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An investigations into the production of chloral by the chlorination of enthyl alcohol

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2015-06-29
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THESIS
SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
IN THE FACULTY OF SCIENCE

UNIVERSITY OF THE WITWATERSRAND

BY

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PART ONE.

AN INVESTIGATION INTO THE PRODUCTION OF CHLORAL BY THE CHLORINATION OF ETHYL ALCOHOL.

PART TWO.

THE CONDENSATION OF ANHYDROUS CHLORAL AND MONOCHLOROBENZENE TO 1:1:1-TRICHLORO-2:2-DI-(4-CHLOROPHENYL)ETHANE.(DDT).

WORK CARRIED OUT UNDER THE DIRECTION OF LT.COL. W. BLELOCH Ph.D.(LONDON), F.R.I.C., M.I.Chem.E. IN THE LABORATORY AND PILOT PLANT AT C.D. FACTORIES (U.D.F.), KLIPFONTEIN.



Thesis.

The writer wishes to express his thanks and appreciation to the Management of C.D. Factories (U.D.F.) in allowing the material in this work to be published in thesis form.

NOTE:

The average barometric height at

KLIPFONTEIN is 627 mm. Hg.

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F O R E W O R D.

The work recorded in this thesis was carried out at the Klipfontein Factory of the C.D. Factories (U.D.F.). It represents the initial stages of a development programme involving the large scale production of chemicals, such as DDT, that were at that time in urgent demand by the Union Defence Force.

The writer, in his capacity as Chief Chemist, was instructed by the Management, early in 1944, to carry out the preliminary work on the manufacture of DDT. It was necessary that any pilot plant should also produce sufficient material for experimental purposes. Though this policy could be criticised in that it might handicap any basic development programme, very little interference was caused. Approximately one ton of DDT was produced at a time when no other supplies were avaiable, and valuable data were gathered for the design of the full scale unit, which has now been operating successfully for a period of one year.

The writer was assisted throughout the investigation by the staff of the Development Laboratory, whose services are duly acknowledged. The pilot plant units were built on the premises by the engineering staff, after due consultation with the General Manager, Lt.Col. W. Bleloch; the Works Manager, Capt. A.Q. Harvey; and the Resident Engineer, Mr. M. J. Swain.

The Management received information through official channels broadly describing the methods adopted overseas. These are referred to under the relevant sections in the text.

PART ONE.

AN INVESTIGATION INTO THE PRODUCTION OF CHLORAL BY THE CHLORINATION OF ETHYL ALCOHOL.

A. INTRODUCTION:

1. The Chemistry of Chloral.

Chloral, or trichloroacetaldehyde, was first obtained by Liebig (1) in 1832 by the extended chlorination of alcohol. The composition of the chief end product, chloral alcoholate, was established by Dumas (2) at a later date.

Chloral, $CCl_3.CHO$, in the anhydrous form is a pungent colourless liquid, boiling at 97 - 98°C. In a very pure state it is stable, though it readily polymerises to metachloral, a white solid, in the presence of traces of acidic substances, such as sulphuric acid or aluminium chloride. Metachloral is insoluble in water, but soluble in most organic solvents. The addition of weak alkalis, such a sodium bicarbonate or even chloral ammonia, generally inhibit the tendency of chloral to polymerise. Chloral undergoes the typical reactions of an aldehyde, forming complexes with ammonia and reducing ammoniacal silver nitrate in a manner similar to acetaldehyde. It differs from acetaldehyde in one important respect, in that it forms hydroxylated compounds with water and alcohol giving solid chloral hydrate, $CCl_3.CH(OH)_2$, and the hemiacetal, chloral alcoholate, $CCl_3.CH(OH)OC_2H_5$, respectively. Both the hydrate and the alcoholate forms yield chloral again on treatment with concentrated sulphuric acid. Metachloral is also reconverted to chloral when heated to above 180°C in the presence of sulphuric acid. As would be expected from the presence of hydroxyl groups, both chloral hydrate and chloral alcoholate are quite stable. In the presence of concentrated sulphuric acid in excess, especially at high temperatures, chloral decomposes to form chloralide, a solid melting at 114°C. The decomposition proceeds as follows:

$3CCl_3CHO$/.....

$$3CCl_3CHO \xrightarrow{H_2SO_4} Cl_3C.CH(O-CH.CCl_3)(CO-O) + COCl_2 + HCl$$

chloralide.

All the derivatives of chloral mentioned above are hydrolysed by strong alkalis to give chloroform and the alkali formate.

$$CCl_3CHO + NaOH \longrightarrow CHCl_3 + H.COONa$$

This reaction is the basis of most analytical procedures for the estimation of chloral. When chloral is estimated in the presence of its polymer, special precautions have to be taken to exclude the polymer from the hydrolysis step. (3, and Appendix).

Chloral hydrate has been the most important derivative of chloral; it is extensively used as a soporific in medicine, and is listed in most pharmacopoeia. It is prepared by the addition of the equivalent of water to anhydrous chloral; the mass becomes hot and solidifies on cooling. It can be recrystallised from benzene, and is the most convenient form to use if a pure chloral derivative is required. The anhydrous chloral produced by the distillation of chloral hydrate or chloral alcoholate over sulphuric acid will always contain some water and hydrochloric acid as impurities. The purest chloral produced in these laboratories, by repeated distillations, has still contained some 1 to 2 per cent of these impurities, though greater purification can be obtained by special methods, such as by distillation through fractionating columns of high efficiency, or by distillation over phosphorus pentoxide (3). The physical properties of chloral, its derivatives, and related compounds are listed in Table I.

TABLE I.

PROPERTIES OF CHLORAL DERIVATIVES AND RELATED SUBSTANCES.

SUBSTANCE	FORMULA	MOL. WT.	DENSITY	B.P. °C	M.P. °C	SOLUBILITY	
						Water	Organic Solvents
Chloral	$CCl_3 . CHO$	147.5	1.5065 (20°C)	97-8	-57	Soluble	Soluble
Chloral hydrate	$CCl_3.CH(OH)_2$	165.5	1.908 (20°C)	96.3 (764 mm)	53	21.3% at 17°C	Soluble
Chloral alcoholate	$CCl_3.CH(OH)OC_2H_5$	193.5	1.143 (40°C)	115-6	50	Soluble	Soluble
Chloralide	$CCl_3.CH-O-CH.CCl_3$ (CO-O)	323.0	-	272-3	116	Insoluble	Sol. in ether Slightly sol. in alcohol
Monochloroacetal	$CH_2Cl.CH(OC_2H_5)2$	152.5	1.023 (20°C)	157	-	-	-
Dichloroacetaldehyde	$CHCl_2.CHO$	113.0	-	90-1	-	-	-
Dichloroacetaldehyde alcoholate	$CHCl_2.CH(OH)OC_2H_5$	159.0	-	110-1	-	-	-
Dichloroacetal	$CHCl_2.CH(OC_2H_5)2$	187.0	1.1383 (14°C)	183-4	-	-	-
1:2-Dichlorodiethylether	$CH_2Cl.CHCl.O.C_2H_5$	143.0	1.174 (20°C)	140.5	-	-	-

2. Methods of Manufacture.

Chloral is manufactured on the large scale by the chlorination of alcohol using methods similar to that described by Liebig. The use of absolute alcohol appears to have no advantage over alcohol at rectified strength (95 per cent.)

$$2C_2H_5OH + 4Cl_2 \longrightarrow CCl_3.CH(OH)OC_2H_5 + 5HCl$$

Other methods have been described, notably that of Reichert, Bailey, and Nieuwland (4), who chlorinated diethylacetal, $CH_3.CH(OC_2H_5)_2$, which was in turn prepared from alcohol and acetylene in a manner analogous to the synthesis of acetaldehyde, and in the presence of a mercury catalyst.

Page (5) chlorinated alcohol with ferric chloride as a catalyst. The reaction mixture was kept cool during the initial stages and was later raised to 100°C. By this process a mixture of chloral and chloral hydrate, rather than chloral alcoholate, was formed. Another process described (6) advocated carrying out a chlorination in three stages. Chlorine was passed into cooled alcohol at a rate such that the density of the liquid reached 1.20 in twenty-four hours. In the next stage the temperature was raised to 50°C, the density reaching 1.3° to 1.39 after the second day. The chlorination was completed on the third day at 95°C, when the density of the product reached 1.50. Recently, a continuous process for the manufacture of chloral has been described (10). It possesses certain novel features in regard to the equipment used, but is based on the chlorination procedure described by Page (5).

The yields claimed on the processes described vary from 60 per cent of chloral (10) to 75 per cent of chloral distillate (6), calculated on the alcohol used. The latter yield would probably be in the neighbourhood of 70 per cent of chloral as it is doubtful whether a distillate produced in the manner described would contain more than 95 per cent CCl_3CHO. Page (5) claimed a yield

greater/.....

greater than that indicated by Liebig's equation (1), though the 525 g. of chloral hydrate, obtained in his experiment from 400 g. of 97 per cent alcohol, would represent a yield of approximately 75 per cent based on the equation giving chloral alcoholate. Official reports received from overseas sources indicated that a yield approaching 80 per cent of chloral on the alcohol is achieved in modern units. Data for the yield based on the chlorine used were not available.

3. Course of the Reaction in the Chlorination of Alcohol:

The course of the reaction is far more complex than that indicated by the simple equation above. Chloroacetals can readily be isolated early in the reaction. Low temperatures favour the formation of chloroacetals, (7) which fact may give the reason for the general use of an initial cold stage in the production of chloral. Chattaway and Backeberg (8) trace the course of the reaction as one essentially involving the oxidation of the alcohol, followed by successive chlorinations with free chlorine and hydrochloric acid taking part. Their scheme can be represented as follows :-

$$C_2H_5OH + Cl_2 \longrightarrow CH_3.CHOCl + HCl$$
ethyl hypochlorite

$$CH_3.CHOCl \longrightarrow CH_3.CHO + HCl$$

$$CH_3.CHO + Cl_2 \longrightarrow CH_2Cl.CHO + HCl$$
monochloroacetaldehyde

$$CH_2Cl.CHO + C_2H_5OH \longrightarrow CH_2Cl.CH(OH)OC_2H_5$$
monochloroacetaldehyde alcoholate

$$CH_2Cl.CH(OH)OC_2H_5 \xrightarrow{HCl} CH_2Cl.CHCl.O.C_2H_5 + H_2O$$
dichlorodiethyl ether

$$CH_2Cl.CH(OH)OC_2H_5 \xrightarrow{C_2H_5OH} CH_2Cl.CH(OC_2H_5) + H_2O$$
monochloroacetal

$CH_2Cl.CH(OC_2H_5)$/....

$CH_2Cl.CH(OC_2H_5)$ —HCl→ $CH_2Cl.CHCl.O.C_2H_5$

—Cl_2→ $CHCl_2.CH(OC_2H_5)$ + HCl

—Cl_2→ $CHCl_2.CHCl.O.C_2H_5$
trichloroethyl ether

—HCl→

$CHCl_2.CHCl.O.C_2H_5$ —H_2O→ $CHCl_2,CH(OH)OC_2H_5$ + HCl
dichloroacetaldehyde alcoholate

$CHCl_2.CH(OH)OC_2H_5$ —Cl_2→ $CCl_3.CH(OH)OC_2H_5$ + HCl
Chloral alcoholate

The formation of ethyl hypochlorite is of interest, as it may give an explanation for the explosions that have been reported. Ethylene hypochlorite is very unstable, and often explodes with violence during its preparation (9). It has been found in these laboratories that when alcohol is chlorinated at sub-zero temperatures, a violent explosion ensues after a few hours (x). It is possible that ethyl hypochlorite accumulates in dangerous concentrations at very low temperatures. It has been our experience that chlorination at elevated temperatures is safe.

B. CHLORINATION OF ALCOHOL.

1. Early Experimental Work:

At the beginning of these investigations the demand for a fairly large supply of chloral took precedence over all other requirements, and a reactor was constructed and put into operation before the process could be studied in the laboratory.

The chlorination of alcohol falls into the class of gas-liquid reactions. In such a unit operation, where the absorption is not rapid or complete, special measures are necessary to ensure an intimate contact between the

gas/....

(x) I. A. Leibbrandt.

gas and the liquid, if high efficiencies are aimed at. Like all chlorinations, where substitution takes place, the operation is also complicated by the large volume of hydrochloric acid gas evolved during the process. In the case of chloral, five moles of hydrochloric acid are evolved for every four moles of chlorine taking part. The hydrochloric acid gas leaving the system will be saturated with the vapour of the reaction mixture, and, unless measures are taken to cool or scrub this effluent gas, losses of product must occur.

Among the many devices in use for promoting intimate contact between a gas and a liquid, the gas distributor and the propeller agitator can be mentioned. The gas distributor can range in form from a simple perforated tube, which is relatively inefficient, to the blocks of porous ceramic material which break down the gas into very fine bubbles. These are similar in action to the sintered glass distributors used in laboratories (10). These "gas diffusion blocks" are most effective, and can successfully replace mechanical agitation. They require relatively high gas pressures for their operation, and this factor, coupled with the rapid formation of lead chloride in lead lined chlorination vessels, excluded their use at Klipfontein, as blockages would soon render them inoperative. The propeller agitator possesses definite advantages. When correctly designed, it not only breaks up the gas stream into minute bubbles in a turbulent flowing liquid, but it also ensures a certain measure of recirculation in that the gas above the surface of the liquid is drawn down the vortex, and broken up on the blades of the propeller, to be redistributed through the mass of liquid (11). This action of the propeller in prolonging the contact is of importance in cases where the gas is

absorbed/.....

absorbed with difficulty.

The design of the first reactor used for the chlorination of alcohol was approached in a very direct manner. It was proposed to pass chlorine into a reactor provided with a propeller agitator and a system for heating and cooling the reaction liquid. In normal practice, when corrosive gases are handled, the propeller is often glass enamelled, and an adequate seal can be made with a gland having a dry asbestos packing against the glass surface of the shaft. As enamelled propellers were not avaiable, a lead coated propeller with a mild steel wearing surface at the gland was used.

The unit employed is shown in Fig. 1. The construction was of lead lined mild steel throughout. C was a vessel of ten gallons capacity, provided with lead coils through which the water from the heater could be passed. The chlorine was weighed off from cylinder A and passed to an indicating flowmeter B, and then into the vessel. The contents of the reactor were agitated by a propeller driven at 500 revolutions per minute by an electric motor. The gland took the form described above. The gas and vapour leaving the reactor passed to a reflux condenser D, and then to the hydrochloric acid scrubber F. The scrubber was made up of 4 inch tile pipe, packed with 1 inch earthenware raschig rings, set in a rubber lined pot fitted with an overflow pipe. No attempt was made to recover the hydrochloric acid, but a good flow of water was maintained and the waste water was taken to an acid proof drain. The water heater is shown in Fig. 2. By suitable adjustment of the steam and water flow, the contents of the reactor could be maintained at any desired temperature up to 90°C. The steam traversed a coil before being injected into the body of water, and this device served to remove most of the latent heat of the steam and so reduced bumping and noisy operation to a minimum. Considerable/.....

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Considerable/.....



FIG. 1 ORIGINAL CHLORINATION UNIT.



Fig 2

Considerable difficulty was experienced in keeping the gland holding the propeller shaft gas tight due to the corrosion that occurred at the mild steel wearing surface. In the absence of suitable materials of construction, the use of mechanical agitation was abandoned when the unit was modified.

The process was carried out along conventional lines. One third of the chlorine was passed in whilst cooling was supplied to keep the temperature down to about 20°C. This took two days, and thereafter the chlorine flow was doubled and the temperature gradually raised to 85 - 90°C. The results on a typical run are given below.

Run 3:

Chlorine:	Excess of theory	30 per cent.
	Weight. Total:	252 lb.
Charge:	Alcohol (93.6 per cent. C_2H_5OH by weight):	67.5 lb.
Cold stage:	Chlorine feed:	1.75 lb. per hour.
	Duration:	48 hr.
	Temperature:	Average of 19.8°C
	Weight of chlorine:	84 lb.
Hot stage:	Chlorine feed:	3.50 lb. per hour
	Duration:	48 hr.
	Temperature:	Raised by 2°C every hour until the thirty-fifth hour when the temperature reached 90°C. It was held at 85° - 90°C until the end of the reaction period.
	Weight of chlorine:	168 lb.
Product:	Weight:	87.1 lb.
	Density:	1.430
	Distillation *	61.7 per cent.
	$CCl_3.CHO$ *	55.5 per cent.

Yield/-----

---

* See Appendix.

Yield: $CCl_3.CHO$ on alcohol 47.8 per cent.

$CCl_3.CHO$ on chlorine 36.6 per cent.

In all, six runs were carried out on this unit. Whilst the yield and the quality of material produced were indifferent, sufficient chloral was prepared to satisfy the immediate demand, and steps were now taken to improve the process.

(a) Examination of Product:

The material produced in Run 3 was examined in the laboratory. A fractional distillation through a 15 inch laboratory column, packed with glass cuts, yielded the following information:-

Conducted at 627 mm. Hg. pressure.

Fraction:	Per cent.
86 - 103°C	45.0
103 - 109°C	30.0
140 - 180°C	21.8
Residue	2.2
Distillation loss	1.0
	100.0

The density and solubility in water were determined on the individual fractions:

Fraction	Density 20°C	Per Cent. Solubility in water
86 - 103°C	1.609	Soluble
103 - 109°C	1.487	Soluble
140 - 180°C	1.201	2

The fractions were then distilled over an equal volume of sulphuric acid.

Fraction:	Per cent yield of distillate (88-92°)
86 - 103°C	80.6
103- 109°C	73.6
140 - 180°C	The whole of the fraction dissolved in the acid and decomposed with charring and evolution of HCl.

It/.....

It was evident, on comparing the properties of those fractions with those listed on Table I, that the fraction 86 - 103°C consisted of chloral and chloral hydrate, the fraction 103 - 109°C was chloral alcoholate and the high boiling fraction 140 - 180°C was a mixture of chloroacetals and possibly chloroethyl ethers.

The presence of these high boiling compounds was strong evidence of an underchlorinated product. A portion of the material was therefore heated to 90°C under reflux and chlorine passed through at a good rate for twelve hours. A distillation following this treatment showed only a slight decrease in the chloroacetal content.

	Per Cent. Composition	
	Before additional chlorination	After additional chlorination
Chlorals	76.0	76.0
Chloroacetals	21.8	18.8
Residue	2.2	3.1
Distillation loss	1.0	3.1
Density 20°C	1.430	1.460

2. Quantitative Laboratory Chlorinations:

Although an adequate excess of chlorine had been used in these initial reactions, subsequent examination had revealed that the absorption was not complete. It also appeared that the chlorine was not readily absorbed during the final stages. After further tests in the laboratory, it was found that alcohol absorbed chlorine readily even at temperatures near the boiling point of the reaction mixture. There appeared to be no valid reason for conducting the initial period of chlorination at low temperatures, and clearly a process that could be carried out without strict control of temperature, offered the attractive features of simplicity of design and operation.

Investigations/.....

Investigations on a quantitative basis were, therefore, commenced in the laboratory on the chlorination of alcohol at temperatures approaching the boiling point of the reaction mixture.

(a) Calibration of Flowmeters for Chlorine:

The method employing tared chlorine cylinders could not be used for the small quantities of chlorine required in these reactions, and, therefore, flowmeters were constructed and calibrated to pass up to 120 grams of chlorine an hour.

The calibration apparatus is shown in Fig. 3. The chlorine from the cylinder A passed to a flow stabiliser B. This stabiliser consisted of a T tube immersed in a cylinder of 70 per cent sulphuric acid. A slight excess of chlorine was allowed to bubble out at the bottom of the T tube and escape to the vent. By adjusting the height of the T tube in the liquid, it was possible to regulate the flow of chlorine through the flowmeter C at rates that held constant over long periods of time. This type of flowmeter was very sensitive to changes of pressure, and, to avoid large errors in the chlorine flow, it was found necessary to incorporate the pressure regulator D. This regulator was filled with calcium chloride solution (density 1.26), and the level of the liquid, and therefore the pressure after the flowmeter, was regulated, by means of the levelling bottle, to give a fixed reading at manometer G (usually 10 ins. of water). The Dreschel bottle at E contained concentrated sulphuric acid which removed the water vapour remaining in the chlorine gas stream. The chlorine was measured in the inverted flask F, of known volume, filled with 80 per cent sulphuric acid. The vapour

pressure/.....



FIG 3

pressure over 80 per cent sulphuric acid is 0.08 mm Hg. at 20°C, so any error due to the volume occupied by vapour could safely be ignored. In order to calibrate the meter, about ten equidistant points were chosen on the scale and a preliminary test carried out at each point by allowing the chlorine to flow into and displace the liquid in F, whilst B was adjusted to give the desired reading at C. Once this had been achieved, the flow could be stopped at H without disturbing the adjustments at A and B. F was refilled, and the time taken to empty the flask down to the level of the liquid in the beaker was measured with a stop watch. Readings usually agreed to within 0.5 per cent. As the displaced volume in F was known, and the chlorine was measured at atmospheric pressure, the chlorine flow in grams per hour could readily be obtained from the density of chlorine at the prevailing pressure. A smooth curve was drawn from the readings and a scale constructed from the curve.

(b) Chlorinations - First Series:

The reaction apparatus used in the first of these experiments is shown in Fig. 4A. The only change from the calibration apparatus was that this reaction flask replaced the inverted metering flask F. The reaction flask was filled about two thirds full with alcohol (93.6 per cent by weight) heated to near its boiling point and chlorine passed in at a predetermined rate whilst the contents of the flask were maintained at reflux temperature. Samples were removed and the density determined, by means of a hydrometer, near the end of the reaction period; all samples being returned to the chlorinator. When the density reached the figure of 1.5 the chlorination was stopped, and the product

cooled/...



Fig 4a

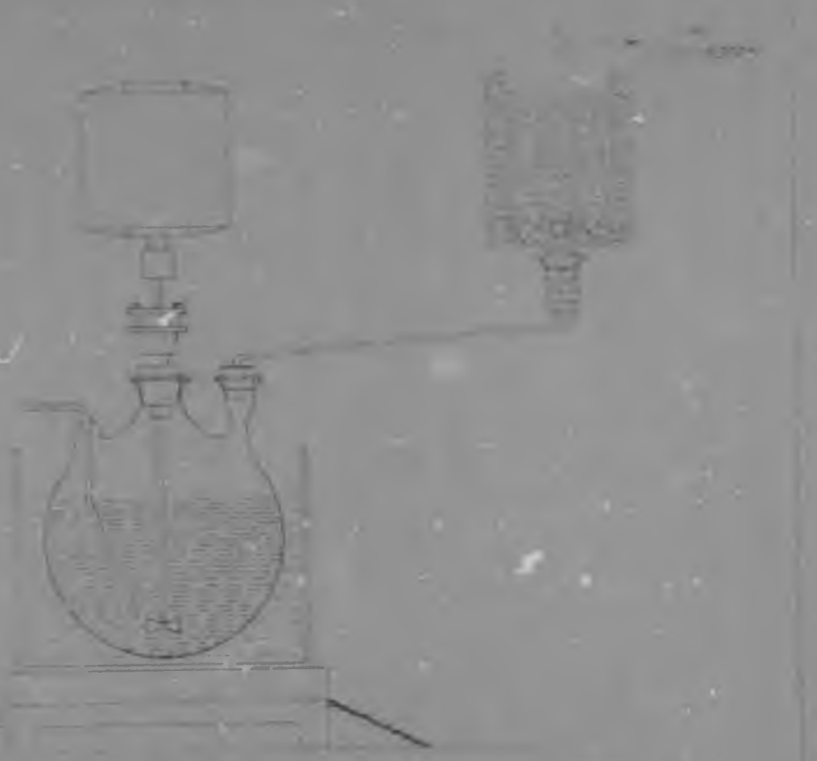

Fig 4b

cooled and weighed. An analysis was conducted and the yield reported in terms of the CCl_3CHO content of the product.

The results on a typical run are given.

Run L3:

Alcohol charged:		2000 g.
Duration:		70 hours
Chlorination rate:		96 g. per hour
Total weight of chlorine		6720 g.
Chlorine required by theory:		5780 g.
Chlorine in excess of theory:		16.3 per cent.
Products:	Weight:	2241 g.
	CCl_3CHO:	65.2 per cent.
Yield:	On alcohol:	48.7 per cent.
	On chlorine:	41.8 per cent.

The yield was not high, though the quality showed a marked improvement in every case over that produced on the original pilot plant unit, and obviously the reaction proceeds in the normal manner at high temperatures. The losses incurred were almost wholly due to the inadequate removal of the vapour from the stream of hydrochloric acid gas. This would be expected, as the relatively large volume of hydrochloric acid evolved would leave a condenser saturated with material at the operating temperature of that condenser. These losses could be reduced, either by scrubbing the exit gases with a cooled liquid, or by passing these gases through a very cold condenser. A refrigerated system was employed for the second series of laboratory runs mainly as it was easier to construct on this small scale.

(c) Chlorinations - Second Series:

The chlorination unit for this series is shown in Fig. 4B, and this replaced the reactor 4a. A major

departure/....

departure was the use of a glass propellor, driven by an electric motor through a cast iron gland fitted in a cork bung, and packed with dry asbestos. Though there was some corrosion of the metal (nickel would have been preferable), the gland remained gas tight and required little attention. It was not intended to revert to the use of propellers on the pilot plant, but they were employed in this instance as it was desirable to operate under conditions that approached the ideal. The gases leaving the reaction flask passed through a half inch diameter glass tube surrounded by a freezing mixture of dry ice in alcohol (at ca.- 70°C). At this low temperature vapour losses were reduced to very small proportions. Some loss did occur, however, and it was noticed that a proportion of the vapours, on passing into the cold zone, condensed to a fog which was swept through the tube by the hydrochloric acid gas stream. This fog formation was reduced by filling the adaptor, fitting to the condenser tube, with glass cuts. This acted as a small scrubber as there was a certain degree of hold up of the reflux from the condenser in the packed portion of the adaptor. The reaction flask was also fitted with a thermowell (Not shown in figure).

Only two experiments were carried out on this apparatus, and details are given of the second experiment. It will be noted that the chlorine could be added at a rate considerably faster than in the previous series, i.e. over forty-eight hours; it is probable that reaction times even shorter than forty-eight hours could be achieved, but the matter was not pursued. The temperature was held high enough to ensure a steady reflux from the condenser. Though the chlorination was commenced at the boiling point of the alcohol, it was

noted/....

noted that a volatile liquid was soon [illegible] which necessitated dropping the temperature to 60°C. This liquid disappeared after twelve hours of chlorination, and it was possible to conclude the reaction at temperatures of between 75 and 85°C. The contents of the reactor were not sampled for density determinations; instead chlorine to the extent of ten per cent. in excess of theory was passed in over 48 hours and the reaction then stopped.

Run L5: (Duration 48 hours)

Alcohol charged:	(93.6 per cent by wt.):	407.13 g.
Chlorine:	Rate:	26.75 g/hr.
	Weight:	1284 g.
	Excess of theory:	10 per cent.
Product:	Weight:	784.31 g.
	Density:	1.498 @ 15°C
	CCl_3CHO:	61.6 per cent.
	Distillation:	72.3 per cent.
Yield:	On chlorine used:	72.3 per cent.
	On alcohol used:	79.1 per cent.

The gases leaving the condenser were sampled periodically and the ratio $\frac{g.Cl_2}{g.HCl}$ determined by analysis. These results are listed with the ratio expressed as percentage chlorine.

Hour.	Per cent. Cl_2 in exit gas.
24.5	0.1
26.5	0.2
30.0	2.5
37.0	6.2
40.5	10.5
42.5	24.0
45.5	25.0
47.0	32.5
48.0	33.5

This/.....

This, the most successful run carried out in this investigation, yielded some important data. Clearly mechanical agitation leads to large economies in chlorine. The efficiency of the chlorine absorption falls after the process is half completed, when the chlorine content of the exit gas increases fairly sharply to a minimum of over thirty per cent. If this gas mixture were led into fresh alcohol, the excess chlorine would be absorbed. Provision of some such scrubber system appears essential in a chlorination unit.

This last experiment terminated the laboratory work, and a modified pilot plant unit was designed and constructed. The description and operation of this unit is now given.

3. Modified Chlorination Process:

(a) Design of Unit:

As a result of the experience gained from the early operations on the original chlorination unit and the experimental work in the laboratory, a new unit was designed which incorporated the following features :-

(i) The reaction was carried out at the reflux temperature of the reaction mass during the entire period of chlorination.

(ii) The exit gas from the chlorinator was passed through cold alcohol (at 20°C).

(iii) Chlorination was continued until the density of the reaction mixture reached a maximum value (usually 1.60 and over),

(iv) Provision was made to return to the chlorinator the material accumulating in the cold alcohol.

The unit is shown in Fig. 5. The chlorine feed

and/ ....

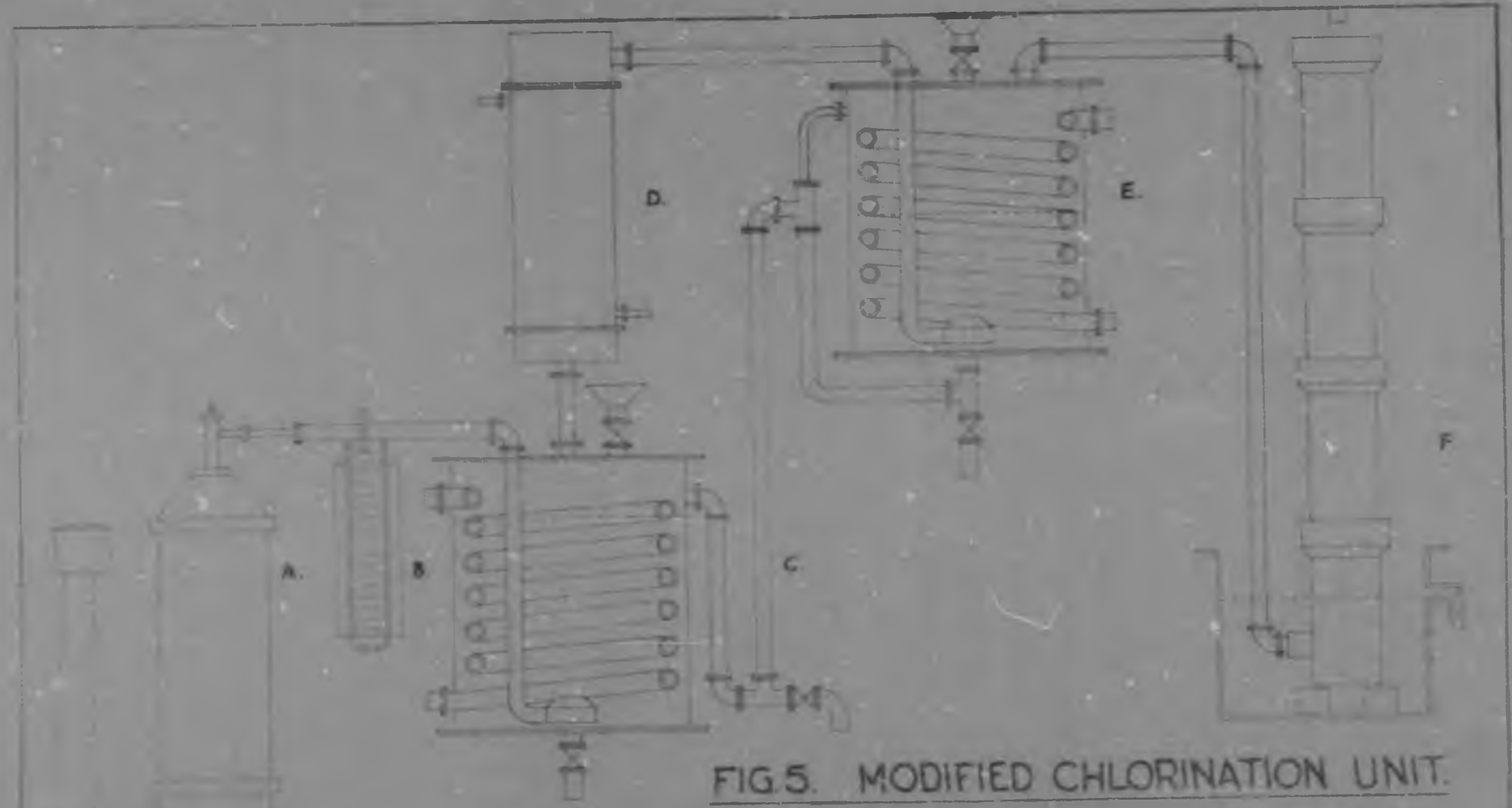

FIG.5. MODIFIED CHLORINATION UNIT.

and hot water system remained, but mechanical agitation was dispensed with; though the rose at the chlorine entry gave some measure of gas distribution. The gas and vapours leaving the condenser D passed directly into cold alcohol held in the vessel E, which was provided with cooling coils and a thermowell (not shown). The cooled alcohol in E absorbed the greater part of the vapour and chlorine in the effluent gas stream. The volume of the liquid in E tended to increase, and any excess was returned to the chlorinator by the overflow device C, which held the liquid in E at the constant level indicated on the figure.

When chloral is prepared in lead vessels there is an unavoidable formation of lead chloride due to the slow corrosion of the metal. This lead chloride caused blockages in C, and it was necessary to remove the accumulated salt after the completion of every run. Valves were fitted at the low points of C for this purpose.

(b) Method of Operation:

These changes simplified the operation of the unit, and the method was standardised after a few variations in technique to suit the new conditions. With the temperature constant, the variables were the rate and quantity of chlorine delivered. In the early runs the tendency was to chlorinate at too rapid a rate with consequent wastage of chlorine, and it required a number of operations to determine the most economical rate. The chlorine could be passed in during the first twelve hours at two to three times this established rate without loss of chlorine. The reason for not making this the usual practice is that the supply of chlorine at Klipfontein, for plant operations, is a cell gas at 90 to 98 per cent chlorine

and 5 lb. per sq. inch pressure, and it is always produced at a constant rate. In view of this fact no operational technique was established on the pilot plant that could not in turn be adapted completely to full scale production.

To commence a cycle of operations alcohol was filled into E until it just overflowed into the chlorinator. The main portion of alcohol was then charged and heated to near the boiling point. Chlorine was fed in at the desired rate, and frequent samples were drawn near the end of the reaction period. When the density reached the figure of 1.50 or over the chlorine feed was stopped, and the product discharged into a weighed glass carboy. Alcohol could again be charged into E and the unit restarted without delay. As each fresh charge of alcohol was filled into E, which was full to the overflow level with partly chlorinated alcohol, some admixture of the fresh charge with the residue of the previous charge took place. This had no apparent effect on the rapidity of the process once regular conditions had been established.

(c) Data and Comments:

The record of ten runs is given in Table II and III. Table II gives the details of the yield of CCl_3CHO obtained on the unit. Certain difficulties arose when computing the true yield. It was necessary that the partly chlorinated alcohol from one run formed a portion of the charge for the one following. It was preferred then to assess the yield on the total performance over a number of runs. In establishing the best chlorination rate, the yield per run could be taken as forming a rough guide; though this could be misleading as, for example, the

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TABLE II.

MODIFIED CHLORINATION UNIT : RECORD OF OPERATIONS.

RUN NO.	LB. ALCOHOL CHARGED	CHLORINE. TOTAL LB WEIGHT	CHLORINE. RATE LB. PER HOUR	CHLORINE. PER CENT IN EXCESS	DURATION HOURS	PRODUCT LB.	PRODUCT ANALYSIS DENSITY	PRODUCT ANALYSIS PER CENT DISTILLATION	PRODUCT ANALYSIS PER CENT CCl_3CHO	PRODUCT LB. CCl_3CHO	PER CENT YIELD ON ALCOHOL	PER CENT YIELD ON CHLORINE
C7	152	562	8.8	-	64	163.0	1.525	72.6	63.0	102.8		
C8	50	266	5.3	-	51	99.5	1.500	70.5	61.7	61.4		
C9	50	198	3.6	-	55	94.25	1.480	70.0	61.7	58.2		
C10	30	274	3.1	-	89	113.25	1.550	75.0	66.2	75.0		
C11	50	233	3.0	-	77	93.5	1.500	71.6	64.4	60.2		
C12	50	171	3.5	-	49	83.0	1.475	70.0	60.9	50.5		
C13	50	195	3.3	-	59	98.5	1.500	72.1	61.8	60.8		
TOTAL	452	1931	-	46.0		745.0	-	-	-	468.9	89.4	47.6
C18	50	184	3.3	-	56	96.0	1.505	71.0	61.6	59.4	-	-
C19	60	202	3.5	-	57	113.0	1.515	70.9	61.8	69.9		
C20	50	188	3.0	-	63	96.5	1.510	70.8	61.6	59.4		
TOTAL	160	574	-	25.0		305.5	-	-	-	188.7	78.6	63.3

fictitiously low chlorine usage in C-12 where an apparent 11 per cent in excess was used, was due to the overchlorination, 60 to 80 per cent, that occurred in C-10 and C-11.

Overchlorination was avoided, however, quite apart from the loss of chlorine involved, as difficulty was always found in completing a charge following a run where overchlorination had occurred. This was the case in Runs C-8 and C-12 which both had a high proportion of high boilers in the crude. Whilst no explanation on an experimental basis for this phenomenon can be advanced, it is possible that the chlorination in the cold, if conducted beyond a certain stage, produces dichloro and trichloroacetals (7) which, according to Chattaway and Backeberg (8), are not intermediates in the formation of chloral, and so would not be converted to it by further chlorination at higher temperatures. Once the danger of overchlorination of the cold alcohol was appreciated, however, no difficulty was experienced in completing the run in about sixty hours.

The next series, C-18 to C-20 represent an average of three runs under good operating conditions. They were carried out in order to assess the efficiency of the unit. The two runs, C-16 and C-17, that preceded the series, were carried out in a similar manner, (except that C-16 was charged with virgin alcohol only) and it could be assumed that the partly chlorinated alcohol left in E (Fig. 6) after run C-17 differed little in composition from that also left in E after C-20 had been completed. The yield calculated on this basis was found to approach the figure established on the best laboratory runs. Some wastage of chlorine was still evident, but is doubtful whether any further improvement

could/.....

could be achieved without recourse to mechanical agitation, or the use of a gas diffusion system. The yield of CCl_3CHO on the alcohol charged was high and equalled the best laboratory performance.

Table III gives details of the analyses carried out on the product of the chlorinations. The Engler distillation range was useful as it showed up any tendency towards an incomplete reaction, and could be carried out more rapidly than a fractional distillation. The composition of the effluent gas was determined on C- 20 periodically. The results were somewhat erratic, but indicated that, though the average loss of chlorine was greater than that experienced in the laboratory, it it did not rise so sharply, and a figure varying between 10 and 20 per cent chlorine was maintained.

Whilst the system could not compete on equal terms with a unit employing mechanical agitation, the results were encouraging in view of the simplicity of construction and operation. The reaction involving the chlorination of alcohol to chloral alcoholate is strongly exothermic, and as no heat need be removed from the reaction mass in the process described, it should be possible to maintain the heat of the reaction without the aid of external heating. Efforts were made to test this procedure on the pilot plant unit, but without success. The comparatively small volume and the exposed locality of the unit made it impossible to maintain the correct temperature, without an external source of heat, during the concluding stages of the reaction. It is interesting to note, however, that on the large scale unit which has been in production for over a year, and where adequate insulation was provided, no external heating is necessary. The alcohol rises rapidly to the reflux

temperature/....

TABLE III.

MODIFIED CHLORINATION UNIT : ANALYSIS OF PRODUCTS.

No.	C7	C8	C9	C10	C11	C12	C13	C18	C19	C20
Distillation Range °C (627 mm. Hg)										
First Drop	-	85.0	92.0	83.0	80.0	84.0	75.0	75.0	86.0	86.0
10 ml.	-	92.0	94.0	92.5	95.0	94.5	93.0	95.0	94.0	94.5
20 ml.	-	92.5	95.0	93.5	95.0	95.5	95.0	95.5	95.0	95.5
30 ml.	-	93.0	95.5	94.0	96.0	96.5	96.0	96.5	95.5	95.5
40 ml.	-	97.0	100.0	94.5	98.0	100.0	98.0	97.0	96.0	96.0
50 ml.	-	103.5	106.0	95.0	101.5	104.5	102.5	98.0	96.5	96.5
60 ml.	-	106.0	107.0	99.0	104.5	107.0	105.5	100.0	98.0	98.0
70 ml.	-	107.0	107.0	107.0	106.5	108.0	107.0	102.5	104.5	104.5
80 ml.	-	107.0	107.0	108.0	107.0	108.0	107.0	104.0	105.5	105.5
90 ml.	-	171.0	108.0	108.0	107.5	139.0	107.0	106.0	107.0	106.0
Dry Point	-	191.0	108.0	108.0	108.0	175.0	108.0	108.0	108.0	108.0
Per Cent Composition by Distillation: (627 mm. Hg).										
Chlorals 87 - 109°C	92.4	85.3	90.0	95.0	94.6	86.7	92.5	91.5	92.0	94.1
Chloroacetals 109 - 180°C	-	10.5	-	-	-	4.2	-	-	-	-
Residue	6.1	1.8	2.5	1.7	1.8	7.1	2.1	3.3	2.5	2.1
Distillation Loss	1.5	2.4	7.5	3.3	3.8	2.0	5.4	5.2	5.5	3.8
Sp. Gravity 20°C	1.525	1.500	1.480	1.550	1.500	1.475	1.500	1.505	1.515	1.510
HCl	-	-	-	-	-	-	-	-	3.7	3.5

temperature and is maintained at that temperature until the completion of the reaction. As the lead lined chlorinators have a limited life, the further simplification in the construction, resulting from the use of the heat of reaction, has an important bearing on the cost of replacements.

C. DISTILLATION OF CHLORAL:

Whilst crude chloral may be used for the preparation of DDT, a product in better yield and quality is obtained if anhydrous chloral is selected. The crude chloral from the chlorination process yields on distillation over concentrated sulphuric acid a material containing some 90 to 95 per cent CCl_3CHO. The impurities are mainly hydrochloric acid and water. By redistillation the purity can be raised to 98 per cent CCl_3CHO, though it is doubtful whether the second distillation is economical in practice.

It was found early in this investigation that both the amount of acid used and the quality of the crude had an important bearing on the finished material. In the earlier runs, where the quality of the crude was indifferent, in that it contained a relatively large proportion of high boiling materials, the direct distillation over sulphuric acid was unsuccessful, as the distillate polymerised very rapidly. Eventually a system was evolved where the crude chloral was first distilled over calcium carbonate to give what was termed "neutral chloral". This neutral chloral was in turn distilled over sulphuric acid in the normal manner to yield an anhydrous chloral that had a life of some weeks, even when low quality crudes were used. Later in the investigation, when the quality of the crude improved, the preliminary distillation over calcium carbonate could safely be omitted.

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* I. A. Leibrandt.

The most important factor in the distillation was the ratio of acid to crude chloral used. If the acid ratio is too low chloral hydrate is formed, whilst too large an excess of acid causes decomposition of the chloral. In a number of distillations carried out on the pilot plant the highest purity and recovery of chloral was obtained with equal weights of crude chloral and sulphuric acid (98 per cent H_2SO_4), though the advantage over other ratios in the vicinity was not marked. It is possible to operate safely at ratios at between 0.80 to 1.20 parts of sulphuric acid per part of crude chloral charged. The ratio of 1:1 was adopted as a standard, however, and the recovery of chloral was satisfactory, as at least 95 per cent of the CCl_3CHO in the crude was found in the distillate.

The equipment used in the distillation of chloral consistedof a ten gallon capacity still pot heated with a mild steel steam coil; a fractionating column 6 ft. high and 4 inch.in diameter packed with ½ inch.earthenware raschig rings; a dephlegmator, or partial condenser, to control the reflux to the column; and a final condenser and receiver for the distillate. It is questionable whether a fractionating column is necessary for the distillation of chloral, but in this case the still was also used to separate benzene from monochlorbenzene, where close fractionation is essential. The still was always operated without reflux when chloral was being distilled, in which case the dephlegmator was employed as a condenser, and the condensate from it was also delivered to the receiver by a special by pass line provided. The whole assembly was fabricated in lead lined mild steel. The mild steel heating coil had a limited life as corrosion was severe. On the scale of operations on the pilot plant, where an average of three distillations were completed in a week, the

life/.....

life of a coil was about three months.

D. SUMMARY AND CONCLUSIONS.

The production of chloral by the chlorination of alcohol has been investigated, both in the laboratory and on a pilot plant. A process has been developed as a result of these investigations that represents a departure from published methods. The handicap of being obliged to operate without suitable mechanical agitation has been offset, to some extent, by chlorinating at the reflux temperature of the reactants, where the absorbtion of the chlorine is more complete. The system has the additional advantage of not requiring a source of external heat, as use can be made of the heat of reaction to maintain the correct operating temperature. Crude chloral was produced at a yield of 78.6 per cent chloral from the alcohol. Laboratory investigations indicated that greater economies in chlorine would result if mechanical agitation were provided.

Anhydrous chloral was produced without difficulty in standard equipment by distilling the crude over an equal weight of 98 per cent sulphuric acid, and this process did not require detailed investigation. The overall yield of chloral in the distillate, from the alcohol used, approached 75 per cent.

NOTE: Since the completion of this work an official report from an American source has been received (12) describing a series of laboratory chlorinations on similar lines to the above. Yields of 70 per cent on the alcohol were claimed.

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REFERENCES.

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PART TWO

THE CONDENSATION OF ANHYDROUS CHLORAL AND CHLOROBENZENE TO 1:1:1-TRICHLORO-2:2-DI-(4-CHLOROPHENYL)ETHANE (DDT).

NOTE: Some confusion often arises in the use of the term DDT.

Throughout this work the following nomenclature is adopted:

i DDT is the name given to the pure 4:4 isomer, 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane.

ii TECHNICAL DDT is the name given to the mixture of the isomers and related products formed in the condensation reaction.

A. INTRODUCTION:

1. History of the Discovery of DDT:

In 1874 Othmar Zeidler, a student working under Baeyer, prepared dichloro-diphenyl-trichlorethane by condensing one mole of chloral with two moles of monochlorobenzene in concentrated sulphuric acid (1). He obtained the main reaction product by crystallising it from absolute alcohol, and correctly inferred to it the formula 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane. (I) This was the class of condensation first observed by Baeyer (15).

Interest in this substance, now known as DDT, was aroused by the discovery of its remarkable insecticidal properties by Paul Muller in 1939 (2). Müller was one of the team of investigators working with Dr. Lauger of the Geigy A.G. of Basle, Switzerland. The discovery of DDT as an insecticide was the result of twenty years work on the development of a moth-proofing agent. Starting with the hypothesis that an effective contact poison should combine the properties of a stomach poison and an inhalation narcotic, these workers prepared an extensive series of compounds for test against insects. Amongst these was DDT, which was found to have phenomenal activity against flies, moths, aphids, and the Colorado beetle. Lauger attributed the high activity of the compound, firstly to the presence of the linked chlorobenzene rings which acted as the poisonous component, and secondly to the chloroform group which conferred the necessary narcotic action. This viewpoint has been criticised and will be dealt with when the mode of action of DDT is discussed.

DDT was used with outstanding success against the

Colorado/....

Colorado beetle which threatened the Swiss potato crop in 1941. Patents were granted in 1942 (3), which disclosed the nature of the compound to the outside world. In view of the grave shortage of pyrethrum and derris then prevailing, the Allied authorities took an active and immediate interest in the claims of the insecticide and production on a large scale had been reached, both in Great Britain and America, by 1944 - 1945. World wide interest was shown as a result of its spectacular success against the winter typhus outbreak in Naples in 1943. Details of the discovery reached Klipfontein in 1944, and the Factory was committed to the manufacture of the insecticide in that year, when the work described in this thesis was carried out; full scale production commencing in July, 1945.

2. The Chemistry of DDT.

Though the principal component of technical DDT is 1:1:1-trichloro-2:2-di(4-chlorophenyl)ethane (I-Fig.6) (always referred to as DDT), it contains, in addition, a number of related compounds. It is fortunate that the principal component is also the most active insecticide.

There have been published recently a number of of papers on the components of technical DDT and their principal reactions (4,5,6,7,8,). DDT is present to some 60 to 80 per cent in the commercial product, from which it can readily be crystallised from alcohol. When pure it has a melting point of 107 - 108°C and a very faint odour. It is quantitatively converted into 1:1-dichloro-2:2-di-(4-chlorophenyl)ethylene (II), with the loss of one mole of hydrochloric acid, by the action of alcoholic potash, as was described by Zeidler (1). The ethylene derivative has little or no insecticidal activity (10). The action of aqueous alkalis on DDT is not marked and it has been reported that no hydrolysis occurs when DDT is subjected to

prolonged/.....

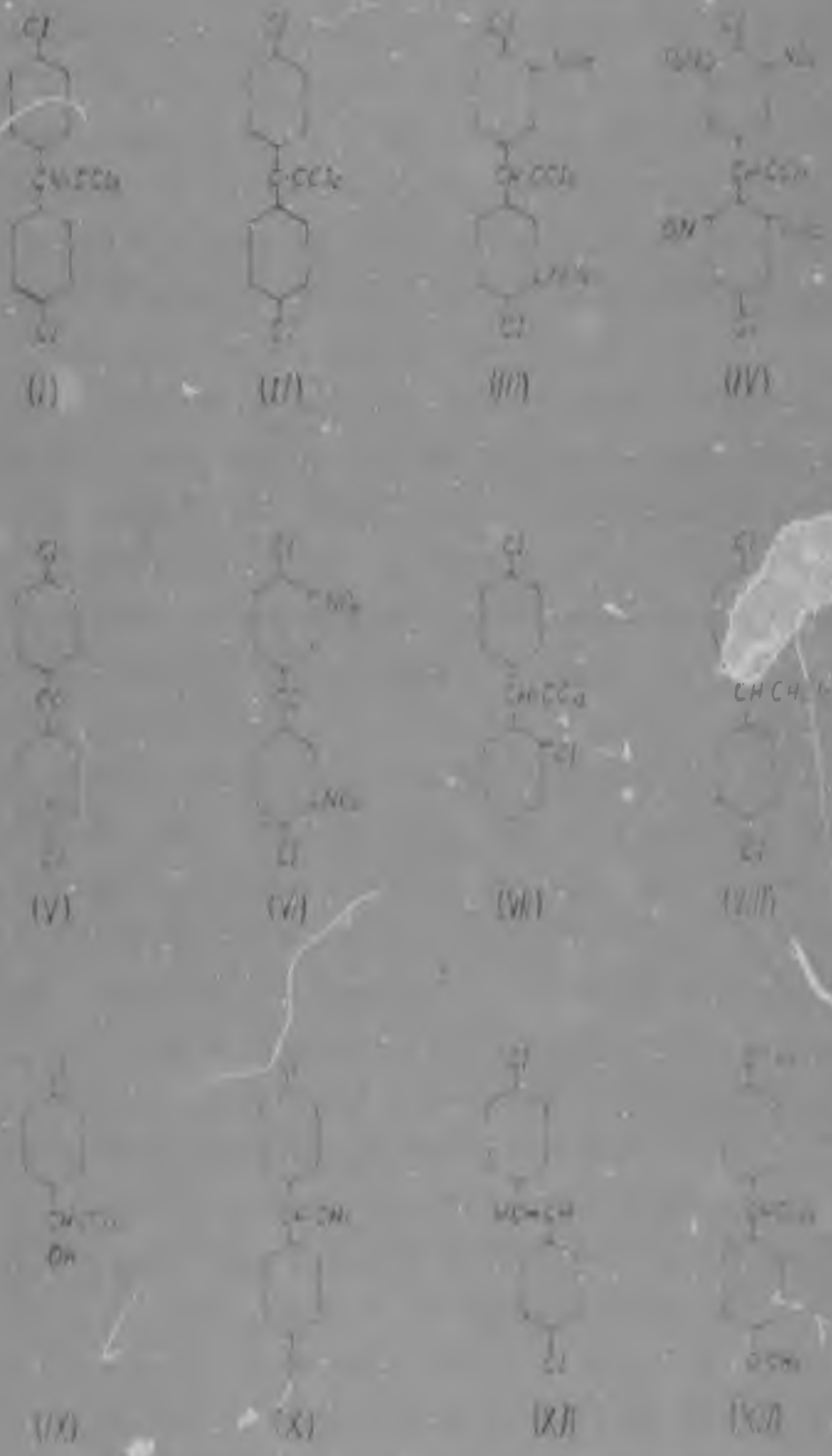

Fig 6

prolonged treatment with aqueous caustic soda at boiling point. (9 - p.33). The remaining chlorine atoms in the molecule resist the strongest action of alkalis. As the hydrolysis of DDT is quantitative, this property is often used as a method for determining the concentration of DDT in mixtures and deposits. The value obtained is generally referred to as the percentage "hydrolysable chlorine". Pure DDT would contain 10.0 per cent hydrolysable chlorine. The reaction is not specific for DDT and has, therefore, only a limited use in analysis.

DDT undergoes nitration by nitric acid in acetic acid solution to 1:1:1-trichloro-2:2-di(4-chloro-3-nitrophenyl)ethane (III), and by more vigorous nitration with fuming nitric acid to the tetranitro compound, 1:1:1-trichloro-2:2:-di(4-chloro-3:5-dinitrophenyl)ethane (IV). Both nitro derivatives are hydrolysed to the corresponding ethylene derivatives by the action of alcoholic potash (6). The nitro derivatives cannot be prepared by direct nitration of 1:1-dichloro-2:2 -di-(4-chlorophenyl)ethylene, as it undergoes oxidation to 4:4'-dichlorobenzophenone (V) or 4:4'-dichloro-3:3'-dinitrobenzophenone (VI). The conversion to 4:4'-dichlorobenzophenone fixes the 4 - position of the nuclear chlorine atoms in DDT.

The other main component of technical DDT is the 2:4 isomer, 1:1:1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane (VII), or iso -DDT, almost devoid of insecticidal activity and present up to 20 per cent in technical DDT. Iso -DDT behaves in an analogous manner to DDT on hydrolysis or nitration. There is also present 1:1-dichloro-2,2 -di-(4-chlorophenyl)ethane, or DDD (VIII), which has an insecticidal activity of about one-third of that of DDT (10). It is evidently formed by the condensation of chlorobenzene with the dichloroacetal or dichloroacetaldehyde present in technical distilled chloral (see Table I).

DDD/...

DDD on hydrolysis yields 1-chloro-2:2-di-(4-chlorophenyl) ethylene which also gives 4:4'-dichlorobenzophenone (V) on oxidation. Another compound found is 1:1:1-trichloro-2-hydroxy-2-(4-chlorophenyl)ethane (IX), or the so called "half condensation product", which is the addition product of chlorobenzene and chloral, and is believed to be the intermediate in the formation of DDT. Chattaway and Mu.. (14), who studied the Baeyer condensation in 1934, prepared the half condensation product of benzene and chloral, 1:1:1-trichloro-2-hydroxy-2-phenyl-ethane, by interrupting a reaction where chloral was in excess and distilling off the half condensation product. It would be expected that the DDT condensation proceeds in a similar manner.

DDT on reduction yields a mixture of DDD, 1:1-di-(4-chlorophenyl)ethane (X), and 4:4'-dichlorostilbene (XI). On chlorination DDT yields 1:1:1:2-tetrachloro-2:2-di-(4-chlorophenyl)ethane.

3. Mode of Action of DDT:

It is generally accepted that DDT acts as a nerve poison causing an initial lack of co-ordination in the insects movements followed by eventual death. At least two theories have been advanced in attempts to explain the action of DDT. Läuger (2) attributes its action to the presence of the chloroform group.

$$Cl \cdot \overset{\cdot}{C} \cdot Cl$$
$$\overset{\cdot}{C}l$$

which imparts lipoid solubility, or the property of the compound to penetrate the hard lipoid structure of the cuticle of the insect, and contact the nerve endings where the toxic component, the linked chlorobenzene rings, acts on the vital centres. Läuger prepared a series of compounds by condensing chlorobenzene with inhalation

narcotics/....

narcotics such as bromoform, methylene chloride, nitromethane, ethylene, and diethyl ether, and produced effective insecticides. Martin and Wain (11), whilst accepting the theory of lipoid solubility, believe on the contrary that it is conferred by the chlorobenzene groups, and that the toxic action is due to the splitting off of hydrochloric acid at the nerve centres, basing this on the fact that 1:1-dichloro-2-di-(4-chlorophenyl)ethylene is almost devoid of insecticidal activity. According to this theory the activity of a compound would depend upon its speed of hydrolysis.

Busvine (10) discounts both these theories and finds no direct correlation between insecticidal activity and any of the properties cited,i.e., speed of hydrolysis, lipoid solubility, or the presence of chlorobenzene rings. For example,1:1:1-trichloro-2-di-(4-methoxyphenyl)ethane (XII) is almost as active as DDT, though it does not contain chlorophenyl groups. The speed of hydrolysis is also much less than DDD which has inferior insecticidal activity. Busvine concludes that there is as yet insufficient evidence to formulate a theory for the mode of action of DDT, and believes that the shape and size of the molecule is important.

4. The Manufacture of DDT:

Little or no work of value, relating to the condensation of chloral and chlorobenzene to DDT, has been published, though it is evident that lengthy investigations preceded the manufacture in Europe and America. Whilst it is known that alternative methods for the synthesis are possible, they have not gained prominence, and, as far as is known, all DDT is manufactured by the condensation of chloral and chlorobenzene in concentrated sulphuric acid. The temperature at which the reaction is conducted and the

strength/...

strength of the acid employed is stated to determine to a large extent the composition and yield of the technical DDT obtained.

The reaction

$$CCl_3.CHO + 2C_6H_5Cl \xrightarrow[(conc H_2SO_4)]{-H_2O} CCl_3.CH(C_6H_4Cl)_2$$

involves the removal of a mole of water for every mole of DDT formed. The reaction is complicated, however, by the sulphonation of the chlorobenzene that occurs concurrently with the main reaction; also with the formation of water which further dilutes the acid.

$$C_6H_5Cl + H_2SO_4 \xrightarrow[(Conc\ H_2SO_4)]{-H_2O} C_6H_4ClSO_3H$$

Whilst the temperature and strength of the acid may be important, other variables have to be considered in an investigation.

The factors that may influence the process can be listed as follows:-

1. Temperature of reaction.
2. Strength of acid employed.
3. Quantity of acid employed.
4. Mode of acid addition.
5. Duration of reaction.
6. Degree of agitation.
7. Form and quality of chloral used.
8. Quantity of chlorobenzene used in excess of equivalent requirements.

It is not surprising, in view of the above, that the process has not advanced much beyond the realm of an industrial art, and there is need for an investigation of a fundamental character into the influence of the various conditions on the kinetics of the reaction and the composition of the reaction product.

Forrest et al (8) believe that the ratio of DDT to iso-DDT remains constant over a wide range of reaction

conditions/.....

conditions. Those workers subjected a large number of samples of technical DDT from various sources, made under different conditions, first to hydrolysis, and then to oxidation, to give the corresponding dichlorobenzophenones. The half condensation product gave 4-chlorobenzoic acid under those conditions, which could be separated quantitatively from the mixture of dichlorobenzophenones by extraction with alkaline water. In all cases they found the mixed ketones to have a fixed setting point, 132 ± 2°C, which corresponded to 26 per cent of the 2:4' isomer. As the percentage of 1:1:1-trichloro-2:2-di(4-chlorophenyl)ethane in technical DDT varies greatly with the reaction conditions, it must be concluded if the ratio of DDT to iso-DDT is constant, that the difference in all cases is made up by the half condensation product, assuming the chloral used is pure and contains no dichloroacetaldehyde which would be converted to DDT.

Once the correct conditions for a condensation have been established there remains the problem of recovering the product from the reaction mixture. A great deal of attention has been paid to this stage of the manufacture and it is in this respect that most processes described differ from one another.

When Klipfontein undertook to investigate the manufacture of DDT, it received through official channels the broad outlines of the manufacturing methods used in Great Britain and America. It was evident at this early stage of the development that optimum conditions for the reaction had not been established.

Two methods appeared to be used, and will be described briefly, as they formed the starting point for the work at Klipfontein.

(a) Chloral Alcoholate Method:

The main advantage of this process lay in the

fact/-....

fact that the crude chloral or "Chloral alcoholate", produced by the chlorination of alcohol, could be used directly in the condensation. Chlorobenzene was mixed with chloral alcoholate in equivalent amounts and concentrated sulphuric acid added. The reactors were of enamelled mild steel and were provided with agitation. The reaction was held at 40°C for five hours, or 30°C for seven hours, and then stopped. The product was then allowed to accumulate at the top of the acid, when the acid layer could be run off and the product washed with water and sodium carbonate solution before being discharged onto a vacuum filter. The dried material contained 50 per cent DDT and was obtained in 65 per cent yield. This corresponded to a yield of 32.5 per cent of DDT (4:4' isomer).

(b) Anhydrous Chloral Method:

This method was more complicated, but resulted in improved yield and quality, and is the basis of present day practice. The crude chloral, or chloral alcoholate, was first refined by distillation over concentrated sulphuric acid as described in the first part of this thesis. The distilled chloral was reacted with up to 25 per cent excess of chlorobenzene in concentrated sulphuric acid at temperatures ranging from 15°C in some cases up to 34°C in others. The yield obtained was in the order of 50 - 55 per cent of the 4:4' isomer at 65 - 75 per cent purity.

In general three methods were used to separate the product from the acid.

(a) Drowning Process:

This was the simplest method and was widely used in Great Britain. It had the one disadvantage

that/.....

that it diluted the spent acid from the reaction, and complicated subsequent recovery of this acid, which was being considered seriously at Klipfontein at this time. The reaction mixture was gradually added to a large volume of water, when the product settled out and could be washed by decantation, filtered, and dried.

(b) Granulation Process:

At the completion of the reaction the agitation was stopped, and the products allowed to rise to the surface of the acid. The spent acid could then be run off without loss of product. The crude DDT was melted by passing steam or hot water through the jacket, and cold water was added with good agitation until the molten product separated out in granules which could be washed without much difficulty.

(c) Solvent Extraction Process:

This process was in vogue in America. At the completion of the reaction a solvent for DDT that was immiscible in sulphuric acid, such as chlorobenzene, was added to the reaction mixture in sufficient quantity to dissolve out all the product. The solution could then be drawn off from the spent acid and washed to neutrality with water and sodium carbonate or ammonia solutions. The solvent was distilled off under reduced pressure and the last traces of solvent removed from the molten product in the still by passing in live steam. The melt was then flaked on a cold drum flaker and the flakes ground to a powder for sale.

Since the completion of this work two papers have been published on processes for the manufacture of DDT. Callaham (12) describes the Brothman continuous

process/....

process. The description deals mainly with the type of equipment used for carrying out the condensation and recovering the product. The solvent extraction method is used to recover the product from the acid, and a yield of 95 per cent of material having a setting point of 90°C is claimed. No details are given for the reaction conditions, and it is doubtful whether the process has been operated on a large scale. Rueggeberg and Torrans (13) employ a novel method using chlorosulphonic acid as the condensation agent. Sufficient chlorosulphonic acid is added to chloral hydrate to form the complex according to the equation

$$CCl_3.CH(OH)_2 + ClSO_3H \longrightarrow CCl_3.CH(OH)_2SO_3 + HCl$$

After the evolution of hydrochloric acid has ceased, chlorobenzene is added, followed by a further slight excess of chlorosulphonic acid. The product is recovered by extraction with carbon tetrachloride, and yields of 77 per cent of a material having a setting point of 88°C are obtained after fourteen hours reaction at 20°C.

5. Quality of Technical DDT:

Whilst the final test for any insecticide is its performance against insects, it is difficult to enforce a test for biological activity in a specification. Therefore, most authorities specify tests that will ensure that the percentage of the active component, 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane, will not fall below a fixed minimum. Before proceeding to the description of the experimental work on condensations carried out at Klipfontein, the methods laid down in the specifications then existing will be dealt with briefly, as the development was carried out with the object of producing a material that would meet the requirements laid down in these specifications.

The British specification required that the technical DDT should contain at least 60 per cent of 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane, estimated by the quantitative crystallisation of the 4:4' isomer from alcohol saturated with pure 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane. This method was originated by Balaban and Calvert and subsequently modified by the Chief Chemical Inspectorate, Ministry of Supply (16). It is often referred to as the Cristol and Hayes method (17). A limit was also laid down for the percentage of hydrolysable chlorine, acidity, alkalinity, water, insoluble matter, and also for the setting point. The setting point should not be below 80 °C.

The American specification placed its reliance on the setting point as an index of purity, and specified a limit of 88°C. This corresponded to about 68 per cent of the 4:4' isomer. Limits for the percentage of organic chlorine, ash, volatile matter, chloral hydrate, water soluble material, matter insoluble in cyclohexanone, and also for the pH of the material were laid down in addition.

It was clear that in order to produce a satisfactory material, the product should contain some 70 per cent of 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane, and it was with this aim that the investigations that will now be described were conducted.

B. THE CONDENSATION REACTION:

When Zeidler first prepared DDT, he did so by mixing the two reactants in the presence of concentrated acid and allowing the mixture to stand for some hours. Unfortunately, this simple procedure does not result in high yields, and the reaction conditions are modified considerably /....

considerably in practice. The experimental work recorded in this thesis forms but a part of a full survey of the effect of reaction conditions on the condensation. The early experimental work, where crude chloral was used, is also included, not on account of its intrinsic value, which was slight, but because it was established there that reactions could be carried out very easily using sulphuric acid at 100 per cent strength (usually called "monohydrate"), where the use of sulphuric acid at the usual commercial strength of 98 per cent was not effective. This early success influenced the trend of the investigation, and in all subsequent experimental work monohydrate was used as the condensation agent.

The amount of chlorobenzene was also fixed at 15 per cent in excess of metathetical requirements, following the work carried out in these laboratories by D. M. Rice, who conducted a series of condensations, using mixtures of monohydrate and sulphuric acid, at temperatures of 15 and 17°C, and also at higher temperatures. In all cases best results were achieved when 15 per cent of chlorobenzene in excess was used. With the concentration of the acid and the excess of chlorobenzene fixed, the investigation resolved into a study of the effect of -

(a) Temperature

(b) Duration of reaction

(c) Quantity of monohydrate

on the composition and the yield of the product. Once optimum conditions had been found in the laboratory, reactions were carried out on a pilot plant unit.

As the object of this investigation was to find the optimum conditions for the formation of the active insecticidal isomer, the composition and yield of the product was expressed in terms of the 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane formed, the product in every case being/.....

being analysed for its DDT content by crystallisation from alcohol under standard conditions. (Appendix). The results were recorded in the following form:-

(a) Purity: The percentage of 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane present in the product.

(b) Material yield: The total yield of material based on the CCl_3CHO used, assuming the product to consist entirely on dichloro-diphenyl-trichloroethanes.

(c) DDT Yield: The yield of the active isomer, 1:1:1-trichloro-2:2-di(4-chlorophenyl)ethane based on the CCl_3CHO used.

The chlorobenzene used was made on site by chlorinating benzene in the presence of iron, and fractionating the mixture in a distillation column to yield the monochlorobenzene. This product was of uniform quality, and contained 1 - 2 per cent of benzene and dichlorobenzene impurities.

1. Early Experimental Work:

The first series of reactions were carried out with the principal object of providing a few hundredweight of DDT for experimental purposes, and a simple reactor was fabricated for this work. It consisted of an open topped lead lined mild steel vessel of ten gallons capacity, provided with a lead coil for heating or cooling the reactants, a thermowell and a propellor agitator driven at 500 revolutions per minute by a vertically mounted one - H.P. electric motor.

Crude chloral, or "chloral alcoholate" was used for the condensation, as equipment for the preparation of anhydrous chloral had not been installed at that time. The reactor was charged with crude chloral, and about 3 moles of chlorobenzene for every mole of CCl_3CHO found by analysis in the crude chloral. Sulphuric acid of 98 per cent strength was fed fairly rapidly into the

reactor/...

reactor with agitation. Thereafter sufficient oleum was added slowly over a period of one to two hours, until the whole reaction mass thickened and finally broke out in a thick suspension of DDT in the acid, resembling curdled milk in appearance. The temperature was held at about 40°C. It was found at this time that positive results were always achieved when the ratio of the sulphuric acid to the oleum used was such as to provide an acid containing 100 per cent H_2SO_4; and subsequently monohydrate was used in place of the mixture of acids. The crude chloral used was of low quality, containing a high proportion of chloroacetals, and this would account partly for the low purity of the product from these reactions.

After the completion of the reaction, the contents of the reactor were allowed to stand undisturbed for from two to three hours. The lower layer of acid was then drawn off through the discharge cock, leaving the product in the reactor. This product was washed free from acid, first with water, and then with dilute sodium carbonate solution, and dried in porcelain dishes in an oven at 60°C. As the material produced by this process was very impure, it was always recrystallised from alcohol to give a product containing 80 per cent DDT.

It will be noted that it was found necessary to add chlorobenzene to the extent of 50 per cent over metathetical requirements. This high consumption of chlorobenzene, coupled with the low yield and quality of the product led to the abandonment of the "Chloral alcoholate" process following successful work in the laboratory using anhydrous chloral as the starting material.

The use of internal coils in the reactor led to troublesome blockages, and they were replaced by a jacketed vessel when the unit was modified.

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In all, about two hundred pounds of recrystallised DDT were prepared by the method described, and though the yields varied considerably, Run No. 3 can be taken as representative of the process.

Run No. 3.

Charge:

Chlorobenzene		20 lb.
Crude chloral	weight	15 lb.
	$CCl_3.CHO$	55.5 per cent
98 per cent sulphuric acid		56 lb.
Oleum (20 per cent free SO_3)		14.5 lb.

Reaction:

Duration	6 hr. 10 min.
Acid feed time	60 min.
Temperature (Average)	26-42°C (38.6°C)

Product:

Weight	18.5 lb.
Purity	45 per cent
Material yield	92.6 per cent
DDT yield	41.7 per cent

2. Quantitative Laboratory Reactions:

(a) Stability of Chloral:

When the initial reactions were conducted on a laboratory scale, it was customary to weigh out freshly distilled chloral and carry out the reaction without delay in order to avoid any loss of chloral due to the polymerisation that occurred. This procedure involved many tedious analyses, as it was necessary, for accurate results, to know the amount of $CCl_3.CHO$ present in the distillate. Any attempt to make up a large stock of chloral distillate was unsatisfactory, as it had a limited life. In any case when reactions were carried

out/....

out on individual distillates, it was difficult to obtain duplication of results, as $CCl_3.CHO$ content varied from batch to batch.

It had been found, quite fortuitously, that if distilled chloral was dissolved in chlorobenzene, it appeared to remain stable over long periods. To test this assumption a solution of chloral was made up in chlorobenzene, and the percentage $CCl_3.CHO$ in the solution estimated by analysis (Appendix). The solution was then stoppered, set aside for a month, and another analysis conducted. No change in concentration, within the limits of the analytical method, was detected over the period of storage. The polymer of chloral is soluble in chlorobenzene, so that should any polymerisation occur it would not show up as visible deposit, as is the case when anhydrous chloral polymerises. The unpolymerised chloral can readily be extracted with water in which the polymer is insoluble, and this is the basis for the current analytical procedure for analysis of chloral in chlorobenzene solutions.

Once it had been established that chloral was stable in a chlorobenzene solution it followed that stock solutions of chloral could be prepared in advance, and adjusted so as to contain $CCl_3.CHO$ and chlorobenzene in the exact ratio for the condensation reaction.

(b) Experimental.

The product from the condensation reaction may be separated from the acid in a number of ways, as has been indicated in the introduction, but it was considered that solvent extraction would be the most suitable method for recovering the product in the laboratory, mainly due to ease with which the reaction, the separation from the acid, the washing of the solvent layer, and the drying of the product could all be completed in the same flask.

A/....

A large number of reactions were carried out before the method gave reproducible results. The procedure described was the outcome of these preliminary trials, and the data recorded were obtained by the standard method that is now given.

Standard Method for Conducting Condensation Reactions:

Reactants:

(i) Chloral-chlorobenzene solution: The chloral was prepared by distilling crude chloral over an equal weight of concentrated sulphuric acid through an 18" column, packed with $\frac{1}{4}$" glass cuts. The distillate was warmed with an excess of calcium carbonate and, when all the effervescence had ceased, was redistilled and the fraction collected between 98 - 91°C at 627 mm. This fraction still contained some chloral hydrate, and so was treated with an equal volume of concentrated sulphuric acid and warmed on a water bath. The chloral layer was then carefully separated from the acid, and distilled in an all glass still protected from the outside atmosphere by a calcium chloride tower. The distillate was collected between 90.5 and 91.5°C at 627 mm Hg, and this gave a product containing 98 per cent $CCl_3.CHO$. A solution of this chloral in redistilled chlorobenzene was prepared and the concentration adjusted until, by repeated analyses, the solution was found to contain 36.3 per cent $CCl_3.CHO$. This percentage would correspond to 15 per cent excess of chlorobenzene, if the chloral used was 100 per cent pure. As the chloral was of 98 per cent purity only, the actual excess of chlorobenzene prevailing was less, and of the order of 13.5 per cent.

(ii)/....

(ii) Monohydrate: Commercial oleum and 98 [illegible]nt sulphuric acid were mixed and the strength adjusted to give an acid containing between 100.0 and 100.2 per cent H_2SO_4.

Reaction Apparatus:

The reactions were carried out in tared 250 ml. round bottom flasks provided with A.29 - B.S.S. ground glass joints (Fig. 7A). These were immersed up to the neck in a thermostat of 15 gallon capacity, the temperature of which was held constant by an "Electro-Methods" mercury thermoregulator. The temperature could be adjusted rapidly and held to within 0.1°C, when operating in the range above the normal atmospheric temperature, by this instrument. The water in the thermostat was kept in circulation by means of a 4 inch motor driven propeller, operating behind a 1 inch perforated baffle screen at the back of the bath. When reactions were carried out at temperatures below atmospheric, the thermoregulator was cut out and the temperature controlled manually by the addition of ice chips. Due to the large capacity and good insulation provided in this thermostat, these lower temperatures could also be controlled to within 0.1°C, without undue adjustment, though it did require the undivided attention of the operator during the experiment. The thermostat was also provided with three vertical shafts, driven by a counter shaft at 1000 revolutions per minute. Small glass propellers were fitted into the chucks of the vertical driving shafts, and these propellers were fitted through the open necks of the reaction flasks with the blades within half an inch of the bottom of the flask. These propellers provided very efficient agitation, despite the fact that the size of the blades had to be restricted in order to pass through the A - 29 socket.

The/....



Fig 7a



Fig 7b



Fig. 7c

The monohydrate was fed from 100 ml. graduated burettes, fitted with calcium chloride guard tubes, and extensions to the tips made from 2 mm. capillary tubing, which also passed down the neck of the flask, clear of the propeller, to above the surface of the liquid in the flask. In the preliminary reactions a thermometer was also fitted into the flask, but when it was found that the temperature did not vary by more than 0.5°C from the bath temperature, and then only during the addition of the acid the thermometer was dispensed with, as the risk of breaking the thermometer was considerable. In order to ensure that the temperature remained within the limits shown, it was necessary to maintain a slow, if regular, feed during the course of the reaction. In all these reactions the acid was added in equal increments every ten minutes over the course of 90 minutes.

During the course of the reaction involving the condensation of chloral and chlorobenzene, there occurs a point where the solid product separates out in the reaction mixture. This point is almost invariably accompanied by a sharp rise in temperature, presumably due to the heat that is evolved when the solid phase separates out. No attempt was made to control this temperature rise, which was about 2°C, and the operating temperature was attained again after the lapse of about 15 minutes.

At the end of the specified reaction period, any further action by the acid was inhibited by the addition of 10 ml. of water for every 100 g. of acid present. The water was run in very slowly drop by drop, from the acid burette whilst agitation was continued in order to avoid excessive rise in temperature. If more than this quantity of water was added, the chlorobenzenesulphonic acids, formed during the reaction, tended to separate out from the acid layer rendering subsequent washing difficult. After the water had been added, 150 ml. of pure carbon tetrachloride was run in,

and/....

and agitation continued until the solid product had dissolved, and two clear layers resulted on standing. The flask was then removed from the thermostat, after washing down the propellor and sides of the flask with 10 ml. of carbon tetrachloride, followed by a little distilled water and allowed to stand undisturbed for twelve hours. During the subsequent operations, involving the removal of the acid layer and the washing of the solvent layer, and where up to 24 flasks were handled at a time, the flasks were conveniently held in long racks labelled to mark the particular stage of the operation.

The acid layer, which occupied the bottom of the flask, was removed by means of the apparatus shown in Fig. 7b. The suction flask was connected by rubber tubes to a vacuum pump and regulator which provided a suction of 16 in. water. The capillary tube was first completely filled with 70 per cent sulphuric acid and the stop cock closed. The tip of the tube could then be inserted down to the bottom of the flask, into the acid layer, without risk of trapping any of the solvent layer. Suction was applied, and, by carefully opening the stopcock, the acid was slowly withdrawn without loss of the solvent layer until about 0.2 ml. of acid remained in the flask. The capillary tube was removed, after washing down with 10 ml. of carbon tetrachloride, the flask filled up to the neck with distilled water, and stirred briskly with a motor driven glass propeller for five minutes. The propeller was withdrawn, after washing down with a jet of water from a wash bottle, and the flask set aside for 24 hours to allow the two layers to settle out completely. The washing of the solvent layer was continued as shown in Fig. 7c. The supernatant water layer was first withdrawn by locating a drawn out capillary tube a few millimeters above the interface and applying suction, care being taken not to

disturb/...

disturb the solvent layer.

Water was then run in at a regulated speed whilst it was withdrawn through the capillary at the same rate. The water in the flask occupied a height of about half an inch during this process, which was carried on until a litre of water had been passed through. The flask was then filled up to the neck with water, stirred for five minutes, and again set aside for 24 hours. This washing process was carried out three times, in all, after which the carbon tetrachloride solution was substantially free of acidic and other water soluble impurities.

The carbon tetrachloride was distilled off through a 12 inch unpacked column and condenser, after the greater part of the water had been removed mechanically. The flask was heated in a glycerine bath up to 100°C, and was removed after all distillation had ceased. The product in the flask still contained some carbon tetrachloride, water, and chlorobenzene, and these volatile materials were removed under reduced pressure in the apparatus shown in Fig. 8.

The flask with its contents was first frozen in dry ice and connected up to the apparatus with the bath removed. The trap at B was immersed in a freezing mixture of dry ice and alcohol (-70°C), and this served to condense the vapours and protect the Hyvac pump D from contamination. The pump was started up and the pressure reduced to 0.5 mm. Hg, as indicated on the gauge C, which pressure was easily held throughout the drying process. The more volatile materials, such as carbon tetrachloride and water, evaporated off smoothly, without spluttering, at a low temperature, and the flask remained frosted for about 20 minutes, and regained room temperature after an hour. At this point the flask was immersed in the bath A, containing cold glycerine-water mixture, and heat was applied so that the temperature rose to 100°C over the course of one hour, whilst the system

was/...



Fig. 8

was still held at reduced pressure. The flask was kept at this temperature until the contents had melted into a clear liquid and all visible ebullition had ceased. The flask was removed, carefully cleaned and dried with a cloth, stoppered, and set aside to cool before weighing. The percentage DDT was estimated, and the material yield and DDT yield calculated from these figures.

(c) Range of Reaction Conditions:

Reactions were carried out at temperatures of 10°C, 15°C, 20°C, and 25°C. The course of the reaction at these temperatures was followed by extending the reaction times, by intervals of two hours, up to a total time of sixteen hours in the case of the reaction at 10°C, and at correspondingly shorter reaction times at the higher temperatures, where the reaction proceeded at a faster rate. The quantity of monohydrate used was also varied for each temperature, acid : chloral ratios of 2:1, 4:1, and 6:1 being employed.

The charge for each reaction of the series was 68.9 g. of the standard chloral-chlorobenzene solution (36.3 per cent $CCl_3.CHO$) which was equivalent to 25 g. of $CCl_3.CHO$. This meant that at acid : chloral ratios of 2:1, 3:1, and 6:1, the quantity of monohydrate fed to the reactions was 50 g., 100 g., and 150 g. respectively.

(d) Data and Comments:

The results obtained in the experimental laboratory condensation reactions are listed in Table IV. The material yield, purity, and DDT yield are given for each set of reaction conditions. The course of the reaction could be followed by plotting the yield and purity of the product against reaction time. In general smooth curves were obtained, such as are shown in Fig. 9, 10, and 11, though certain anomalies became apparent when the purity values were used. The method for estimating the DDT content of the reaction product by crystallisation

from/.....

TABLE IV. - LABORATORY CONDENSATION REACTIONS - YIELD AND PURITY OF THE PRODUCT FORMED DURING THE COURSE OF THE REACTION AT DIFFERENT TEMPERATURES.

Temp. °C	Acid: Chloral Ratio	REACTION TIME - HOURS											
		2			4			6			8		
		Material Yield	Purity	DDT Yield	Material Yield	Purity	DDT Yield	Material Yield	Purity	DDT Yield	Material Yield	Purity	DDT Yield
25	6:1	75.0	64.8	48.6	87.8	66.5	58.4	85.2	60.9	51.9			
	4:1	55.5	64.8	36.0	83.2	68.4	56.9	84.1	61.6	51.8			
	2:1	30.8	53.8	16.6	49.1	58.9	29.0	-	-	-			
20	6:1	67.2	63.1	42.3	85.8	65.6	56.3	86.5	66.7	57.7	88.9	69.6	61.9
	4:1	55.2	60.0	34.9	76.9	63.8	48.5	84.3	65.0	54.8	89.2	68.5	61.2
	2:1	35.8	34.5	12.4	43.7	53.8	23.5	56.6	55.3	31.3	55.2	58.7	33.4
15	6:1	67.6	63.6	43.0	85.5	65.8	56.2	89.0	66.4	59.1	87.6	66.7	58.5
	4:1	49.5	59.2	29.3	71.4	61.7	44.1	78.2	64.2	50.2	87.4	64.7	56.5
	2:1	43.7	47.7	11.3	32.6	50.8	16.6	31.2	50.1	15.6	46.7	54.3	25.6
10	6:1	87.7	51.9	35.7	82.4	61.6	50.8	90.0	66.1	59.5	89.0	66.4	59.1
	4:1	47.7	57.0	27.2	71.1	59.8	42.5	80.5	62.8	50.6	86.1	64.9	55.9
	2:1	22.8	43.0	9.8	38.0	49.5	18.8	43.7	50.8	22.2	49.7	53.3	26.5

TABLE IV. (CONTD.)

Temp. °C	Acid: Chloral Ratio	REACTION TIME - HOURS											
		10			12			14			16		
		Material Yield	Purity	DDT Yield	Material Yield	Purity	DDT Yield	Material Yield	Purity	DDT Yield	Material Yield	Purity	DDT Yield
25	6:1												
	4:1												
	2:1												
20	6:1	88.4	70.4	62.2	82.0	65.5	53.7						
	4:1	90.2	70.8	63.9	92.0	63.5	58.4						
	2:1	58.7	60.7	35.6	68.5	54.3	31.7						
15	6:1	90.0	67.4	60.7	84.3	64.9	54.7	84.5	64.6	54.6			
	4:1	91.0	66.6	60.6	92.5	66.0	61.0	92.5	63.5	58.8			
	2:1	49.5	55.1	27.2	57.6	56.0	32.4	56.7	54.4	30.8			
10	6:1	92.5	68.1	63.0	91.0	67.0	61.8	92.6	65.5	60.7	93.6	66.8	61.5
	4:1	88.1	64.1	56.5	90.7	64.2	58.2	90.8	64.6	58.7	93.0	66.5	62.3
	2:1	50.3	52.4	26.4	54.0	51.3	27.7	52.0	49.5	25.8	56.7	54.5	30.9

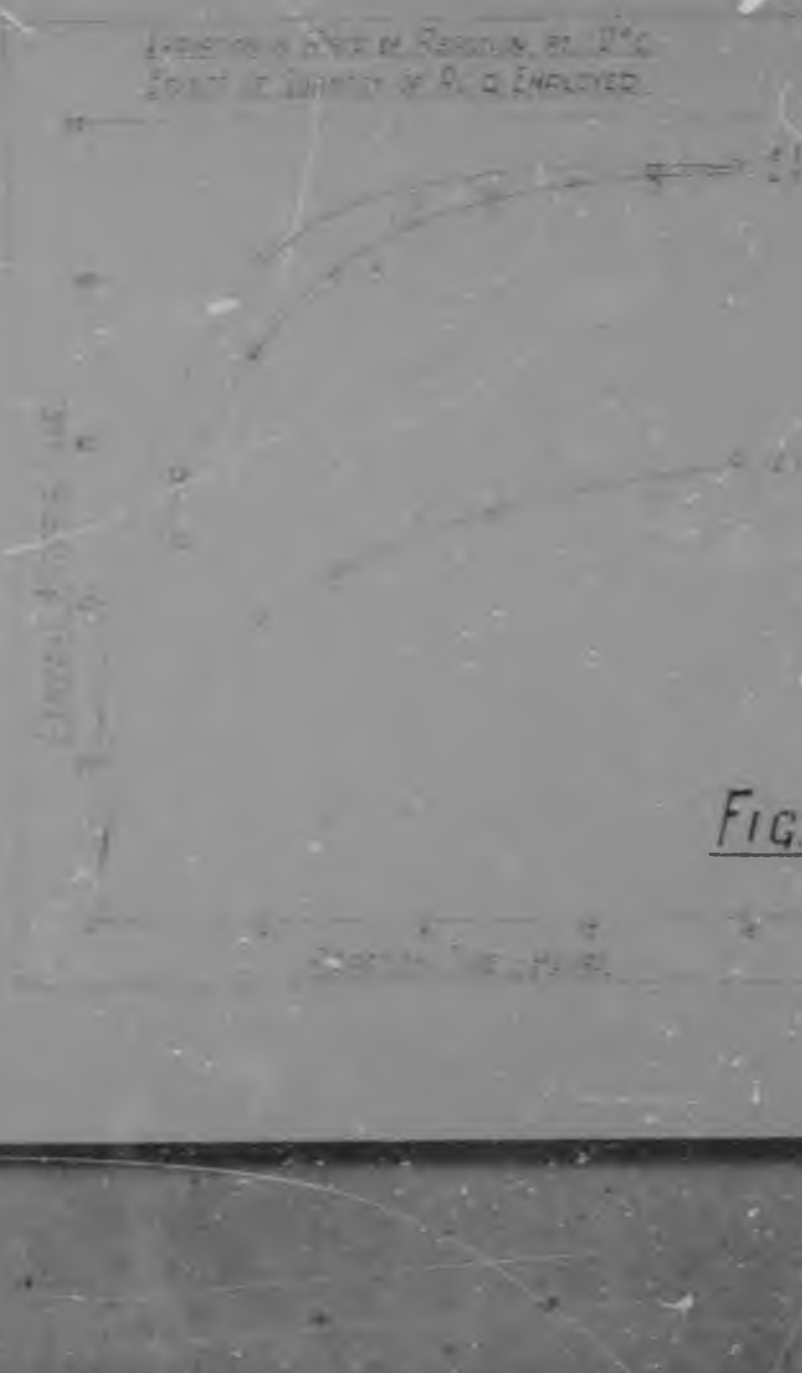

Fig. 9a

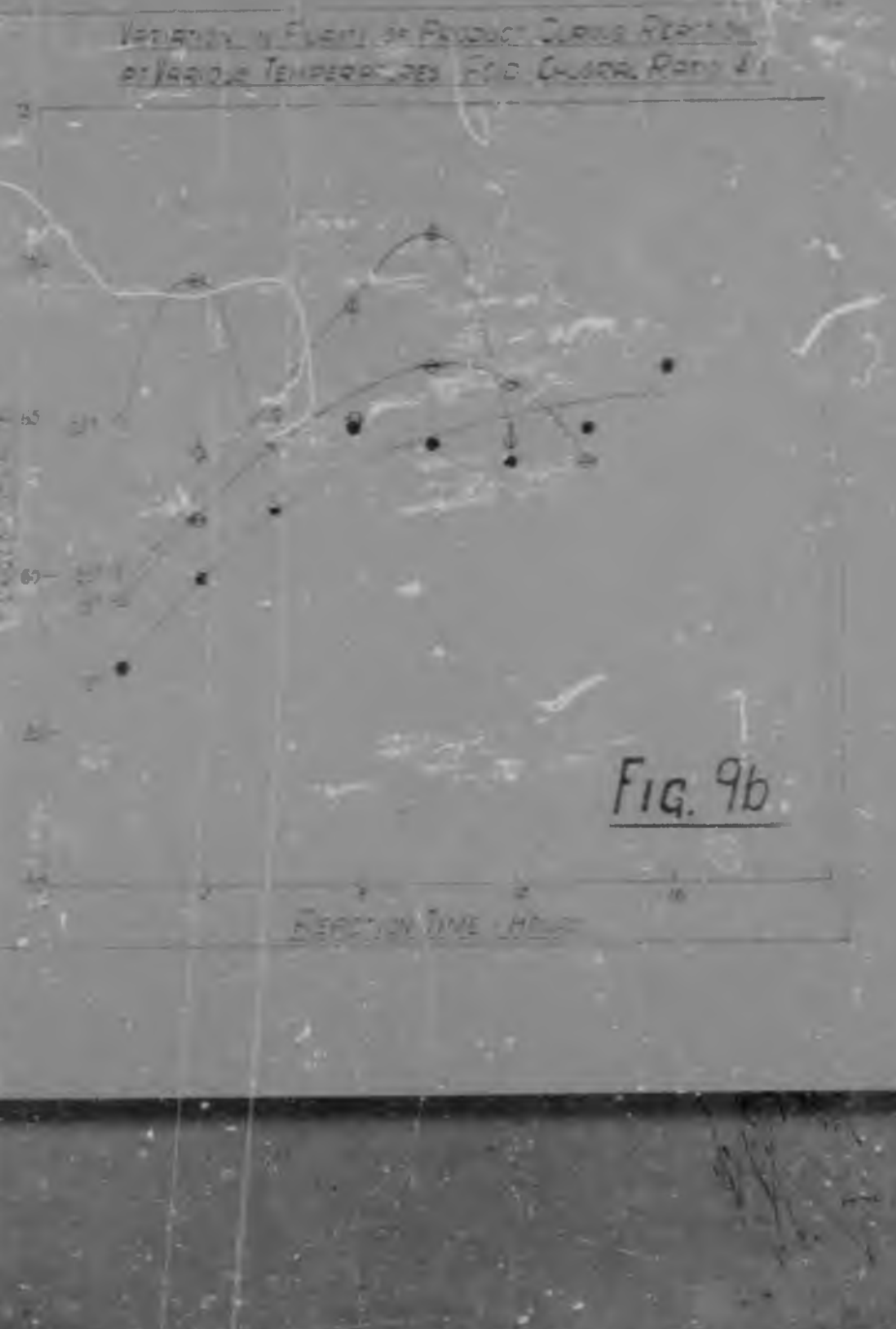

Fig. 9b

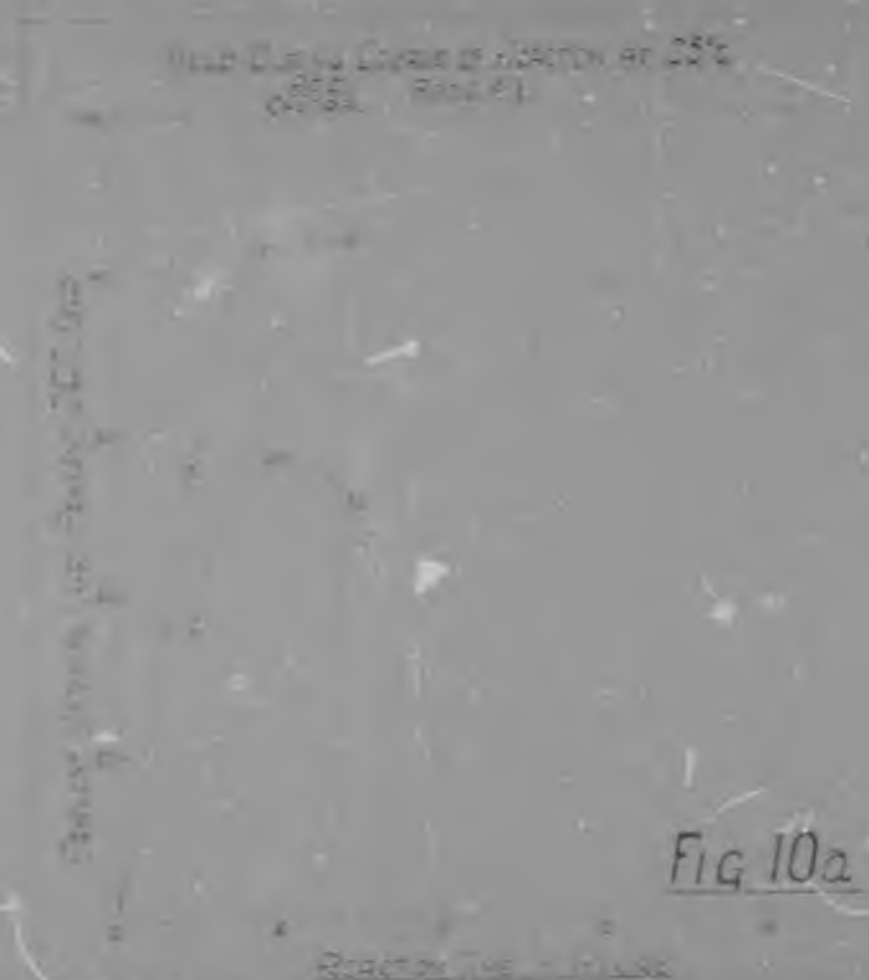

Fig 10a

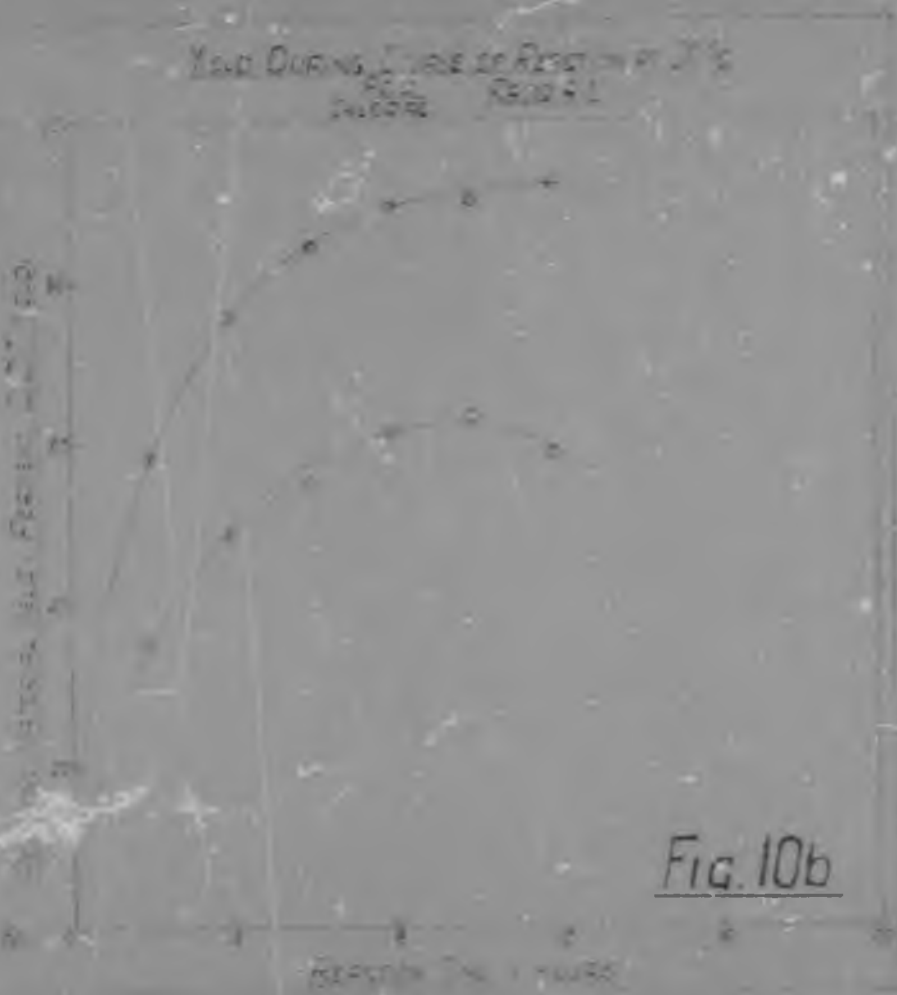

Fig. 10b

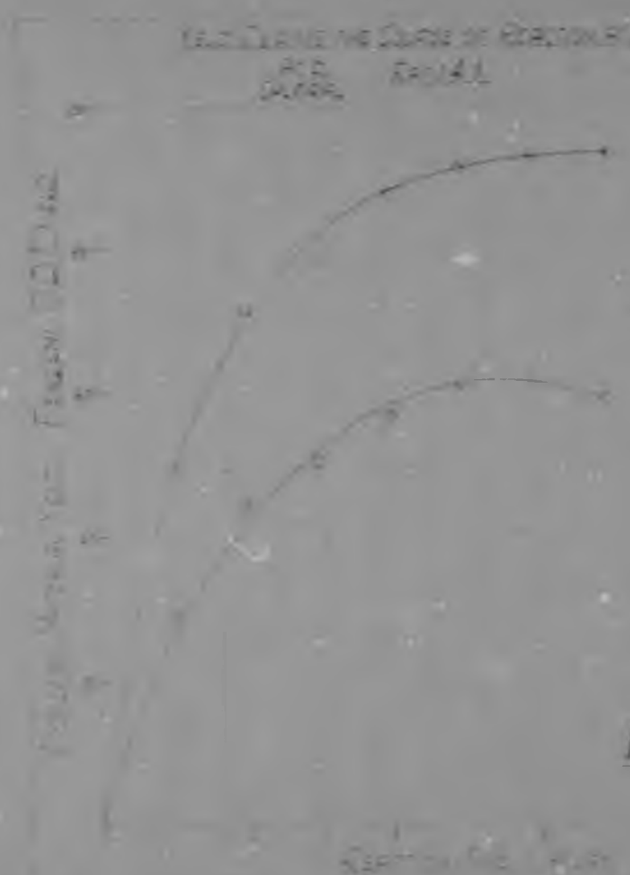

Fig 11a



Fig 11b

from alcohol had an accuracy of 1.0 to 2.0 per cent, though greater errors could occur when low purity materials were examined. It will be noticed that there was an apparent decrease in the purity of the product near the end of the reaction period, whilst the material yield remained unaffected. At first sight it would appear that the DDT formed was being removed, possibly by either undergoing sulphonation, or by hydrolysis, as the loss of DDT was greater than could be accounted for by the error in the analytical method. It is known, however, that DDT hydrolyses with difficulty under aqueous conditions, and it can also be shown that pure DDT resists sulphonation to a marked degree. For example, 50 g. of pure DDT, M.P. 10[illegible]°C, was mixed with 300 g. of C.P. concentrated sulphuric acid in a flask and agitated at 20°C for five hours. The product was extracted with carbon tetrachloride, and the solvent layer separated, washed, and dried by the standard procedure for condensation reactions. This treatment yielded 49.84 g. of material having a melting point of 106°C. The loss of DDT was therefore negligible.

In the light of these facts it is difficult to correlate the curve for the DDT yield, where a drop in purity ocurred, with the curve for the material yield which proceeded normally. One fact emerges, however, when the curves on Fig. 9b are examined. The tendency for the purity to pass through an optimum value decreased as the temperature was lowered, and at 10°C disappeared entirely. This would be in keeping with a theory that the loss was due to some chemical action.

The quantity of acid used had a marked influence on the course of the reaction. This is clearly shown in Fig. 9A., where the material yield is plotted against reaction time at 10°C for the three acid: chloral ratios employed. This relationship also held closely at the other temperatures. The ultimate yield at the 4:1

acid/.....

acid : chloral ratio was identical with that using a 6:1 ratio, though the initial reaction rate was slower. Reducing the ratio to 2:1 had a marked effect on the course of the reaction, as the material yield did not exceed 60 per cent with low purities prevailing. Whilst the low yield obviously was due to the accumulation of water from the reaction, which diluted the acid down to the point where the reaction rate became imperceptible, the low purities found could only be attributed to the formation of substances other than DDT. The washing and drying treatment would effectively remove the reactants, chloral and chlorobenzene, still remaining in the product; therefore, if the ratio of the formation of DDT to iso-DDT is constant, as is maintained by Forrest et al (8), the low purity found under these conditions could be explained most satisfactorily by the accumulation of the half condensation product (I - Fig. 6). The Baeyer condensation takes place in two stages (14), and in the case of chloral and chlorobenzene would proceed as follows:-

(I) $CCl_3.CHO + C_6H_5Cl \longrightarrow CCl_3.CH(OH)C_6H_4Cl$

(II) $CCl_3.CH(OH)C_6H_4Cl + C_6H_5Cl \longrightarrow CCl_3.CH.(C_6H_4Cl)_2 + H_2O$

Whilst the treatment of the kinetics of this reaction is not possible with the data available, it would appear that the process takes the form of two successive reactions of the second order. It could be surmised that the velocity of the first stage would be less effected by the dilution of the acid than the second stage, where one mole of water is liberated, and under these conditions there would be an accumulation of the half condensation product, accompanied by a drop in purity. Apart from procedures based on chemical analysis, the presence of the half condensation product could be tested by treating the product of a reaction, where an acid : chloral ratio of 2:1 was employed, with further quantities of monohydrate and

noting/--

noting the effect. A simple experiment was carried out recently which illustrates this point. Solutions of chloral in chlorobenzene obtained from the commercial plant were used.

Three reactions were carried out on a solution of chloral in chlorobenzene containing 36.0 per cent $CCl_3.CHO$ by weight. The chloral used for making up the solution contained 92.0 per cent $CCl_3.CHO$. The equivalent of 25.0g.$CCl_3.CHO$ was used in each case, and the product was separated and dried in the usual way. The conditions for each reaction were varied as follows:-

(a) 50 g. of monohydrate, equivalent to an acid : chloral ratio of 2:1, were added to 69.4 g. of chloral - chlorobenzene solution over 90 minutes. The reaction was held at 20°C and halted after eight hours. The product was recovered, weighed, and analysed.

(b) The reaction was carried out as in (a) up to the end of the eighth hour when, instead of halting the reaction by the addition of water, the agitation was stopped, and the neck of the flask sealed with rubber tape to prevent undue absorption of water vapour. The flask was then left standing overnight in the thermostat, and the following morning the reaction was continued by a further addition of 100 g. of monohydrate over 90 minutes to bring the total addition of monohydrate up to an acid : chloral ratio of 6:1. After the second eight hour reaction period had been completed the product was recovered.

(c) The reaction was carried out as in (a), but 150 g. of monohydrate equivalent to an acid : chloral ratio of 6:1 were used

The experiment can be summarised as follows:-

Reaction Conditions/.....

Reaction Conditions.	Material Yield	Purity
(a) 2:1 acid : chloral ratio for eight hours. 20°C.	53.6	55.0
(b) 2:1 acid : chloral ratio for eight hours, followed by a further eight hours with the acid : chloral ratio raised to 6:1. 20°C.	87.2	64.4
(c) 6:1 acid : chloral ratio for eight hours	82.5	63.3

It is clear from these results that the substances which caused the low purity in (a) were converted by the further addition of acid into a product of approximately the same composition as that found in (c), where the full quantity of acid was used at the beginning of the reaction. The yield in (b) was rather higher than that found in (c), and could be attributed to the longer period of reaction. These results are good evidence of the presence of accumulated half condensation product in these uncompleted reactions.

The presence of the half condensation product was also found in the initial stages of the reaction where the normal quantity of acid was employed. This is shown in the first portion of the curves in Fig. 9b, where the purity of the product is plotted against reaction time. If the latter portions of the curves, where drops in purity occur, are ignored, it will be seen that the purity of the product increased with time of reaction, and that the rapidity of this process, that is, the slope of the curve, is a function of temperature; increase in temperature being accompanied by a more rapid increase in purity. This indicates that the second stage reaction is, in general, more sensitive to changes in temperature than the first stage.

In view of the general interest in the preparation of the half condensation product, 1:1:1-trichloro-2-hydroxy-2-(4-chlorophenyl)ethane, which is used as a starting point

for/.....

for the synthesis of unsymmetrical analogues of DDT, it would be of interest to speculate on the conditions necessary for the maximum concentration of this substance to appear. From the curves it is probable that this would occur when the reaction was carried out at a low temperature, with the minimum quantity of acid, and with comparatively short reaction periods.

The effect of temperature on the material yield was found to be slight. The velocity of the reaction increased with temperature, as would be anticipated, and the yield at 25°C was poor; but this could be attributed to the disappearance of one of the reactants, chlorobenzene, due to the increased rate of sulphonation at this temperature, rather than any other factor. The amount of chlorobenzene used in the condensation, therefore, is more important than was realised at the time these reactions were commenced, and it could be assumed that a result more in accord with the others would have been found, had a larger excess of chlorobenzene been used when the reactions were conducted at 25°C. It is concluded that, provided the reaction temperature is within reasonable limits (for example at 50-60°C a syrup results) identical yields will be obtained over a comparatively wide range of temperatures, and that the main advantage of conducting the reaction at the lower temperatures lies in the decreased amount of sulphonation that occurs.

The temperature was found to have some effect on the purity of the product, and the optimum yield of DDT occurred at 20°C after a reaction period of ten hours, when the purity exceeded 70 per cent.

These laboratory investigations proved very useful in formulating the best conditions for the reaction on a larger scale, but at the same time they emphasised the fact that all important factors had not been included.

The/.....

The results indicate that the percentage chlorobenzene used in excess of metathetical requirements will also influence the course of the reaction, and secondly, if the quantity of acid used is important, the probability that the strength of the acid will be equally important, cannot be ignored, and the logical extension of this work would be to carry out condensation reactions with acid at oleum strength, with sufficient chlorobenzene in excess, and at low enough a temperature, to minimise the effect of the sulphonation of the chlorobenzene.

3. Pilot Plant Reactions.

(a) Design and Operation of Unit:

A large number of reactions had been carried out on the pilot plant scale, at arbitrarily chosen conditions, before the pilot plant unit was used to confirm the laboratory findings on the larger scale. It was customary to react the equivalent of one mole of $CCl_3.CHO$ with 2.30 moles of chlorobenzene for six hours at 150°- 170°C, using monohydrate at an acid: chloral ratio of 6:1. The reaction vessel was originally fabricated in lead, but later, when at the instance of the General Manager, Lt.Col. W. Bloloch, the units in the commercial plant were made up in mild steel and successfully operated, the pilot plant unit was also modified in this way.

The unit in its final form is shown in Fig. 12. The principal feature was the provision made for cooling the water circulating through the jacket with a freezing mixture of salt and ice, which made it possible to conduct reactions at temperatures below atmospheric. The reaction vessel proper consisted of a mild steel jacketed vessel C of ten gallon capacity, provided with a 6 inch propeller agitator, driven at 800 revolutions per minute by a 3 H.P. electric motor and a

crossed/...

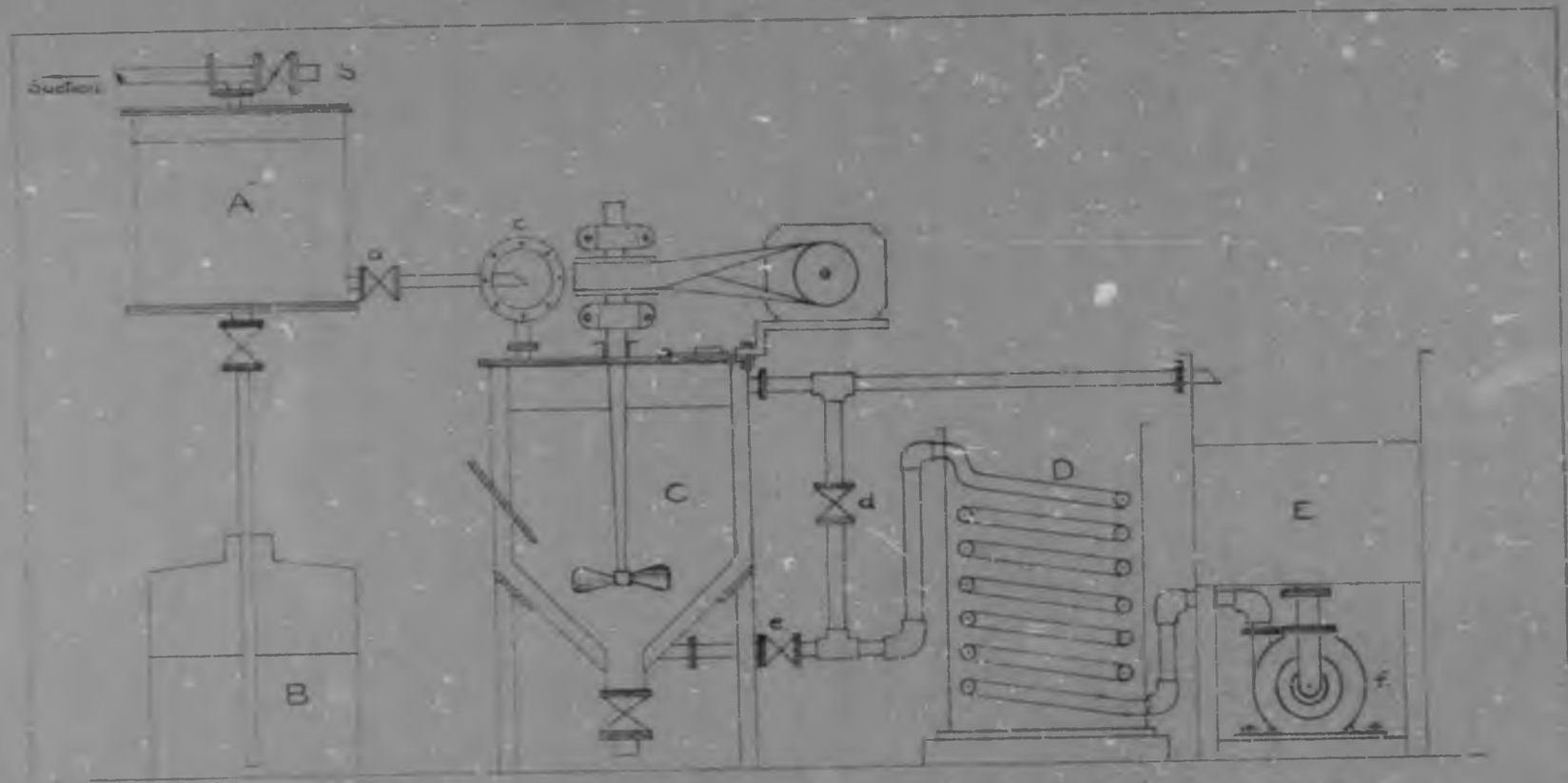

FIG.12. PILOT PLANT CONDENSATION APPARATUS.

crossed flat belt drive. The agitation produced was probably excessive, but as it operated without splashing, no attempt was made to alter it. The lid of the reactor was provided with a semicircular flap on hinges, which was normally closed down firmly during the reaction, but could be opened when an inspection of the contents was required. The circulating cooling water was drawn from a reservoir at E and forced through a cooler consisting of a coil immersed in the salt - ice freezing mixture D, and then into the base of the reactor cooling jacket; the water leaving the top of the jacket was returned to the reservoir. Both the reservoir and the cooler were insulated with cork. The flow of cooling water through the jacket could be controlled by adjusting the by-pass valve 'd' and valve 'c', without throttling down the flow of circulating water through the cooler, which prevented accidental freezing. This arrangement made the use of brine as a cooling medium unnecessary. In any case the temperature rarely fell below 7°C, which was adequate for the correct control of the reaction.

The monohydrate was loaded into the head tank A by drawing up the acid from a steel carboy B set upon a platform scale. The valve on the dip pipe was closed and suction applied. By regulation of the valve, the correct weight of acid could be drawn up into the head tank. When this weight was indicated on the scale, the dip pipe valve was closed, the suction turned off, and the tank vented to atmosphere through valve 'b'. In weighing in the acid a correction was made for the acid remaining in the dip pipe.

The reactants were charged in through the cover, and when the correct temperature had been attained, the monohydrate was run in at a steady rate through valve 'a' and the bulls eye sight glass 'c'. After some experience, the correct flow of acid could be judged quite accurately

at/.....

at 0, so that the addition was made over the customary 90 minutes. However, the addition of acid was also controlled in relation to the temperature of the reaction, and provided that the acid was not run in at a rate such as to affect the temperature, small variations in the time of acid addition had no measurable effect.

At the completion of the reaction the product was recovered by discharging the contents into a lead vessel of about two cubic feet capacity provided with a perforated base. The perforations consisted of 1/16 inch holes drilled through the lead base at one inch intervals. When monohydrate was used, the product was found in the form of fairly large buttery particles, and this screen separated the acid from the product with negligible loss. The product was drained for 30 minutes, tipped into an open topped lead lined vessel, and worked up with successive changes of water, and finally with sodium carbonate solution, until virtually free of acid. The washed product was dried in a tray drier in a current of air at 60°C for twelve hours, when it contained less than one per cent of moisture.

(b) Data and Comments.

In carrying out the pilot plant reactions no attempt was made to depart from the optimum conditions found in the laboratory, where this was possible, and these runs served merely to confirm the findings on a considerably larger scale. There were, however, certain differences which might have influenced the results. In the first place, the product was not recovered on the plant by solvent extraction as in the laboratory, and secondly, the purity of the chloral was much lower than the specially purified material used in the laboratory experiments. Whilst a large scale reaction using pure chloral would have been of considerable interest, the purification on a laboratory scale of the comparatively large quantity

required/...

required was impracticable at the time.

The data on three typical runs are listed in Table V. In runs No. 1 and 2 the conditions for the reaction were identical and, after a ten hour reaction period at 20°C, there was close agreement in the yield and purity obtained. In run No. 3 the quantity of chlorobenzene used in excess was doubled without influencing the result, beyond increasing the material yield slightly. It is obvious, then, that the charge for large scale production could be based on weights of chloral (90 to 95 per cent $CCl_3.CHO$), chlorobenzene, and monohydrate, without much variation in yield. This was borne out by subsequent reactions, and the charge became:

Distilled chloral	20 lb.
Chlorobenzene	33 lb.
Monohydrate	75 lb.

Needless to say, the freshly distilled chloral was always premixed in the ratio required for the condensation and stored in this condition; 53 lbs of the mixture being used for each reaction. On this basis the process worked smoothly, and about one ton of technical DDT of approximately 66 per cent purity was produced.

C. BIOLOGICAL ACTIVITY OF TECHNICAL DDT.

It was important that the biological activity of the technical DDT produced by this process be assessed. Tests were recently carried out by Mr. Potty of the Division of Entomology, Department of Agriculture, Pretoria, and these are being published (18). These tests formed a part of a whole series of experiments on the efficacy of technical DDT from various sources and processes, but they will serve to illustrate the potency of the technical DDT produced by the monohydrate process, which was included. The material used for the tests was not produced on the pilot plant, but represented a sample of a weeks output

on/.....

EAGLE V:

PILOT PLANT CONDENSATION REACTIONS.

RUN NO.	CHLORAL			CHLORO-BENZENE		MONOHYDRATE		REACTION			PRODUCT			YIELD	
	LB.	% CCl_3CHO	LB. CCl_3CHO	LB.	% IN EXCESS	LB.	ACID CHLORAL RATIO	PERIOD of FEED Mins.	HOURS	TEMP. °C	LB.	% PURITY	% WATER	MATERIAL	DDT.
1	20	93.0	18.6	32.6	15.0	74.4	4:1	90	10		40.0	66.0	0.9	89.5	59.1
2	20	95.9	19.8	33.2	15.0	75.2	4:1	90	10	20	40.0	67.3	0.5	88.6	59.6
3	20	92.0	19.8	39.5	30.0	79.2	4:1	90	10	20	44.1	66.0	0.6	92.7	61.2

on commercial units.

The materials examined were:-

(a) Technical DDT containing 66.6 per cent of 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane.

(b) Pure DDT isolated from (a) by crystallisation from absolute alcohol.

(c) The mother liquor from the purification step in (b) evaporated down to give a product of low purity, containing 24.7 per cent of 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane.

Two sets of solutions were made up from these materials, containing in the first instance 3.5 per cent of the material under examination dissolved in kerosene, and in the second the equivalent of 3.5 per cent of 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane dissolved in kerosene.

The test insects were workers of the termite 'Trinervitermes Havilandi'. The test surfaces were 3½ inch petrie dishes. The application was 0.3 ml. of the test solution sprayed onto the test surfaces in a spray tower of standard dimensions. Each dish was exposed to this spray for two minutes. With these small deposits the relative effectiveness of the various solutions was sharply defined. Forty insects were used for each experiment, and they were exposed to the treated surface for six hours, removed to clean dishes, and the final mortality noted after 120 hours. Tests were conducted 24 hours, 14 days, and one month after the application of the solution. Controls were also carried out in the usual way.

The per cent mortality for each solution is given on Table VI, and it is clear from these results that no great advantage is gained by purifying the technical DDT before use in an insecticidal spray, as a kill of 25.0 per cent is obtained after one month as against 33.2 per

cent/.....

TABLE VI BIOLOGICAL ACTIVITY OF DDT.

MATERIAL UNDER EXAMINATION	CONCENTRATION	MORTALITY PER CENT		
		AFTER 24 HOURS	AFTER 14 DAYS.	AFTER 1 MONTH
TECHNICAL DDT PURITY: 66.6 PER CENT.	3.5 PER CENT OF MATERIAL	98.3	37.3	25.0
	3.5 PER CENT OF 4:4 ISOMER	100.0	69.1	65.3
PURE DDT.	3.5 PER CENT OF MATERIAL	96.7	46.2	33.2
	3.5 PER CENT OF 4:4 ISOMER			
IMPURITIES FROM CRYSTALLISATION PURITY 24.7 PER CENT	3.5 PER CENT OF MATERIAL	98.3	33.5	11.1
	3.5 PER CENT OF 4:4 ISOMER	100.0	90.8	96.1

cent for pure DDT. Even more important is the conclusion that, if the solutions are made up on a basis of the active ingredient, 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane, as is now common practice in South Africa, an even more effective insecticide is produced when technical DDT is used, for example the residual toxicity after one month is raised to 65.3 per cent. This result is no doubt due to the presence of other substances, such as DDD and iso-DDT, which have some insecticidal activity. This is emphasised, if in an exagerated form, by the extraordinarily high kill after one month, 96.1 per cent, achieved by the solution which contained the equivalent of 3.5 per cent of the active 4:4 isomer, made up from material of 24.7 per cent purity. In this case the concentration of substances other than DDT was 10.7 per cent, and undoubtedly contributed to the activity of the mixture.

D. SUMMARY.

As a result of a prolonged series of reactions that were carried out using a standard method of procedure, the optimum conditions for the condensation of chloral and chlorobenzene to DDT, using sulphuric acid at monohydrate strength, have been established. Chloral was stored for long periods in a stable condition by dissolving it in the amount of chlorobenzene necessary for the condensation. When a charge of one mole $CCl_3.CHO$, 2,30 moles chlorobenzene, and 6 moles sulphuric acid (100 per cent strength - acid : chloral ratio 4:1) was reacted with vigorous stirring at 20°C, a yield of 90 per cent was approached after ten hours reaction time. The product contained from 66 to 70 per cent of 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane, giving a yield of 60 per cent of this substance based on the $CCl_3.CHO$ used.

The temperature was found to have little direct effect on the ultimate yield of technical DDT, but did

influence/....

influence the reaction, in that the rate of sulphonation of the chlorobenzene increased with temperature. The optimum purity was found at 20°C after ten hours reaction, which led this to be chosen as the operating temperature on the large scale units. The mechanism of the reaction is discussed in some detail.

The amount of acid used was critical, and the most economical of the three quantities employed in the laboratory (6 moles acid per mole chloral) was also used successfully on the pilot plant unit.

The development of these laboratory experiments to pilot plant scale was undertaken, and a description is given of the ultimate process. The product manufactured here was of somewhat lower purity than that produced in the laboratory, which could be accounted for by the lower purity of the chloral used. The yield, however, confirmed the laboratory findings.

The technical DDT produced by this process has been examined for biological activity, in relation to pure DDT, by the Division of Entomology, Pretoria, and excellent results were obtained on termites. The relationship between purity and biological activity is discussed.

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APPENDIX.

ANALYTICAL METHODS:

1. Chloral:

(a) Estimation of $CCl_3.CHO$ in crude and distilled Chloral by reduction of mercuric chloride:

NOTE: This method was received through official channels: Full details have since been published. (See Part One - page 2.)

REAGENTS:

Buffered mercuric chloride solution: Dissolve 200 g. mercuric chloride, 300 g. hydrated sodium acetate, and 80 g. sodium chloride in water, and make up to one litre. Leave standing overnight, and filter before use.

Hydrochloric acid solution: Approximately normal strength.

Caustic soda solution: Approximately normal strength.

Methyl red indicato 0.1 per cent methyl red in 40 per cent alcohol.

Weigh out accurately 10 g. of material, using a Lunge-Rey pipette, into 500 ml. of distilled water in a litre standard flask. Shake well and make up to one litre. Filter through dry filter paper, rejecting the first portion of the filtrate. The filtration is necessary in order to remove any of the insoluble chloral polymer present in the material. Transfer 25 ml. of the filtrate, with a pipette, into 100 ml. of saturated lime water held in a 600 ml. beaker. Swirl the contents and bring to boil as rapidly as possible over a hot flame, and boil for ten minutes. Cool somewhat, add a few drops of methyl red indicator, and acidify with HCl, taking care to add sufficient acid to dissolve any solid calcium hydroxide or carbonate adhering to the side of the beaker. Make the clear liquor alkaline with N NaOH, and then just acid with one drop of N HCl. Dilute the solution to about 400 ml. with distilled water, and add 25 ml. of the buffered mercuric

chloride/.....

chloride reagent. Heat over a flame until the solution becomes cloudy, and the place the beaker on a water bath for two hours. Filter hot through a tared sintered glass crucible, complete the transfer of the precipitate, and wash using the minimum quantity of hot distilled water. Dry to constant weight at 105°C.

$$\text{Percent } CCl_3.CHO = \frac{\text{g.precipitate} \times 1000 \times 0.3122 \times 100}{\text{g. material} \times 25}$$

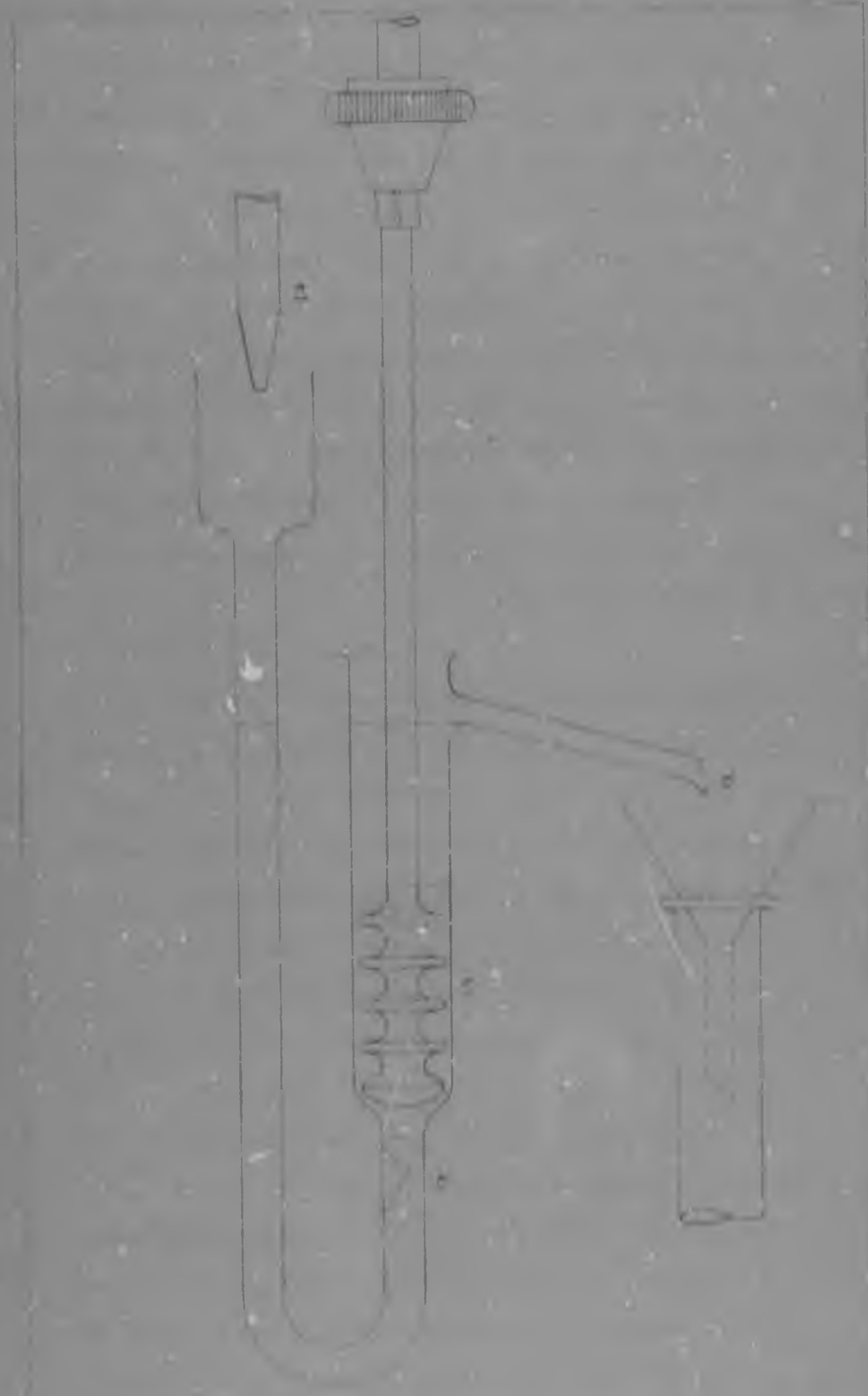
(b) Estimation of $CCl_3.CHO$ in chlorobenzene solution:

It is not possible to prepare an aqueous solution directly with this material, and if it is known that the solution is free from polymer the estimation may be carried out by weighing out a portion of the solution directly into the lime water by means of a Lunge-Rey pipette, and proceeding with the analysis as described under (a).

Unfortunately, any polymer present will also react with the mercuric chloride and cause errors. To avoid this, a method was evolved recently where the chloral is quantitatively extracted with water from the chlorobenzene solution by means of the apparatus shown in Fig. 13. The procedure is as follws:-

The apparatus is cleaned, set up vertically in a stand, and filled with distilled water until it just overflows at 'd'. A funnel, resting in the neck of a clean one litre volumetric flask, is set up under 'd', and distilled water is added drop-wise at a steady rate at 'a'. About 30 g. of the chloral chlorobenzene solution is weighed accurately (from a Lunge-Rey pipette) into 'c', and being heavier than water, displaces it, and takes up a position above the orifice at 'b'. The function of the orifice is to prevent the escape of any of the chlorobenzene solution into the U portion of the tube where it will escape the action of the agitator. The motor driven agitator is

started/.....



EXTRACTION APPARATUS
FOR THE ESTIMATION OF CHLORAL

FIG. 13

started, and the speed adjusted to about 3 revolutions per second, when an intimate contact is affected between the two phases and the extraction proceeds rapidly. The extraction may be so energetic that the contents become hot, due to the heat liberated with the hydration of the chloral. In such cases it is best to slow down, or even stop the agitation and increase the flow of water in the initial stages so that the apparatus never becomes more than just warm to the touch. When the litre flask is nearly full to the neck it is removed, made up to the mark with distilled water, and shaken well. An analysis for the $CCl_3.CHO$ is conducted on an aliquot as described in (a). In doubtful cases the extraction up to a second litre can be conducted, but normally, no more than a trace of chloral is found to be present.

Apart from its present use, the apparatus should prove generally useful for the extraction of a liquid phase by a lighter immiscible solvent.

NOTE: Whilst this method has proved its usefulness, recently, in establishing the stability of chloral in chlorobenzene solution, in all the quantitative condensation reactions conducted in the laboratory the direct method was used for the estimation of chloral.

(c) Distillation analysis of crude chloral:

75 ml. of crude chloral is weighed into a 250 ml. round bottom flask, together with 75 ml. of C.P. concentrated sulphuric acid. The flask is connected to an 18 inch by 1 inch insulated laboratory column, packed with ¼ inch glass cuts. Distillation is commenced at an even rate, and all product distilling between 88° and 92°C at 627 mm. Hg. pressure is collected and weighed. The distillation is halted at the appearance of fumes in the distillation flask. The weight of chloral distillate is reported as

a/.....

a percentage.

The method is of limited value only, and was used in the early stages of the investigation, when the mercuric chloride method was not avaiable. It is retained only for reasons of comparison with large scale distillations.

All glass apparatus with ground glass interconnecting joints is used exclusively for this distillation, due to the rapid deterioration of ordinary bungs.

2. DDT.

(a) Estimation of the percentage 1:1:1-trichloro-2:2-di-(4-chlorophenyl)ethane in condensation reaction products and commercial DDT. (Purity). (British Specification for DDT.)

Reagents: Solution A.

Dissolve 60 g. of pure DDT crystals (M.P. not less than 106°C) in 500 ml. of hot absolute alcohol. Dilute to two litres with cold absolute alcohol. Add about 2 g. of the solid crystals and allow to stand overnight, preferably at 15°C. Store in a cool place as near 15°C as possible.

Method:

Weigh out accurately 10 g. of material, preferably in a boiling tube of 100 ml. capacity provided with a ground glass joint fitting to a reflux condenser. Add 50 ml. of Solution A, attach to reflux condenser, and heat carefully until all the material has dissolved and the alcohol is just brought to the boiling point. Allow the tube to cool somewhat, detach from condenser, stopper, and leave standing for one hour at room temperature. Transfer to a bath held at 15°C ± 1°C and leave for two hours. Filter the entire contents of the tube onto a tared sintered glass or Gooch crucible under suction. Use two 10 ml. portions of Solution A to complete the transfer, and to wash the crystals on the crucible. Apply suction for five minutes and dry to constant weight at 75 to 80°C. Determine the melting point of the crystals. Should this

fall/....

fall below 105°C the analysis is repeated using a greater quantity of Solution A.

$$\text{Purity per cent} = \frac{\text{Wt. of crystals} \times 100}{\text{Wt. of material.}}$$

ACKNOWLEDGMENTS.

The writer wishes to place on record his appreciation to:

(1) Professor H. H. Stephen for his interest in the work carried out at Klipfontein and for making the submission of this thesis possible.

(2) Lt. Col. W. Blaloch for his whole hearted support and encouragement during the whole course of this investigation. This work would not have been concluded, had not many of the innumerable difficulties encountered in connection with equipment, design, and policy been surmounted by the General Manager.

(3) Capt A. G. Harvey, Mr. M. Swain and the Engineering staff for the close co-operation and advice in the matter of fabrication of equipment.

(4) Mr. T. Higman, and the staff of the Drawing Office for preparing tracings and prints for this thesis from the drawings submitted.

(5) The staff of the Development Laboratory, on whom fell the main burden of conducting the laboratory experiments and operating the pilot plant. Amongst others the services of Messrs I.A. Leibbrandt, D. M. Rice, W. Hofmeyr, M. S. Chazan, J. Allen Leven, and more recently R. A. Aling, H. Retief, and I. D. Groenwald are acknowledged.

(6) My father, Mr. B. Jacobson, who undertook the onerous task of preparing the stencils from an unfamiliar text, and to whom all credit for accuracy in presentation is due.



Author Jacobson A C B
Name of thesis An investigation into the production of chloral by the chorination of Ethyl Alcohol 1947

PUBLISHER:
University of the Witwatersrand, Johannesburg
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