rapid decline in cholinesterase indicative of a dangerous situation, and atmospheres containing 6.2×10^{-9} lb/ft³ or more can cause a steady reduction of the enzyme; only when its concentration is less than this level can an atmosphere be considered safe to breathe.

These levels of course, do not represent sharp lines of demarcation as between one degree of hazard and another, and the resistance of individuals to anticholinesterase must also vary. But figures did tell us quite clearly the conditions to avoid in order to make the plant safe for the manufacture of 'B'.

Vapour pressure data

Some of the available data on the vapour pressure of 'B' and its solutions are given below :—

Vapour pressure of 'B' in the range 10–50°C is given by:²
 $\log p = 8.009 - 2522/T$

Partial pressure of 'B' in a 10% w/w solution of toluene is given by :

$$\log p = 5.88 - 2012/T$$

in a 15% w/w solution the partial pressure of 'B' is given by :

$$\log p = 6.05 - 2012/T$$

Partial pressures of a 5% w/w aqueous solution are given by :

$$\log p = 13.61 - \frac{4700}{T}$$

In the above expressions p is the vapour pressure (in mm Hg) and T is the temperature (°C).

From the expression for the pure toxicant, it can be shown that an atmosphere saturated with 'B' at 25°C would contain a fatal concentration of toxicant.

Elimination and Reduction of Hazards

The above data were useful for investigating the inhalatory dangers likely to arise at various parts of the plant. The original design is shown in Fig. 1; this was a plant out in the open. This was considered to be of some advantage since the prevailing winds could assist in dispersing emissions of

noxious fumes. Other circumstances conducive to safety were the small area occupied by the plant and the small output of product. The first task was to examine each part of the plant and its every operation for emission or leakage of toxicant.

So far as the two main reactions stages were concerned there was no possibility of rendering them continuous and on that account less hazardous to operate.

A number of more or less obvious practices were adopted in order to remove the various sources of danger. To avoid contact hazards, the plant had to be absolutely free of liquid leaks. Pumps or valves with glands could not be used: pipelines carrying 'B' or its solutions had a minimum of joints. Where joints could not be avoided they were of the heavy-flanged type with narrow-faced joints. The pipelines were arranged to drain completely once the transference of liquids through them was complete.

Where gravity flow could not be used, transference from one vessel to another was carried out by first partially evacuating the receiving vessel and then opening the line connecting the two vessels. Pumps were used only for the transference of harmless fluids such as fresh or distilled toluene.

Protective clothing of non-absorbent, water-proof material was worn by the plant operators; this clothing was washed down in warm water before being removed by an operator so that when he returned to his job it would be in clean, uncontaminated clothing.

Making the main reaction safe

Clearly one of the main sources of hazard in the entire process would be where the reaction producing 'B' was carried

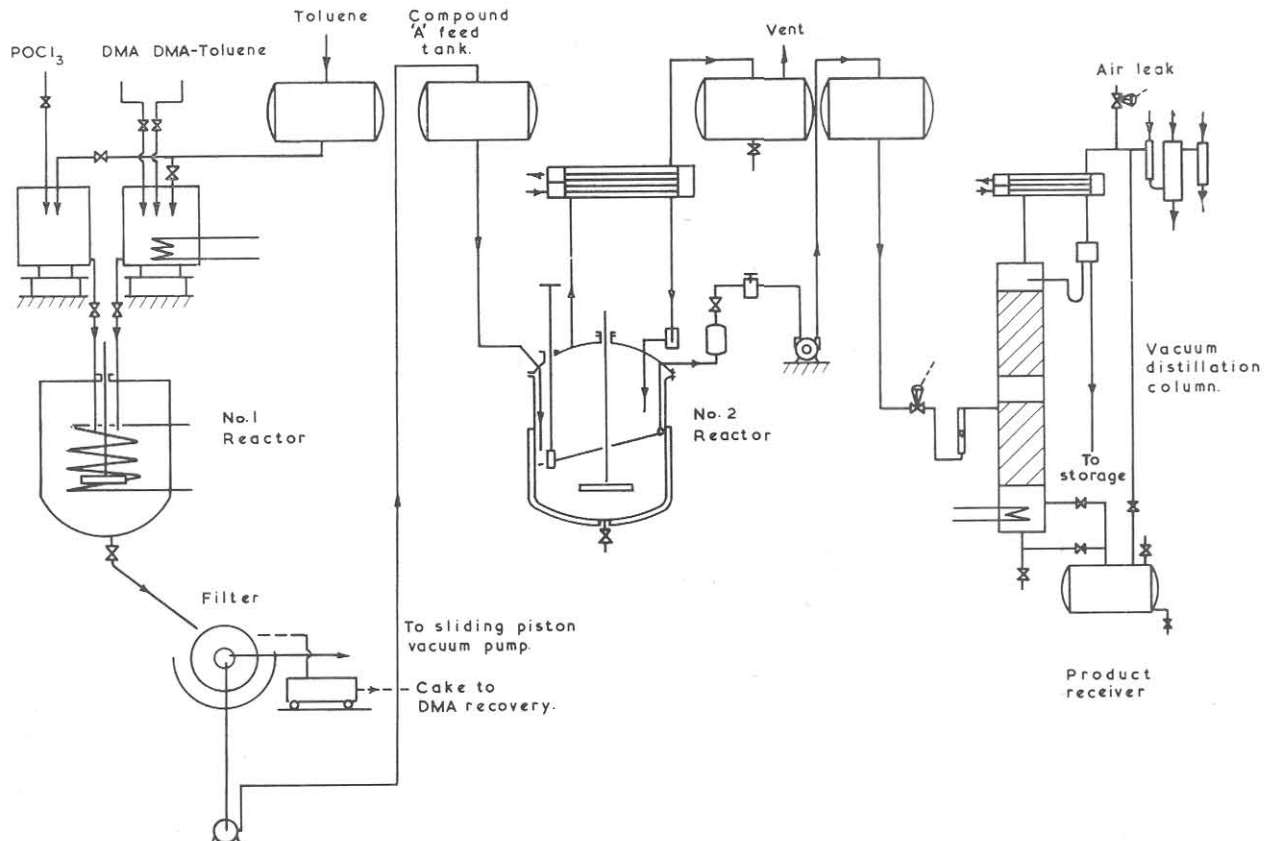


Fig. 1.—Plant before modification

out. The main features of the reaction vessel as originally available are shown in Fig. 2. Its purpose had been to react together solid potassium hydroxide with a solution of 'A' in toluene, the product being considerably less toxic than 'B'. After the reaction the products were cooled and allowed to settle. The clear solution would then be transferred to storage by means of the rotary pump and the dip-pipe.

In the modified arrangements at this reactor the pump was discarded. The dip-pipe was operated manually by means of a stainless steel rod which passed through a stuffing box on the cover of the vessel. The exposed end of the rod was clearly a source of contact hazard, despite any wiping action of the packing, and it was therefore totally enclosed in an elongated leather bellows. At the same time it was arranged that the rod could be operated remotely by means of a small compressed-air hoist.

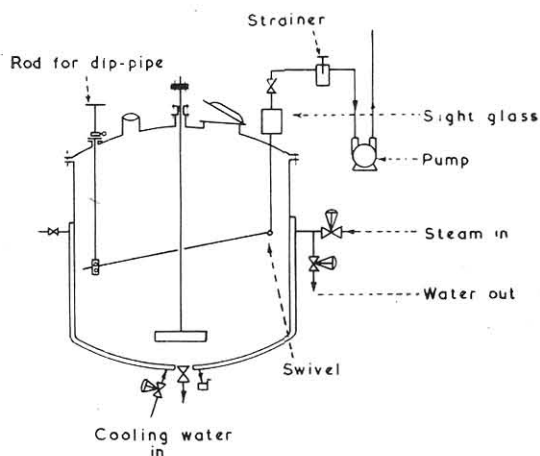


Fig. 2.—Reaction vessel as originally available

The dip-pipe was connected to a packed swivel fitted inside the vessel. The swivel was removed altogether and replaced by a short piece of flexible stainless steel hose, the open end of which was positioned by the rod. The dip-pipe connection on the vessel was connected through a sightglass of enlarged section to a tank of somewhat greater capacity than that of the vessel. In order to transfer the contents of the reactor, the receiver tank would be partially evacuated. After this operation the solution of 'B' would be run by gravity to one of two storage tanks, in readiness for distillation.

Another possible source of contact hazard was the gland of the agitator shaft; it was possible for toxicant solution to creep past the packing on to the exposed length of shaft near the motor gear unit coupling. To reduce this danger the lantern ring of the gland was put under a positive pressure of several feet of water.

The arrangements which were adopted at the main reaction stage to eliminate the contact hazards are summarised in Fig. 3.

Inhalatory risks at the main reaction stage

From the vessel in its original form hazards through inhaling vapours of the compound 'B' could arise from at least three causes, the emission in each case being through the vent of the reflux condenser. These were:—

(a) displacement of the vessel atmosphere during the charging of reactants;

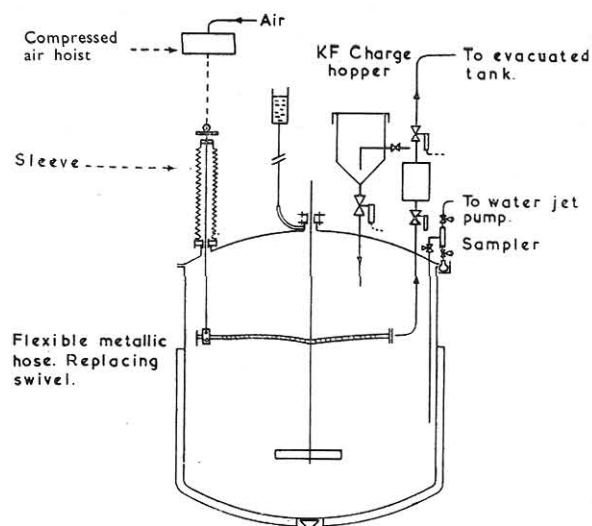


Fig. 3.—Arrangements of main reaction stage to eliminate contact hazards

(b) expansion of the vessel atmosphere in heating the contents from the ambient temperature to the reaction temperature of 90–95°C;

(c) carryover with non-condensable gases liberated during the course of the reaction.

To estimate the amount of 'B' through the first of these mechanisms it was assumed that the condenser, which was not designed as a cooler-condenser, would cool the outgoing gases to 30°C, but not below this temperature. It was also assumed that the atmospheres discharged from the vessel were saturated with respect to 'B'. The estimated amounts discharged through the condenser through causes (a) and (b) were 0.0025 and 0.0033 lb, or a total in round figures of 0.006 lb. This would be discharged within 10–15 minutes.

Mechanism (c) did not appear to enter the picture although as shown below, provision was made for dealing with its possible occurrence.

The quantity of 0.006 lb is capable of rendering 60 ft³ air lethal. For absolute safety it would have to be dispersed through a volume of 900 000 ft³. Clearly there were serious inhalatory risks at the main reactor and they were reduced to a safe level by the means shown in Fig. 4. A condenser with

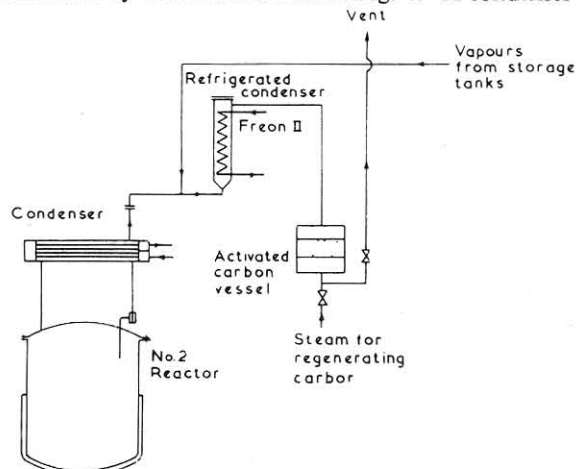


Fig. 4.—Recovery of dangerous non-condensable gases

Freon 12 evaporating inside the coils was fitted downstream of the reflux condenser and beyond this a shallow bed of activated carbon was installed to remove the last traces of 'B' and toluene. The additional vessels were arranged to allow safe regeneration of the carbon. Thus the steam-plus-solvent and toxicant would condense in the refrigerated condenser and flow from it by gravity back into the reactor.

A final point about the reactor is the method of adding the solid reactant, potassium fluoride. In the process previously carried out in this vessel the charge of solid caustic potash was introduced into the vessel through a quick-opening lid on the cover. This practice could not be contemplated in the case of compound 'B'. Instead a 4-inch connection was welded to the cover of the vessel, and to this was attached a compressed-air operated lubricated plug-cock. Above this valve was fitted a small hopper just sufficient to carry the charge of fluoride necessary for a single reaction. At one time the use of a double-valve feed hopper had been contemplated but the idea was abandoned as being too complicated. The charge was added with the valve closed—indeed the lid of the hopper could only be lifted when the valve was in this position. Once the operator had retired to a safe distance the discharge valve would be opened and the charge of fluoride emptied into the vessel. It was possible to sluice the hopper with a small quantity of water after each charge.

Other methods of making this addition were tested; one suggestion was to fluidise the fluoride and to pump it by means of a positive displacement screw pump directly into the vessel. Although a number of finely divided solids have been pumped successfully by this method potassium fluoride has not proved to be one of them and the idea was discarded. Another method was to convey the charge as a slurry in toluene to the reactor, but this too proved unpractical.

Hazards at storage tanks

The filling and breathing of storage tanks containing solutions of 'B' also constituted a hazard. A 500-gallon storage

tank containing a small quantity of 15% solution of 'B' in undergoing a rise of temperature from 10–25°C would discharge about 0.000 56 lb of 'B' to atmosphere. This small quantity would be sufficient to produce a fatal level of concentration in a volume of 9 ft³ and for complete safety would have to be dispersed in a volume of some 90 000 ft³. However, this quantity is evolved over a comparatively long period.

When the filling emissions are considered the figures are much more serious; if the tank and contents are initially at 10°C then about 0.0039 lb of toxicant is emitted. This is sufficient to render lethal a volume of 50 ft³ and for safety would have to be dispersed in a volume of over 600 000 ft³. If the temperature of tank and contents were 25°C the situation would be even worse since the quantity discharged would be about 0.008 lb and this would render lethal a volume of 112 ft³ and for safety would have to be evenly distributed through a volume of over a million cubic feet.

The emissions were dealt with by connecting the tank vents to a point between the reflux condenser and the refrigerated condenser shown in Fig. 4.

Treatment of solvent

After it is distilled from the main pocket, toluene is returned to the process for further use. It is for example mixed with phosphorus oxychloride to provide one of the reactants for No. 1 reaction. It is used also for the absorption of recovered DMA and for washing the cake of DMA hydrochloride arising from the first reaction.

The safety of No. 1 reaction and its preparatory operations, the filtration following it, and the recovery of DMA depends therefore to some extent upon the use of a solvent substantially uncontaminated by 'B'.

The distillation column available was found to be capable of reducing the level of contamination to somewhere in the range 15–200 p.p.m. This was not considered to be low enough since something like 0.2 p.p.m. was required for

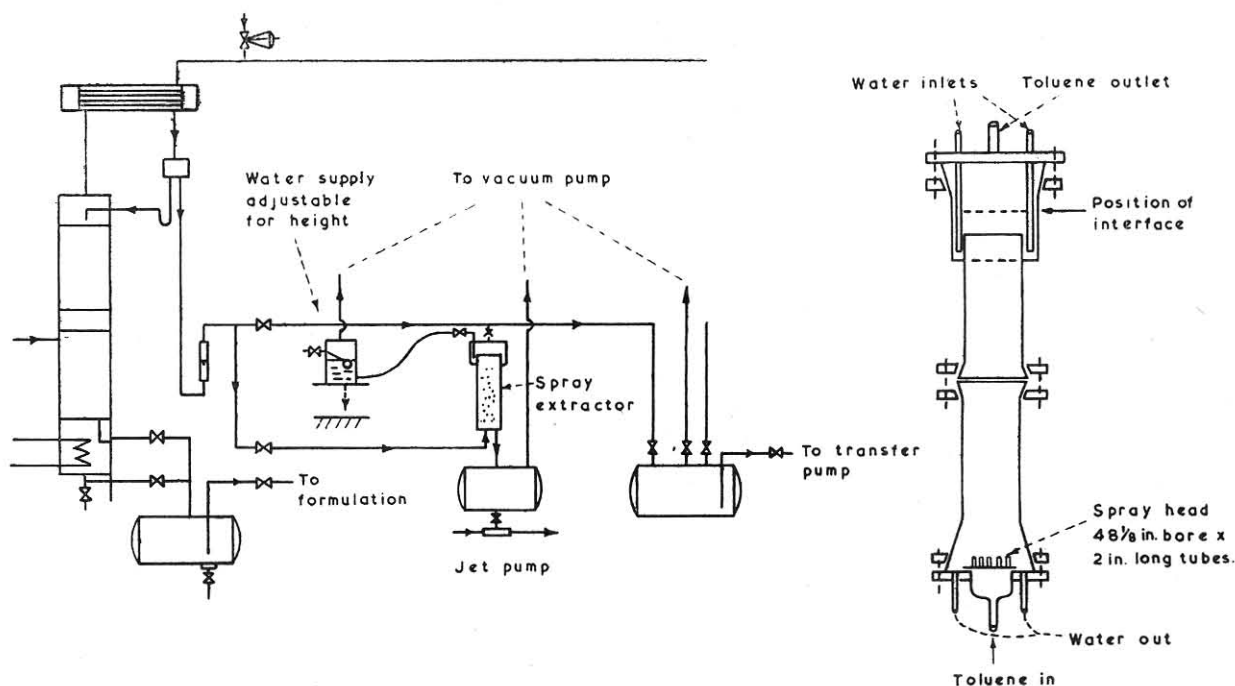


Fig. 5.—Spray column for extraction of toxicant

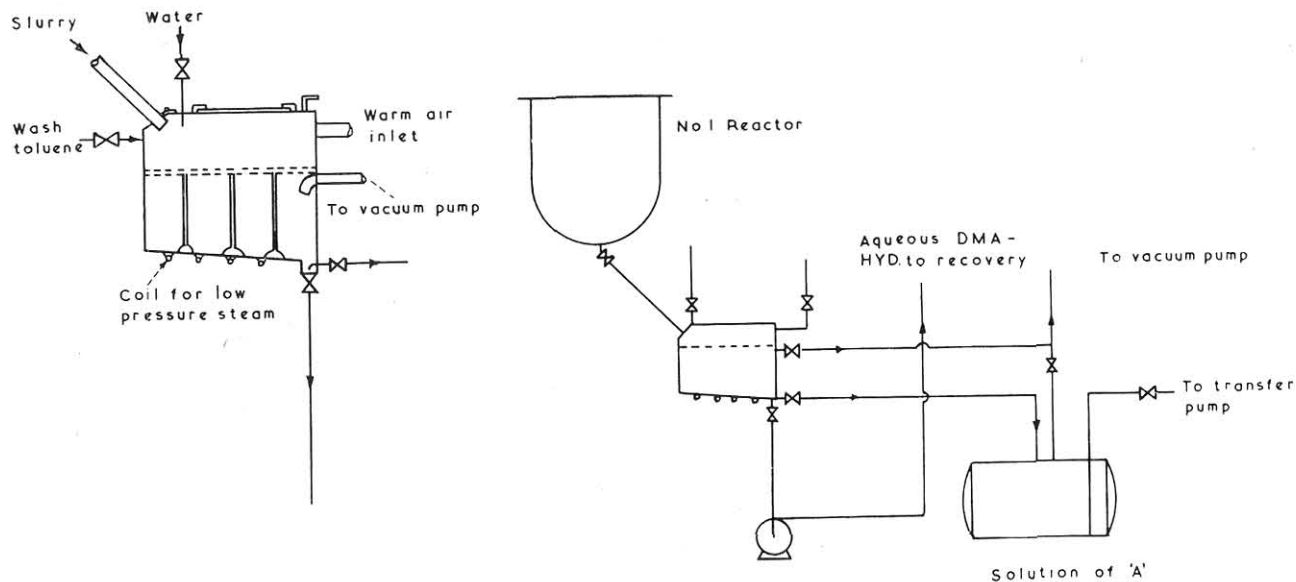


Fig. 6.—Home-made Nutsch filter

reasonable safety. It seemed doubtful whether this level of purity could be obtained by distillation.

The column, which was designed to operate at a vacuum of 28½ in. Hg, was provided with a water-ring vacuum pump in place of a two-stage ejector set used previously. The substitution was made because uncontrollable fluctuations in steam supply to the ejectors had previously led to upsets in operating vacuum. While this change was conducive to more stable operation for the production of purer toluene another measure was necessary.

This consisted of making use of the greater solubility of 'B' in water compared with toluene; thus the toxicant was extracted with water from toluene, by means of a small spray column fitted between the distillation column and the toluene collecting tanks. In this unit (Fig. 5) toluene is bubbled through the extracting water which passes downwards through the apparatus. The extractor was designed to reduce the 'B' content of 30 gal/h of toluene from 200 p.p.m. to 0.2 p.p.m. A greater extracting effect could have been obtained, if required, by interposing another cylindrical section between the main joint.

Although the provision of a very pure toluene was an important contribution to the safety of the earlier stages of the process additional measures were taken to improve safety. Thus the pumps used for the transference or circulation of toluene were arranged to have their glands under suction when in operation. A further measure was the filter for the hydrochloride. This piece of equipment replaced a small rotary vacuum filter which was not mechanically reliable enough to be a safe means of filtration. The replacement was a home-made Nutsch filter (Fig. 6). Contact with the cake could be avoided by dissolving it, after washing, in water and by pumping the aqueous hydrochloride solution to the recovery process. The filter cloth after this operation can be dried by drawing warm air through the filter. The design still allowed for the manual removal of cake, but the dissolution method was much the safer since it eliminated contact with the cake.

Transfer of toxicant and its solutions

As indicated earlier in this paper, compound 'B' or its solutions were not transferred by pumping direct but by

evacuating the receiving vessels. The pumps used for evacuation were of the water-ring type and they were particularly suitable for this purpose because their service water supply served to condense to toxicant vapours. The air-discharge pipes from the pumps were taken to a height to ensure that any uncondensed toxicant would be carried away beyond the operating area. The water discharged from the pumps passed through beds of activated carbon to remove the traces of dissolved toxicant.

For filling containers at the final stage of the process, glove boxes fitted with quick opening air locks were employed. The amount fed to a container was controlled by means of a conductance electrode system which worked in conjunction with a solenoid valve.

In addition to the steps described other safeguards were provided. For emergencies, respiratory apparatus was available, the air being supplied from a small diaphragm compressor with its intake situated well clear of the plant area. In order to provide a ready source of decontamination in the event of a spillage of 'B' or its solutions, a header tank containing a supply of hypochlorite solution was also installed. A highly desirable feature at this plant would have been a system of monitoring continuously the condition of the atmosphere at various danger points. Unfortunately no such equipment appeared to be available at the time of making the modifications described, and reliance had to be placed upon frequent manual sampling and chemical analysis for this purpose.

Finally the operating and maintenance staff were given frequent and regular medical examinations to ensure that their cholinesterase levels had not suffered through their presence on the plant.

The foregoing were some of the main steps which were taken to make an existing plant safe for the manufacture of a useful but extremely dangerous chemical.

References

- 1 Pianka, M. and The Murphy Chemical Co. Ltd. *British Patent 742 699.*
- 2 Schrader, G. "Die Entwicklung Neuer Insectide auf der Base der Fluor und Phosphor Verbindungen."

The manuscript of this paper was received on 15 March, 1960.