SOME FACTORS AFFECTING THE VAPOR PHASE CHLORINATION OF ACETALDEHYDE

by

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I. INTRODUCTION

During World War II a new insecticide, Dichloro-diphenyl-trichloroethane, commonly known as DDT was introduced. The synthesis of DDT consists of the condensation of chlorobenzene with chloral. Prior to 1943 there was little use for chloral other than for biological research; therefore, it was only necessary to produce chloral on a small-batch basis. However, the demand for DDT by the armed forces became so great that it was necessary to produce chloral in large quantities, preferably on a continuous production basis. The monthly consumption of chloral now averages over 1,300,000 pounds.

A considerable amount of research has been conducted in the United States, as well as in Great Britain and Canada, on the optimum conditions required for the preparation of chloral, but most of these research results have not been disclosed. One of the known processes now in use for the production of chloral consists of the chlorination of ethyl alcohol to form chloral alcoholate. To release the chloral from the chloral alcoholate an equivalent quantity of 96% sulfuric acid is required. Actually very little of the sulfuric acid is recovered, because the reclamation of sulfuric acid is both cumbersome and costly. Furthermore, the use of ethyl alcohol involves close governmental control.

Another method that has been used for the production of chloral is the chlorination of acetaldehyde in the liquid phase; that is, by keeping the temperature below 21 degrees Centigrade. The flow of fluids is more difficult to control in a chemical process than is the flow of gases. Since both acetaldehyde and chlorine are gases at room temperature, an investigation of the feasibility of chlorinating acetaldehyde in the vapor phase seems to warrant an investigation.

The purpose of this investigation is to undertake vapor phase chlorination of acetaldehyde for the production of chloral and to determine the effects of variables on the yield and quality of chloral produced.

II. LITERATURE REVIEW

History

Discovery. Chloral was first synthesized by Liebig[10] in 1832 while he was conducting experiments on the chlorination of ethyl alcohol. In 1834 Dumas[4] verified Liebig's synthesis and furnished quantitative data for the production of chloral by the chlorination of ethyl alcohol. Stadeler[19] studied the composition of chloral in 1847.

Physiological Properties. It was not until 1869 that Liebrich,[11] inspired by Liebig's observation that chloral yields chloroform under the influence of alkalis, formed the idea of studying its physiological action, with hope that the small amount of alkali in the blood would be sufficient to effect the transformation of chloral into chloroform and formic acid, with the result that he discovered the interesting and unexpected physiological qualities of chloral. Harnack and Ramertz[7] found that chloral was also a hypnotic and an antipyretic. In 1905 Rohde[18] studied the action of chloral on the heart.

Chemical Reactivity. The vast range of compounds formed from condensation reactions are found in the literature which suggest that chloral is very reactive. It reacts with phenols, alcohols, acids, various bases, as also with reagents like hydrogen sulfide, halogens, phosphorous halides, cyanides, cyanates, and oxidizing agents. With aldehydes and chloral, an aldol type of condensation takes place. Koenigs[9] obtained from chloral and paraldehyde chloral aldol and from

butyl chloral, paraldehyde butyl chloral. In the presence of pyridine, sulfuric acid, or aluminum chloride Boeseken and Schimmel[2] obtained a polymer.

Insecticidal Properties. In 1874 Zeidler[23] condensed chlorobenzene with chloral to obtain di-monochlorphenyl-trichlorethane. This compound was forgotten until a few years ago when Muller, a research worker for the J. R. Geigy Company of Basle, Switzerland, in routine testing of a number of formulae, synthesized the product from Zeidler's account of his early work in the proceedings of the German Chemical Society and discovered its surprisingly good insecticidal properties. In 1939 the Geigy Company supplied a test quantity of the material, later assigned the trade name of "Gesarol", to Dr. R. Weisman for use in experiments designed to control the Colorado potato beetle on the Swiss potato crop. His experimental work confirmed the Geigy findings as to the insecticidal value of this remarkable compound. Today this compound is known as DDT. In 1943 Muller[13] was given a patent for the use of DDT as an insecticide.

Production of Chloral

Chlorination of Ethyl Alcohol. The production of chloral by the chlorination of ethyl alcohol[3] [4] [6] [10] [12] [14] [20] consists of passing gaseous chlorine into an enameled vessel containing ethyl alcohol. Page[14] states that a large yield is obtained when the alcohol used for the preparation of chloral is treated with a five per cent solution of ferric or thallium chloride previous to the introduction of chlorine. The reaction vessel must be fitted with internal coils for heating and cooling and a means provided for distributing the chlorine throughout the alcohol. The operation requires about five days. During the first day, chlorine is passed into the alcohol at 20 to 25 degrees Centigrade. On the second day the temperature is increased to approximately 50 degrees Centigrade. When the liquid has a specific gravity of 49 degrees Baumé the maximum amount of chloral alcoholate has been formed. The reaction mixture is then cooled and an equal volume of concentrated sulfuric acid is added to release the chloral. By rectification the chloral is separated from the other products formed during the reaction. The side products formed are ethylidene chloride, ethylene chloride, and chloro-ethylene chloride.

Chlorination of Acetaldehyde. Pinner and Kraemer[17] studied the action of chlorine on liquid acetaldehyde. Chlorine was first passed into acetaldehyde, initially cooled in a freezing mixture, and only heated to 100 degrees Centigrade at the end of the reaction. The first few bubbles caused the separation of a small quantity of solid metaldehyde. As the reaction proceeded the evolution of hydrogen chloride

started and every trace of chlorine was absorbed. The reaction was complete at the end of twenty-four hours. The main product distilled over between 163 and 165 degrees Centigrade and proved to be crotonic chloral. Pinner[15] later determined that it was butyl chloral and not crotonic chloral as previously stated. Pinner and Kraemer[17] explained the formation of butyl chloral by the results of Kekulé who showed that acetaldehyde is readily converted into crotonic aldehyde by the action of dehydrating agents of which hydrogen chloride is one. The hydrogen chloride was formed by the action of chlorine on acetaldehyde. Pinner[16] carried out further experimentation with the idea in mind to eliminate the hydrogen chloride as fast as it is formed. To do this he added marble chips to moist acetaldehyde; the greater proportion of the acetaldehyde was oxidized in the presence of the water. Fifty grams of acetaldehyde by this treatment yielded 15 to 20 grams of a distillate bearing the characteristics of chloral.

Wurtz and Vogt[22] concluded that "the reaction of acetaldehyde and chlorine results in the formation of acetyl chloride as the aldehyde grouping is attacked. However, when the aldehyde grouping in acetaldehyde is replaced by $CHCl(OC_2H_5)$, by passing a current of hydrogen chloride into a mixture of absolute alcohol and acetaldehyde, the action of chlorine in the presence of iodine gave rise to $CCl_3CH\begin{pmatrix}OC_2H_5\\Cl\end{pmatrix}$. When heated with water this tetra-chlorinated ether was readily converted to chloral.

$$CCl_3CH\begin{pmatrix}OC_2H_5\\Cl\end{pmatrix} + H_2O \longrightarrow HCl + CCl_3CHO + C_2H_5OH$$

The use of alcohol instead of water yielded hydrochloric acid and tri-

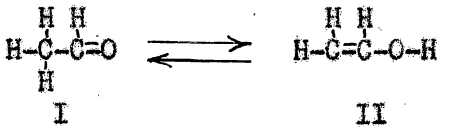
chlor-acetal, $CCl_3CH\begin{pmatrix}OC_2H_5\\OC_2H_5\end{pmatrix}$. The action of sulfuric acid on trichlor-acetal yielded chloral. The tetra-chlorinated ether also gave ethyl chloride and chloral when distilled with sulfuric acid. It is by these successive changes that chloral is formed in the ordinary process for its manufacture; namely, by passing chlorine into ethyl alcohol. The water necessary for the decomposition of the tetra-chlorinated ether results, independently of that which may be present in the alcohol, from the action of hydrogen chloride generated, upon the alcohol and acetaldehyde.

$$CH_3CHO + C_2H_5OH + HCl \longrightarrow CH_3CH\begin{pmatrix}OC_2H_5\\Cl\end{pmatrix} + H_2O$$

The acetaldehyde was formed by the action of chlorine on alcohol, but it did not accumulate as it was at once attacked by the alcohol and hydrochloric acid. From the preceding explanation it should be possible to substitute water for alcohol. Under such circumstances the formation of the compound $CH_3CH\begin{pmatrix}OH\\Cl\end{pmatrix}$ is conceivable. This compound corresponds to monochlorinated ether and may be regarded as the chlorhydrin of ethylidene glycol, $CH_3CH\begin{pmatrix}OH\\OH\end{pmatrix}$. The action of chlorine on such a compound should yield chloral. With this point in mind it is a fact that chloral is readily formed in notable quantity when chlorine is passed into a cooled mixture of acetaldehyde and hydrogen chloride, or even of acetaldehyde and water."

Theory. Williams[21] advances the following theory on the chlorination of acetaldehyde. "The reactions of acetaldehyde with the halogens are rationally explained if acetaldehyde is assumed to be a mixture

of two substances represented below, in equilibrium.

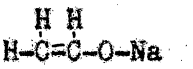


I II

Either substance may change to the other by shifting of a hydrogen atom from carbon to oxygen, or vice versa. Such a change as this may take place spontaneously in both directions maintaining an equilibrium.

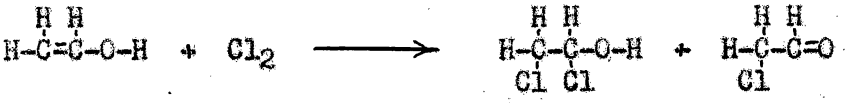
The change from I to II is analogous to that which takes place in the aldol condensation. The C-H bonds in the methyl group are weakened by the influence of the carbonyl group, and an addition to the carbonyl group takes place within the one molecule. The change from II to I consists of an intramolecular addition of an alcohol to a C=C linkage.

Alkali, if present, will react with component II, because of its acidic character, forming the following substance



and this will decrease the amount of component I in the mixture.

If such an equilibrium mixture as has been described is treated with chlorine, the chlorine will be added by component II which has doubly bonded carbon atoms in its structure, because, as has already been noted, addition reactions of this kind are much faster and take precedence over substitution reactions.



When a chlorine atom and a hydroxyl group become attached to the same carbon atom, the combination is unstable and hydrogen chloride

breaks off. This reaction is especially favored by the presence of the alkali which immediately neutralizes the acid. By this reaction there is formed a chlorine-substituted aldehyde, which like acetaldehyde itself should exist in two forms as indicated:

This unsaturated form may then add on another molecule of chlorine, and the formation of dichloro-acetaldehyde. The process may repeat and form trichloro-acetaldehyde. When acetaldehyde is treated with chlorine under these conditions, trichloro-acetaldehyde or chloral is actually formed".

III. EXPERIMENTAL

A. Purpose of Investigation

The purpose of this investigation is:

1. To determine the effect of time, temperature, concentration and catalysis in the vapor phase chlorination of acetaldehyde.
2. To determine the yield and quality of the chlorinated derivatives produced.

B. Plan of Investigation

The plan of this investigation is as follows:

1. A review of the literature will be conducted in order to obtain previous data on the vapor phase chlorination of acetaldehyde.
2. Design and construction of the experimental apparatus.
3. Development of the process to determine the effect of different catalysts on the vapor phase chlorination of acetaldehyde with an increase in temperature and concentration of reactants. A summation of experimental tests to be conducted is as follows:

a. A series of experimental tests will be conducted using the following conditions:

Variants	Non-Variants
Catalyst Concentration of reactants	Total rate of flow of reactants - 100 liters/hr. Time of each test - two hours Pressure - atmospheric Temperature - 30 degrees C.

Test Number	Catalyst	Conc. of reactants (vol%) Chlorine	Acetaldehyde
1	none	67	33
2	none	75	25
3	none	80	20
4	activated carbon	67	33
5	activated carbon	75	25
6	activated carbon	80	20
7	aluminum chloride	67	33
8	aluminum chloride	75	25
9	aluminum chloride	80	20
10	ferric chloride	67	33
11	ferric chloride	75	25
12	ferric chloride	80	20

b. A series of experimental tests will be conducted as in a. above with the exception that the temperature of the test will be increased to 55° Centigrade.

c. A series of experimental tests will be conducted as in a. above with the exception that the temperature of the test will be increased to 80° Centigrade.

d. The experimental test giving the best results in series a., b., and c. above will be used as a basis for making tests with the total rate of flow of reactants increased to 500 liters per hour and 1000 liters per hour.

C. Materials

The following materials were used during the investigation:

Acetaldehyde. Liquid, 99% purity, 30 pounds. Obtained from United States Vanadium Corp., Niagara Falls, N. Y.

Chlorine. Cylinder no. 98, 99.5% purity, 105 lbs., 84 lb/sq.in. (569 cu.ft.). Obtained from Matheson Company, Inc., East Rutherford, N. J.

Sulfuric Acid. C.P., 95.5% (sp.gr. 1.84), lot number 122844. Used in the U-tube differential manometer and in the atmospheric expansion flask. Obtained from the J.T.Baker Chemical Company, Phillipsburg, N. J.

Ammonium Hydroxide. 28% solution. Used for detecting chlorine leaks in the equipment. Obtained from the Chemistry Department Stock Room.

Soy Bean Oil. Refined. Used as a medium in the chlorine preheat bath. Obtained from I.F.Laucks, Inc., Portsmouth, Va.

Sodium Hydroxide. Pellets. C.P., lot no. 82246. Used to prepare a test solution for hydrochloric acid determinations. Obtained from the J.T.Baker Chemical Company, Phillipsburg, N. J.

Potassium Acid Pthalate. Granular, C.P., lot no. 390511. Used to standardize sodium hydroxide solutions. Obtained from the Coleman and Bell Company, Norwood, Ohio.

Methyl Orange. Powder, C.P., Used as an indicator for hydrochloric acid determinations. Obtained from Phipps and Bird Company, Richmond, Va.

Feldspar. Crushed to pass through 8 mesh screen and retained on 16 mesh screen (U.S. standard sieve). Used as an inert filler in the catalyst chamber. It was also used as an extender for the ferric chloride. Obtained from Seaboard Feldspar Company, Moneta, Va.

Aluminum Chloride. Granular, anhydrous, C.P., lot no. 41776. Used as a catalyst for the reaction between chlorine and acetaldehyde. Obtained from Merck and Company, Rahway, N. J.

Ferric Chloride. Sublimed, anhydrous, C.P., lot no. 463957. Used as a catalyst for the reaction between chlorine and acetaldehyde. Obtained from Eimer and Amend Company, New York, N. Y.

Activated Carbon. Granular, size 4x10. Used as a catalyst for the reaction between chlorine and acetaldehyde. Obtained from Cliffs-Dow Chemical Company, Marquette, Mich.

D. Apparatus

The following apparatus was used in the investigation:

Acetaldehyde Bath. A fifty-five gallon drum was cut in half across the vertical axis. Into the bottom of the drum was fitted a 200 watt, 230 volt immersion heater.

Reaction-Gases Condenser. The apparatus used as a condenser for the reaction gases was constructed as shown in drawing no. 1, page 26. The heat exchanger was fabricated from 7mm Pyrex tubing and consisted of ten lengths of 4-foot tubing welded together and bent at an angle of 175° every three feet. The condenser bath was constructed from 24-gauge galvanized iron which was brazed together and placed in a frame of 3/4" angle iron. The size of the bath was 30"x48"x6".

Hydrogen Chloride Absorber. A 4-foot length of 37mm Pyrex tubing placed in the vertical position was used as the hydrogen chloride absorber. Each end of the column was fitted with a no.8 two-hole rubber stopper. Glass marbles 1/2" in diameter were used as packing in the column.

Reactor-A. Pyrex tubing 48mm in diameter and 14 inches long was used as a reactor. Each end of the reactor was fitted with a no.10 rubber stopper. Details of the apparatus are shown in drawing no.2, page 27.

Reactor-B. Pyrex tubing 34mm in diameter and 8 inches long was used in the case of reactor-B. Into each end of the reactor was inserted a no. 8 rubber stopper. A detail drawing of reactor-B is shown in drawing no. 3, page 28.

Chlorine Preheater. The apparatus that was used as the chlorine preheater is shown in detail in drawing no.4, page 29. The heat exchanger was fabricated from six and one-half 4-foot lengths of 7 mm Pyrex tubing that were welded together and bent to fit within the preheat bath. The preheat bath was constructed from a rectangular, five-gallon, galvanized iron can which had been lagged with a ½" layer of asbestos. Into the end of the bath was inserted a 1000 watt, 110 volt automatic heater. The heat transfer medium used was soy bean oil.

Chlorine-Pressure Stabilizer. A 2000 cc, three-necked flask was used as the chlorine-pressure stabilizer. The center neck was fitted with a no.7 one-hole rubber stopper through which was inserted a 3-foot length of 8mm Pyrex tubing one end of which extended to within 1/8" of the bottom. The other end was open to the atmosphere. The flask contained 400 cc of concentrated sulfuric acid.

Manometer. A U-tube differential manometer was constructed in the laboratory from a 2-foot length of 7 mm Pyrex tubing.

Rotameter. Glass, size 1-R, etched scale 0-250mm, drilled out aluminum rotor; used to measure the rate of flow of gaseous acetaldehyde. Obtained from Schutte and Koerting Company, Philadelphia, Pa.

Timer. Precision "Time-it", 100 volts, 60 cycles, tenths of seconds. Used to calibrate the chlorine manometer. Obtained from Precision Scientific Company, Chicago, Ill.

Balance. Triple beam, agate bearings. Used for weight determinations. Obtained from the Chemical Rubber Company, Cleveland, Ohio.

Jar. Cylindrical, Pyrex, Outside diameter 12", height 18", capacity 7 gallons. Used as a bath for the reactor. Obtained from Fisher Scientific Company, Pittsburgh, Pa.

Electric Stirrer. (two) Motor driven, variable speed, rheostat controlled. Used to agitate the oil in the chlorine preheater and the water in the reactor bath.

Oven. Electric drying, 110 volts, 600 watts, range 35 to 180 degrees Centigrade, thermostat controlled, no. 100-2761. Used for drying glassware and catalyst samples. Obtained from Precision Scientific Company, Chicago, Ill.

Automatic Heater. Immersion, stainless steel clad, length of element 12", 115 volts, 1000 watts, maximum rated temperature 350 degrees F., no. 3-589. Used to heat the chlorine preheater. Obtained from American Instrument Company, Silver Springs, Md.

Balance. Analytical, chainweight, dampened, no. 11G3039. Manufactured by Seederer-Kohlbusch Inc., Jersey City, N. J.

Aspirator. (filter pump) Brass, side arm and water outlet serrated. Used to evacuate chlorine and acetaldehyde from the system at the end of a run.

Heater. Immersion, copper clad, 230 volts, 2000 watts, no. 15x831. Used to heat the acetaldehyde bath. Obtained from General Electric Company, Schenectady, N. Y.

Valve. Non-automatic needle, no. 51, constructed from cold rolled steel, silver seat and needle. Used to control the rate of flow of chlorine from the cylinder. Obtained from the Matheson Company, East Ruther-

ford, N. J.

Jar. Narrow neck, soft glass, capacity five gallons. Used to collect the hydrochloric acid formed in the hydrogen chloride absorber.

Three-Necked Flask. Pyrex, 2000cc capacity. Used as a pressure stabilizer for chlorine gas leaving the cylinder.

Tubing. Pyrex, 7mm outside diameter, 5mm inside diameter, 120 feet. Used to pipe the gases through the system. Obtained from Fisher Scientific Company, Pittsburgh, Pa.

Valve. (three) Needle point, 1/2", globe with brass point, cat. no. 120. Used to regulate the flow of chlorine and acetaldehyde through the system. Obtained from the Walworth Company, New York, N. Y.

Fractionation Column. The column was constructed from a 3-foot length of 10mm Pyrex tubing that was welded to a condenser tube two feet long and 10mm in diameter. To the flared end of the condenser was welded a six-inch length of 7mm Pyrex tubing that served as a side arm. The side arm was inserted into a 240mm Liebig condenser. The column was packed with 5mm lengths of 5mm soft glass tubing. The lower part of the column was encased by a four foot length of 25mm Pyrex tubing which had been wrapped with fifty-five feet of no. 24 nichrome wire and then covered with a one-inch layer of asbestos lagging. The upper section of the column was encircled by a one-foot length of 37mm Pyrex tubing which served as a dephlegmator.

Beakers, Erlenmeyer Flasks, Liebig Condensers, Clamps, "Tygon" Tubing, Thermometers, and various Assorted Glassware was obtained from the Chemical Engineering Department Stock Room.

E. Method of Procedure

Calibration of U-Tube Differential Manometer

The rate of flow of chlorine through the orifice of the manometer was determined by the water displacement method. The calibration was conducted at 25°C. at which temperature the solubility of chlorine in water is 0.64%[1].

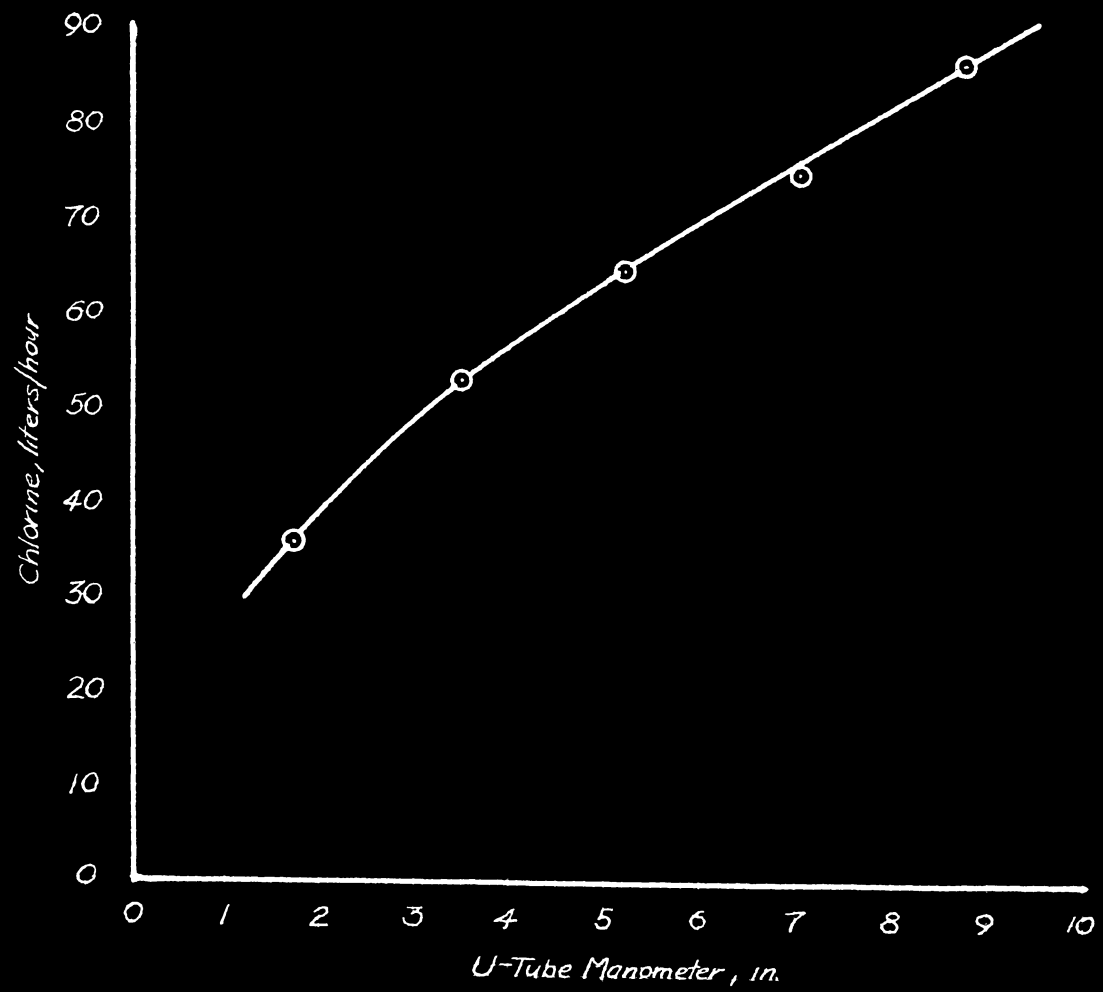
The following procedure was used for the calibration of the U-tube differential manometer:

1. The manometer was filled with 95.5% sulfuric acid to the zero mark on the manometer scale which was graduated in tenths of inches.
2. The orifice was cleaned with acetone and inserted between the legs of the manometer.
3. The needle valve attached to the cylinder was opened and the system allowed to fill with chlorine, and reach a constant pressure differential between the level of sulfuric acid in each leg.
4. The pressure differential was adjusted to the desired level. Differences between the levels in the manometer legs were tested at 2, 4, 6, 8, and 10 inches.
5. When the pressure differential had reached a constant level a liter of chlorine-saturated water was displaced from a volumetric flask. The time required for the displacement was recorded.

A calibration graph for the chlorine manometer is shown in figure 1, page 19.

FIG. 1

Calibration Curve
for
U-Tube Manometer
U-Tube Manometer-in. Vs. Chlorine-liters/hour



Calibration of Rotameter

The rate of flow of gaseous acetaldehyde through the rotameter was measured by condensation in the reaction-gases condenser and a weight determination of the liquid acetaldehyde collected at the end of one hour.

The procedure used for the calibration of the rotameter was as follows:

1. The outlet end of the rotameter was connected directly to the reaction-gases condenser which had an erlenmeyer flask of known weight attached to its outlet end. The erlenmeyer flask was immersed in a water bath maintained at 15°C. The temperature of the water in the reaction-gases condenser bath was constant at 10°C.
2. The liquid acetaldehyde container was heated in a water bath, maintained at 30°C., for one hour prior to the time when the calibration was conducted.
3. The gate valve and the needle valve attached to the acetaldehyde container were opened and the system filled with acetaldehyde, and the rotor was allowed to reach a constant reading on the etched scale of the rotameter.
4. The height of the rotor was adjusted to the desired level. The rotor was tested at levels of 10, 50, 100, 150, and 200 millimeters.
5. The liquid acetaldehyde that was collected at the end of each test was weighed and converted to a volume basis. A calibration chart for the rotameter is shown in Figure 2, page 21.

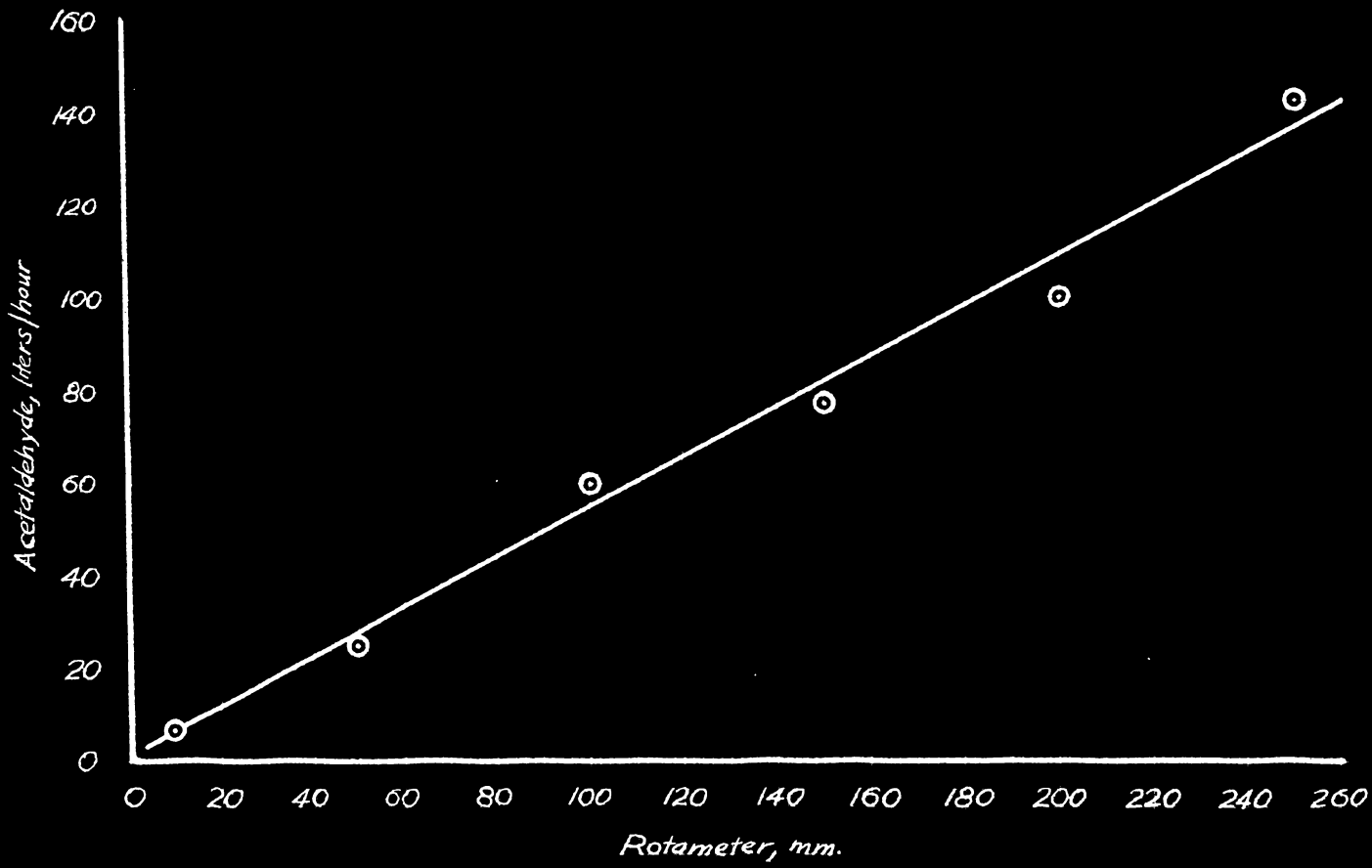
FIG. 2

Calibration Curve

for

Rotameter

Rotameter-mm. Vs. Acetaldehyde-liters/hour



Procedure for Flow of Gases Through System

The chlorination apparatus was constructed from glassware and metallic equipment using "Tygon" tubing for connections and was supported by iron ring stands.

The chlorine from the cylinder passed through a special needle valve and then through 7mm Pyrex tubing into the pressure stabilizer which smoothed out small pressure changes from the cylinder.

The outlet end of the pressure stabilizer was connected to the U-tube differential manometer which measured the rate of flow of chlorine through the system.

From the manometer the chlorine gas was piped through 7 mm Pyrex tubing into the chlorine preheater. The soy bean oil bath was agitated by an electric stirrer and contained a thermometer for temperature measurement.

The outlet end of the chlorine preheater was connected to 7mm Pyrex tubing which piped the chlorine into a thermometer well at which point the temperature of the chlorine gas was measured.

From the thermometer well the chlorine passed into the reactor where it met the incoming acetaldehyde.

The acetaldehyde, in the liquid state, was contained in a galvanized iron drum which had a capacity of thirty pounds. The drum was immersed in a constant temperature water bath kept at 30°C. The gasified acetaldehyde was controlled by a 1/4" needle valve into 7mm Pyrex tubing through the rotameter which was used to measure the rate of flow of gaseous acetaldehyde through the system.

The outlet end of the rotameter was connected to a thermometer well at which point the temperature of the gaseous acetaldehyde was measured.

From the thermometer well the gaseous acetaldehyde passed into the reactor where it met the incoming chlorine.

When reactor-A was used in the system the reactants were brought together by a ring-bulb method. The chlorine was released into the reactor through eight small holes that were spaced 45° apart along the inner circumference of a ring fabricated from 7mm Pyrex tubing. The ring was placed perpendicular to the vertical axis of the reactor. The acetaldehyde entered the reactor from a bulb, 1/2" in diameter, that was positioned inside the annular space of the chlorine ring. The bulb contained eight small holes spaced 45° apart around its circumference that was perpendicular to the vertical axis of the reactor. The incoming gases produced an impinging effect as they entered the reactor.

During the latter stages of the investigation reactor-A was modified and designated as reactor-B. In the case of reactor-B the gases were released into the reactor through 1/2" diameter bulbs, each of which contained eight small holes spaced 45° apart around the circumference of the bulb perpendicular to the vertical axis of the reactor. The bulbs were centered with reference to the vertical axis of the reactor and were spaced two inches apart between centers. The chlorine entered the reactor at the bottom and passed through two inches of catalyst bed before it met the incoming acetaldehyde.

The bottom of the reactor was fitted with a no.10 one-hole rubber stopper that was coupled to a no.5 one-hole rubber stopper by a short

length of 7mm Pyrex tubing. The no.5 one-hole rubber stopper was fitted in a 200cc round-bottom flask that was used to collect the liquid chlorinated derivatives formed in the reactor. The no.10 rubber stopper in the top of the reactor contained the two gas inlet tubes, a thermometer, and a 7mm Pyrex line through which passed the gaseous products of reaction plus the unreacted chlorine and acetaldehyde. The reactor and the attached round-bottom flask were immersed in the reactor bath.

The reaction gases passed out of the reactor through the 7mm Pyrex tubing and into a 250cc erlenmeyer flask fitted with a 2-hole rubber stopper. The flask was used as a trap to collect liquified chlorinated derivatives.

From the trap the gases passed into the reaction-gases condenser. The temperature in the water bath was measured by a thermometer immersed in the top of the bath.

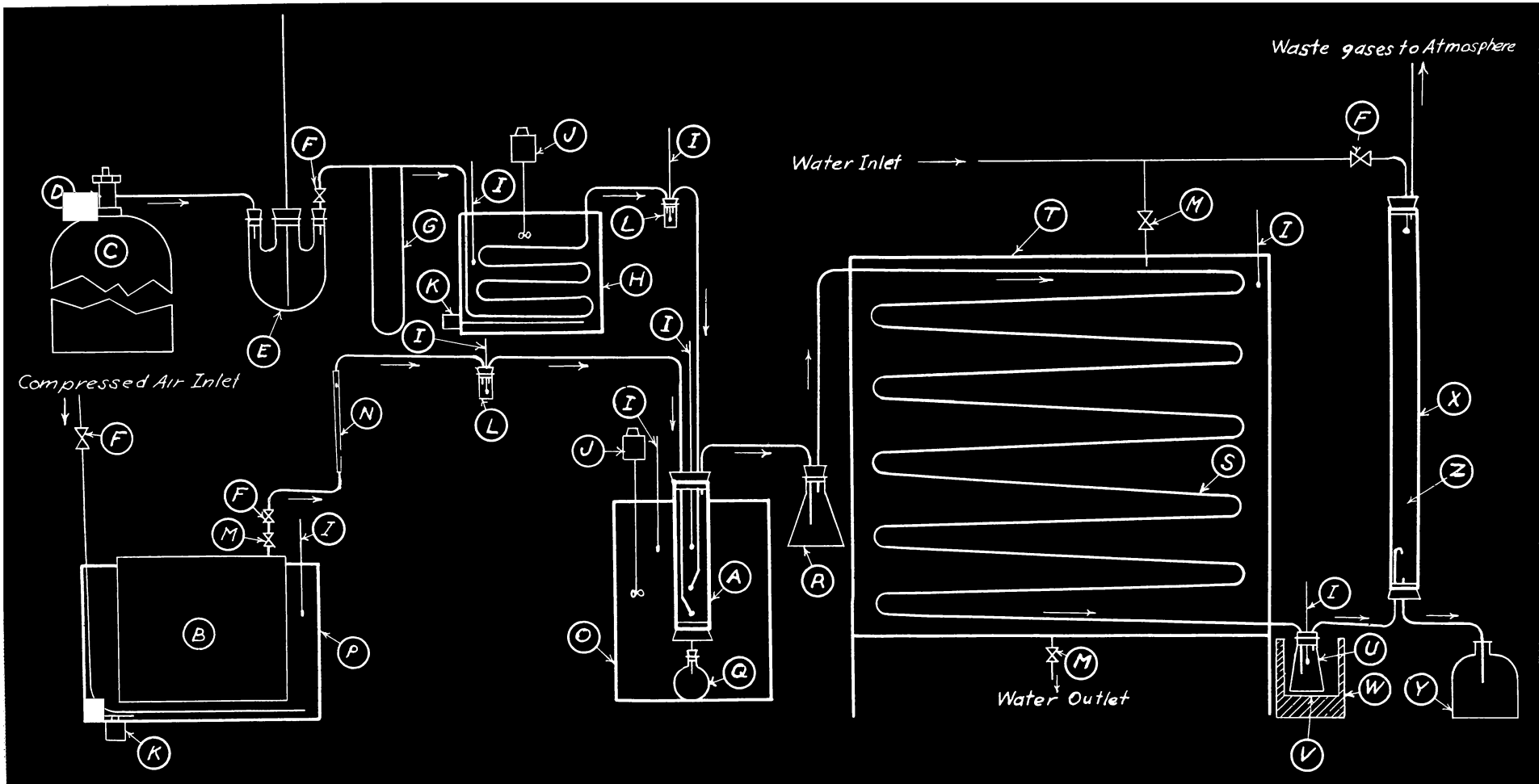
The condensed acetaldehyde, liquid chlorinated derivatives, hydrogen chloride, and the unreacted chlorine flowed into a 250cc erlenmeyer flask which was fitted with a no.7 three-hole rubber stopper. A thermometer was inserted through the stopper and was used to measure the temperature of the gases leaving the condenser.

The unreacted chlorine and the hydrogen chloride formed during the reaction were piped through 7mm Pyrex tubing into the hydrogen chloride absorber.

The hydrogen chloride and the chlorine entered the absorber at the bottom and were met by a stream of water flowing down through the packing. The hydrogen chloride was absorbed by the water, and the resulting hydro-

chloric acid was removed at the bottom of the absorber and collected in a five-gallon glass jar. The undissolved chlorine passed out the top of the absorber and was released to the atmosphere.

A schematic diagram of the chlorination apparatus is shown in drawing no.1, page 26.



— LEGEND —

A - Reactor
B - Acetaldehyde Drum
C - Chlorine Cylinder
D - Special Needle Valve
E - Pressure Stabilizer
F - ¼" Needle Valve
G - Differential Manometer
H - Chlorine Preheat Tank
J - Electric Stirrer
K - Immersion Heater
L - Thermometer Well & Trap
M - ½" Gate Valve
N - Rotameter
O - Reactor Bath
P - Acetaldehyde Bath
Q - Product Receiver
S - Reaction Gases Condenser
T - React. Gases Condenser Bath
U - Condensate Receiver
V - Condensate Rec. Bath
W - Insulated Container
X - Hydrogen Chloride Absorber
Y - Hydrochloric Acid Receiver
Z - Packing - ½" Glass Marbles

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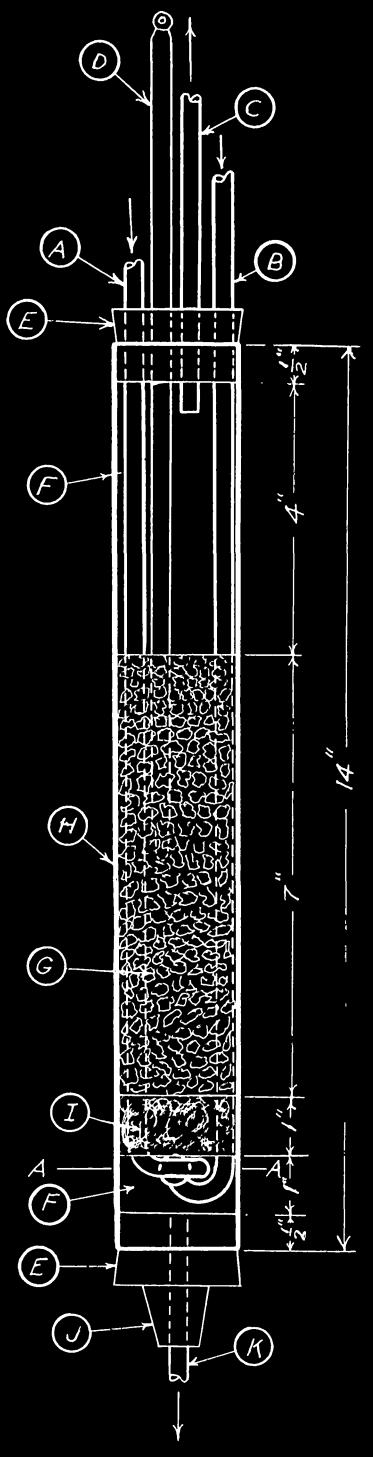
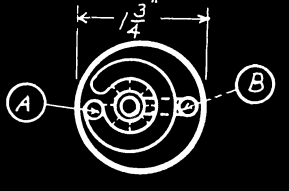
Schematic Diagram
ACETALDEHYDE CHLORINATION APPARATUS

Drawn by: [illegible]	Case: PG	Drawing No: 1
Checked by: F.C.V	File: 539	Scale: None
Approved by: F.C.V	Date: 4-8-47	Figure: 3





Section A-A

— LEGEND —

A - Chlorine Inlet, 7mm. Pyrex
B - Acetaldehyde Inlet, 7mm. Pyrex
C - Reaction Gases Outlet
D - Thermometer
E - No. 10 Rubber Stopper
F - Empty Space
G - Feldspar Filler
H - Pyrex Reactor Tube
I - Glass Wool
J - No. 5 Rubber Stopper
K - Product Drain

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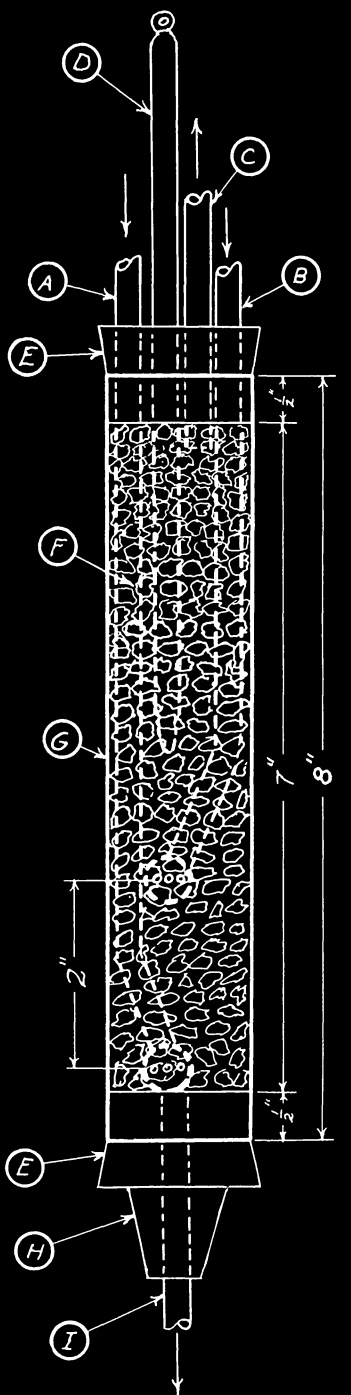
Detail Drawing
REACTOR - A

Drawn by: [illegible]	Case: PG	Drawing No: 2
Checked by: [illegible]	File: 539	Scale: 1" = 3"
Approved by: [illegible]	Date: 4-10-47	Figure: 4



LEGEND

A- Chlorine Inlet, 7mm. Pyrex
B-Acetaldehye Inlet, 7mm. Pyrex
C- Reaction Gases Outlet
D- Thermometer
E- No. 8 Rubber Stopper
F- Catalyst Bed
G- Pyrex Reactor Tube
H- No. 5 Rubber Stopper
I- Product Drain

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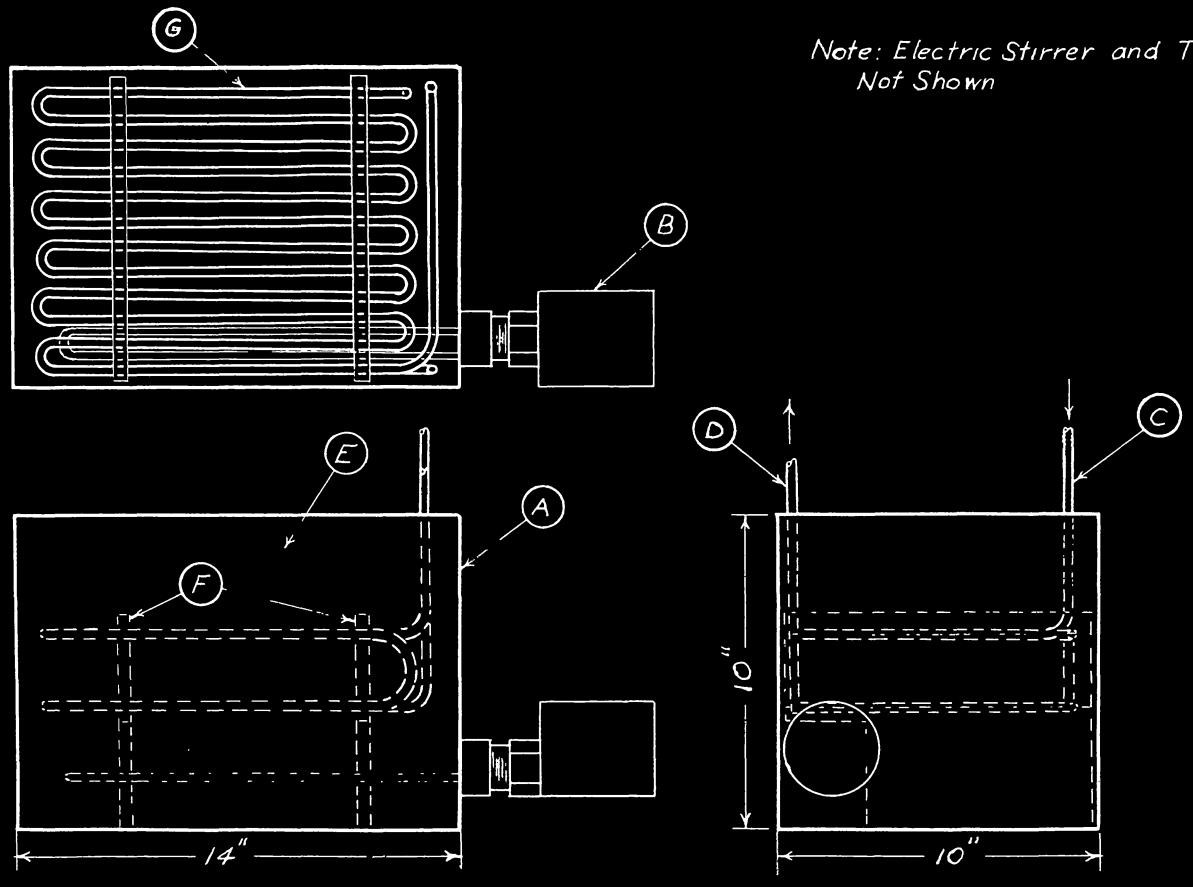
Detail Drawing
REACTOR-B

Drawn by: [illegible]	Case: PG	Drawing No. 3
Checked by: [illegible]	File: 539	Scale: 1" = 2
Approved by:	Date: 4-11-47	Figure: 5



Note: Electric Stirrer and Thermometer Not Shown

LEGEND

A- Rectangular 5 gallon Tank- Lagged with $\frac{1}{2}$" Asbestos
B- Automatic Immersion Heater
C- Chlorine Inlet
D- Chlorine Outlet
E- Soy Bean Oil Medium
F- Supports
G- Heat Exchanger Tubing (26'- 7mm. Pyrex)

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Detail Drawing
CHLORINE PREHEAT TANK

Drawn by: [illegible]	Case: PG	Drawing No: 4
Checked by: F.C.J.	File: 539	Scale: 1" = 6"
Approved by: F.C.J.	Date: 4-12-47	Figure: 6

Chlorination Procedure

The outlined procedure listed below was used for the chlorination of acetaldehyde:

1. The following steps were taken prior to the start of a run:

   a. The acetaldehyde drum was placed in the preheat bath, connected to the system, and preheated to a temperature of 30°C. for one hour prior to the start of a run.

   b. The reactor receiver, trap, and condensate receiver were weighed.

   c. the reactor was filled with 7" of inert filler or catalyst, assembled, weighed on a triple-beam balance, immersed in the reactor bath that was maintained at a temperature of 17°C., and connected to the system.

   d. The reaction-gases condenser bath was filled with process water.

   e. The condensate receiver was immersed in the insulated ice bath and connected to the system.

   f. The water inlet valve on the hydrogen chloride absorber was turned on and adjusted to maintain an approximate rate of flow of one liter of water every five minutes.

2. The chlorine valve at the cylinder was turned on, adjusted to the required rate of chlorine flow measured by the manometer, and the system allowed to fill with chlorine.

3. After the chlorine had been passed through the system for five minutes, the flow of acetaldehyde was adjusted by means of a needle valve

to that required for the run, measured by the rotameter.

4. The following data were recorded, at five minute intervals, during the course of a run:

a. Temperature of the acetaldehyde preheat bath.

b. Reading of the acetaldehyde rotameter.

c. Temperature of acetaldehyde entering the reactor.

d. Reading of the chlorine manometer.

e. Temperature of the chlorine preheat bath.

f. Temperature of chlorine entering the reactor.

g. Temperature of the reactor bath.

h. Temperature within the reactor.

i. Temperature of the gases leaving the condensate receiver.

j. Temperature of the reaction-gases water bath.

k. Room temperature.

5. The following steps were taken at the end of each run:

a. The chlorine valve and the acetaldehyde valve were closed.

b. The water inlet valve into the hydrogen chloride absorber was closed and the volume of absorber water collected during the run was measured.

c. The reactor was removed from the system, the receiver flask detached, and the reactor weighed.

d. The chlorine remaining in the system was removed by a water aspirator that was connected to the condensate receiver.

e. The reactor receiver, trap, and condensate receiver were weighed.

Analytical Procedure

The following analytical procedure was used during the course of the investigation:

Hydrochloric Acid. The amount of hydrochloric acid formed during a run was determined by titrating duplicate 50cc samples of the absorber water with a 0.2305N solution of sodium hydroxide. Methyl orange was used as the indicator.

Chlorinated Derivatives. Separation of the chlorinated derivatives from the acetaldehyde was accomplished as follows:

1. Fractionation. The contents of the condensate receiver, trap, and reactor receiver were poured into a 200cc round-bottom flask which was attached to the bottom of the fractionating column. Heat was furnished to the flask by an electric heater that was placed beneath the round-bottom flask. The water into the Liebig condenser was then turned on. The temperature in the column was controlled by adjusting a variable rheostat that was connected in series with the nichrome winding around the column. The collection of distillate from the column was maintained at approximately 10cc every two minutes by raising or lowering the cooling water level in the dephlegmator.

2. Simple Distillation. The contents of the condensate receiver, trap, and reactor receiver were poured into a 200cc side-neck distilling flask which was fitted with a mercury bulb thermometer whose bulb was even with the exit tube. The distilling flask was immersed in a water bath beneath which was placed an elec-

tric heater. A 400 centimeter Liebig condenser was connected to the side neck of the distilling flask and the distillate was recovered in a 100cc evaporating dish that was immersed in an ice bath.

The fraction distilling over between 10° C. and 50° C. was collected in the evaporating dish, weighed, and allowed to stand exposed to the atmosphere for twelve hours at 25° C., and weighed again. The difference in weight of the evaporating dish before and after the twelve hour exposure period was designated as unreacted acetaldehyde.

F. Data and Results

The experimental data and results obtained from the chlorination experiments are presented as follows:

No-Yield Tests Without a Catalyst

Reactor-A, which contained a 7" filling of feldspar, was used during each of the below mentioned tests.

Chlorination Tests 1a and 2a. For test 1a the chlorine manometer reading was 5.7", the acetaldehyde rotameter reading was 67mm., and the pressure was 711 mm. The conditions for test 2a were: chlorine manometer - 7.0", acetaldehyde rotameter - 50 mm., and the pressure was 723 mm.

As soon as each test was started a flammation was propagated in the reactor. The flammation was propagated in the lower part of the reactor during test 1a and in the upper part of the reactor during test 2a. The instant that the flame occurred in the reactor during each test, the test was stopped for a period of one minute and then turned on again. No further flammation occurred in the reactor for the duration of the tests.

Each test was ended after a period of approximately ten minutes as the rotor in the rotameter became engulfed by a liquid that formed in the metering tube; thereby, preventing the measurement of the flow of acetaldehyde through the system.

By replacing the rubber tubing connections on each end of the rotameter with Tygon tubing the formation of liquid in the measuring tube was eliminated.

Chlorination Tests 1b and 3b. The conditions for test 1b were: chlorine manometer - 5.7", acetaldehyde rotameter - 67 mm., and the pressure reading was 712 mm. For test 3b the chlorine manometer reading was 7.8", the acetaldehyde rotameter reading was 39 mm., and the pressure was 712 mm.

Within a period of three minutes after the tests were started the reactor trap, which was exposed to diffused sunlight, exploded, thereby, ending the tests.

The reactor trap was enclosed with a black cloth bag in test 3c and no explosion occurred; subsequent runs avoided explosions in the reactor trap by this procedure.

Table I

Data Sheet on Chlorination Test No. 2b

Reactor-A
Catalyst - none (7" Feldspar)
Pressure - 712 mm.

Chlorine Manometer - 7.0"
Acetaldehyde Rotameter - 50 mm.

Data:

Time	Temperature								
	Acetaldehyde		Chlorine		Reactor	Reactor	Condenser		Room
	preheat bath	into reactor	preheat bath	into reactor	preheat bath		water bath	exit gases	
(min)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
0	30.5	28.0	42.5	28.5	25.0	27.0	13.5	20.0	27.5
5	30.5	31.5	42.0	30.0	25.0	28.0	13.5	22.0	27.5
10	30.0	31.5	42.0	30.0	25.0	28.0	13.5	23.0	27.5
15	30.0	31.5	41.5	30.0	25.0	30.0	13.5	23.0	27.5
20	30.0	31.5	41.0	30.0	25.0	30.0	13.5	21.0	27.5
25	30.0	31.5	41.0	30.0	25.5	31.0	13.5	21.0	27.5
30	29.5	31.5	40.0	30.0	25.5	32.5	13.5	21.0	27.5
35	31.0	31.5	40.0	30.0	25.5	33.0	13.5	20.0	27.5
40	30.5	31.0	40.0	30.0	25.5	34.0	13.0	20.0	27.5
45	30.5	30.0	40.0	30.0	25.5	34.0	12.0	19.0	27.5
50	30.0	30.0	39.5	30.0	25.5	34.0	11.0	18.0	27.5
55	30.0	30.0	39.0	30.0	25.5	35.0	10.5	18.0	27.0
60	30.0	30.0	39.0	29.5	25.5	36.0	10.0	18.0	27.0
65	30.0	30.0	39.0	29.5	25.5	37.0	10.0	18.0	27.0
70	30.0	30.0	38.5	29.5	25.5	37.0	10.0	18.0	27.0
75	30.0	30.0	38.5	29.5	25.5	37.0	10.0	18.0	27.0
80	30.0	30.0	38.0	29.5	26.0	37.0	10.0	19.0	27.0
85	30.0	29.5	37.5	29.5	26.0	37.0	10.0	19.0	27.0
90	29.5	29.5	37.5	29.5	26.0	38.0	10.0	20.0	27.0
95	30.5	29.5	37.0	29.5	26.0	38.0	10.0	20.0	27.0
100	30.5	29.5	37.0	29.5	26.0	38.0	10.0	21.0	27.0
105	30.5	29.5	37.0	29.5	26.0	38.0	10.0	23.0	27.0
110	30.5	29.5	37.0	29.5	26.0	38.0	10.0	28.0	27.0

Results: A spontaneous flame was propagated in the upper part of the reactor. System was turned off and then on again after a lapse of one minute. No further flammation occurred in the reactor.

Fractionation caused polymerization of the chlorinated derivatives in the column.

The weight of chlorinated derivatives formed during the test was 74.7 grams.

The weight of unreacted acetaldehyde was 63.0 grams.

Table II

Data Sheet on Chlorination Test No. 3a

Reactor-A
Catalyst - none (7" Feldspar)
Pressure - 706 mm.

Chlorine Manometer - 7.8"
Acetaldehyde Rotameter - 39 mm.

Data:

Time	Temperature								
	Acetaldehyde		Chlorine		Reactor	Reactor	Condenser		Room
	preheat bath	into reactor	preheat bath	into reactor	preheat bath		water bath	exit gases	
(min)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
0	30.0	30.0	41.0	28.0	26.0	26.0	9.5	14.0	25.0
5	29.5	31.0	40.5	28.0	26.0	27.5	9.5	15.0	25.0
10	31.0	31.0	40.0	28.0	26.0	28.0	9.5	15.0	25.0
15	31.0	31.0	40.0	28.0	26.0	28.5	9.5	14.0	25.0
20	31.0	31.0	40.0	28.0	26.0	28.5	9.5	14.0	25.0
25	30.5	31.0	39.5	28.0	26.0	29.0	9.5	14.0	25.0
30	30.5	31.0	39.0	28.0	26.0	29.0	9.5	14.0	25.0
35	30.0	30.5	39.0	28.0	26.0	29.0	9.5	14.0	25.0
40	30.0	30.0	38.5	28.5	26.0	29.0	9.5	14.0	25.0
45	30.0	30.0	38.0	28.5	26.0	29.0	9.5	14.0	25.0
50	31.0	30.0	38.0	28.0	26.0	29.0	9.5	15.0	25.0
55	30.5	30.0	37.5	28.0	26.0	29.0	9.5	15.0	25.0
60	30.5	30.0	37.5	28.0	26.0	29.0	9.5	15.0	25.0
65	30.0	29.0	37.0	28.0	26.0	29.0	9.5	15.5	25.0
70	30.0	29.0	27.0	28.0	26.0	29.0	9.5	15.5	25.0
75	30.0	28.5	36.5	28.0	26.0	29.0	9.5	16.0	25.0
80	30.5	28.0	45.0	28.0	26.0	29.0	9.5	16.0	25.0
85	30.0	28.0	52.0	28.5	26.0	29.0	9.5	16.0	25.0
90	30.0	28.0	52.0	29.0	26.0	29.0	9.5	16.5	25.0
95	30.0	28.0	51.5	29.0	26.0	29.0	9.5	17.0	25.0
100	30.0	28.0	51.0	29.0	26.0	29.0	9.5	18.0	25.0
105	30.0	28.0	50.0	29.0	26.0	29.0	9.5	18.5	25.0
110	30.0	28.0	50.0	29.0	26.0	29.0	9.5	18.5	25.0
115	30.0	28.0	49.0	29.0	26.0	29.0	9.5	19.0	25.0
120	30.0	28.0	49.0	29.0	26.0	29.0	9.5	19.0	25.0

Results: A spontaneous flame was propagated in the upper part of the reactor. System was turned off and then on again after a lapse of one minute. No further flammation occurred in the reactor.

Fractionation caused polymerization of the chlorinated derivatives in the column.

The weight of chlorinated derivatives formed during the test was 105.6 grams.

The weight of unreacted acetaldehyde was 35.0 grams.

Table III

Data Sheet on Chlorination Test No. 2c

Reactor-A
Catalyst - none (7" Feldspar)
Pressure - 709 mm.

Chlorine Manometer - 7.0"
Acetaldehyde Rotameter - 50 mm.

Date:

Time	Temperature								
	Acetaldehyde		Chlorine		Reactor	Reactor	Condenser		Room
	preheat bath	into reactor	preheat bath	into reactor	preheat bath		water bath	exit gases	
(min)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
0	30.0	24.0	24.0	25.0	17.5	17.5	10.0	15.0	24.0
5	30.0	32.0	24.0	24.0	18.0	24.0	10.0	21.0	23.0
10	30.0	33.5	24.0	24.0	18.0	26.0	10.0	22.0	23.0
15	30.0	35.0	24.0	24.0	18.5	28.0	10.0	25.0	23.0
20	29.5	35.0	24.0	24.0	19.0	29.0	10.0	19.0	23.0
25	29.5	35.0	24.0	24.0	19.0	30.0	10.0	20.0	23.0
30	30.0	35.0	29.0	24.0	19.5	30.0	10.0	21.0	23.0
35	29.5	34.0	35.0	24.0	20.0	30.0	10.0	21.0	23.0
40	30.5	34.0	35.0	25.0	20.5	30.0	10.0	20.5	23.0
45	30.5	34.0	35.0	25.0	20.5	31.0	10.0	20.0	23.0
50	30.0	34.0	34.0	25.0	21.0	31.0	10.0	20.0	23.0
55	30.0	33.5	34.0	25.0	21.0	31.0	10.0	19.5	22.5
60	30.0	33.5	34.0	25.0	21.5	31.0	10.0	19.0	22.5
65	30.0	33.0	33.0	25.0	21.5	31.0	10.0	19.0	22.5
70	31.0	33.0	33.0	25.0	22.0	30.5	10.0	19.0	22.5
75	30.5	33.0	33.0	25.0	22.5	30.5	10.0	18.5	22.5
80	30.5	33.0	33.0	25.0	22.5	30.5	10.0	18.5	22.5
85	30.5	33.0	33.0	25.0	22.5	30.5	10.0	18.5	22.5
90	30.5	32.5	33.0	25.0	23.0	30.0	10.0	18.5	22.5
95	30.0	32.0	32.0	25.0	23.0	30.0	10.0	18.0	22.5
100	30.0	32.0	32.0	25.0	23.0	30.0	10.0	18.0	22.5
105	30.0	31.5	32.0	25.0	23.5	30.5	10.0	18.0	22.5
110	30.0	31.5	32.0	25.0	23.5	31.0	10.0	18.0	22.0
115	30.5	31.5	32.0	24.5	24.0	31.5	10.0	21.5	22.0
120	30.0	31.5	32.0	24.5	24.0	31.5	10.0	22.5	22.0

Results: A spontaneous flame was propagated in the lower part of the reactor. The flame burned itself out within a period of 3 min.

The weight of chlorinated derivatives formed during the test was 279.6 grams.

The weight of unreacted acetaldehyde was 41.7 grams.

The absorber water collected during the run (30 liters) contained 143.5 grams of hydrochloric acid.

Table IV

Data Sheet on Chlorination Test No. 3c

Reactor-A
Catalyst - none (7" Feldspar)
Pressure - 712 mm.

Chlorine Manometer - 7.8"
Acetaldehyde Rotameter - 39 mm.

Data:

Time	Temperature								
	Acetaldehyde		Chlorine		Reactor	Reactor	Condenser		Room
	preheat bath	into reactor	preheat bath	into reactor	preheat bath		water bath	exit gases	
(min)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
0	30.0	26.5	26.0	27.0	21.5	21.5	9.5	12.5	26.0
5	30.0	34.0	26.0	27.0	22.0	26.0	9.5	12.5	26.0
10	30.0	34.0	26.0	27.0	22.0	29.0	9.5	12.0	26.0
15	30.0	35.0	26.0	27.0	22.0	32.0	9.5	12.0	26.0
20	30.0	35.0	26.0	27.0	22.5	33.0	9.5	12.0	26.0
25	30.0	35.0	26.0	27.0	22.5	39.0	9.5	12.0	26.0
30	30.0	35.0	26.0	27.0	23.0	40.0	9.5	12.0	26.0
35	30.0	35.0	25.5	27.0	23.5	40.0	9.5	12.5	25.5
40	30.0	36.0	25.5	27.0	23.5	36.5	9.5	13.0	25.5
45	30.0	40.0	25.5	27.0	24.0	40.0	9.5	14.5	25.5
50	29.5	40.0	25.5	27.0	24.0	36.5	9.5	15.0	25.5
55	30.0	40.0	25.5	27.0	24.0	36.0	9.5	15.5	25.5
60	30.0	40.0	25.5	27.0	24.0	33.5	9.5	16.0	25.5
65	29.5	40.0	25.5	27.0	24.5	36.0	9.5	16.0	25.5
70	30.0	40.0	25.5	27.0	25.0	35.0	9.5	16.5	25.5
75	30.0	40.0	25.5	27.0	25.0	34.0	9.5	16.5	25.5
80	30.0	40.0	25.5	27.0	25.0	34.0	9.5	16.5	25.5
85	30.0	40.0	25.5	27.0	25.5	34.0	9.5	16.5	25.5

Results: The apparatus was blacked out, but a spontaneous flame was still propagated in the lower part of the reactor. The flame burned itself out within a period of 3 min.

The weight of chlorinated derivatives formed during the test was 110.9 grams.

The weight of unreacted acetaldehyde was 22.8 grams.

The absorber water collected during the run (22 liters) contained 115.5 grams of hydrochloric acid.

Table V

Data Sheet on Chlorination Test No. 1c

Reactor-B
Catalyst - none(7" Feldspar)
Pressure - 712 mm.

Chlorine Manometer - 5.7"
Acetaldehyde Rotameter - 67 mm.

Data:

Time	Temperature								
	Acetaldehyde		Chlorine		Reactor	Reactor	Condenser		Room
	preheat bath	into reactor	preheat bath	into reactor	preheat bath		water bath	exit gases	
(min)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
0	30.0	27.0	26.5	27.0	19.0	19.0	10.0	17.5	26.5
5	30.0	35.0	26.5	27.0	19.0	28.0	10.0	18.0	26.0
10	30.0	35.0	26.5	27.0	19.0	30.0	10.0	17.0	26.0
15	30.0	35.0	26.5	27.0	19.0	30.0	10.0	16.0	25.5
20	30.0	35.0	26.5	26.5	19.0	31.0	10.0	15.5	25.0
25	30.0	34.0	26.5	26.5	19.0	31.0	10.0	15.5	25.0
30	30.0	33.5	26.5	26.0	19.0	30.5	10.0	15.5	25.0
35	30.0	33.0	26.5	25.5	19.0	30.5	10.0	15.5	25.0
40	30.0	32.5	26.5	25.5	19.5	30.5	10.0	15.5	25.0
45	30.0	32.0	26.5	25.5	19.5	30.5	10.0	15.0	25.0
50	30.0	31.5	26.5	25.5	19.5	30.5	10.0	15.0	25.0
55	30.0	31.5	26.5	25.5	19.5	30.5	10.0	15.0	24.5
60	30.0	30.0	26.5	25.0	19.5	30.5	10.0	15.5	24.5
65	30.0	30.0	26.5	25.0	20.0	30.5	10.0	16.0	24.5
70	30.0	30.0	26.5	25.0	20.0	30.5	10.0	16.0	24.5
75	30.0	29.0	26.5	25.0	20.0	30.0	10.0	16.5	24.5
80	30.0	29.0	26.5	25.0	20.0	30.0	10.0	17.0	24.5
85	30.0	28.0	26.5	25.0	20.0	30.0	10.0	17.0	24.5
90	30.0	28.0	26.5	25.0	20.0	30.0	10.0	18.0	24.5
95	30.0	28.0	26.5	25.0	20.0	30.0	10.0	18.0	24.5
100	30.0	27.5	26.5	24.0	20.0	29.5	10.0	19.0	24.0
105	30.0	26.5	26.0	23.0	20.0	29.5	10.0	20.0	21.0
110	30.0	26.0	26.0	23.0	20.0	29.5	10.0	21.0	20.0
115	30.0	26.0	26.0	23.0	20.0	29.0	10.0	22.5	20.0
120	30.0	26.0	26.0	23.0	20.0	29.0	10.0	30.0	19.0

Results: No flammation occurred in the reactor.

The weight of chlorinated derivatives formed during the test was 164.0 grams.

The weight of unreacted acetaldehyde was 45.7 grams.

The absorber water collected during the run (26 liters) contained 67.4 grams of hydrochloric acid.

Table VI

Data Sheet on Chlorination Test No. 2d

Reactor-B
Catalyst - none (7" Feldspar)
Pressure - 708 mm.

Chlorine Manometer - 7.0"
Acetaldehyde Rotameter - 50 mm.

Data:

Time	Temperature								
	Acetaldehyde		Chlorine		Reactor	Reactor	Condenser		Room
	preheat bath	into reactor	preheat bath	into reactor	preheat bath		water bath	exit gases	
(min)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
0	30.0	25.0	24.0	24.0	17.0	17.0	9.0	13.5	24.0
5	30.0	33.0	24.0	24.0	17.0	31.0	9.0	15.0	23.5
10	30.0	34.0	24.0	24.0	17.0	31.5	9.0	15.0	23.5
15	30.0	34.0	24.0	24.0	17.0	32.0	9.0	15.5	23.5
20	30.0	34.0	24.0	24.0	17.0	32.5	9.0	15.5	24.0
25	30.0	34.0	24.0	24.0	17.0	32.0	9.0	15.5	24.0
30	30.0	34.0	24.0	24.0	17.0	32.0	9.0	15.5	24.0
35	30.0	34.0	24.0	24.0	17.5	32.5	9.0	16.0	24.0
40	30.0	34.0	24.0	24.0	18.0	32.5	9.0	17.0	24.0
45	30.0	37.0	24.0	24.0	18.0	30.0	9.0	17.0	24.0
50	30.0	39.0	24.0	24.0	18.0	31.0	9.0	20.0	24.0
55	30.0	39.0	24.0	24.0	18.0	31.5	9.0	21.0	24.0
60	30.0	39.0	24.0	24.0	18.0	31.5	9.0	22.5	24.0
65	30.0	39.0	24.0	24.0	18.0	31.5	9.0	24.0	24.0
70	30.0	39.0	24.0	24.0	18.0	31.5	9.0	25.5	24.0
75	30.0	39.0	24.0	24.0	18.0	31.0	9.0	27.5	24.0
80	30.0	39.0	24.0	24.0	18.0	31.0	9.0	28.5	24.0
85	30.0	38.5	24.0	24.0	18.0	31.0	9.0	29.0	24.0
90	30.0	38.0	23.5	23.5	18.5	31.0	9.0	29.0	24.0
95	30.0	37.5	23.5	23.5	18.5	31.0	9.0	29.0	23.5
100	30.0	37.0	23.5	23.5	19.0	31.0	9.0	28.0	23.5
105	30.0	36.5	23.5	23.5	19.0	31.0	9.0	27.0	23.0
110	30.0	36.0	23.5	23.5	19.0	31.0	9.0	25.5	22.5
115	30.0	35.5	23.5	23.5	19.0	31.0	9.0	25.0	22.0
120	30.0	35.0	23.5	23.5	19.0	31.0	9.0	25.0	21.0

Results: No flammation occurred in the reactor.

The weight of chlorinated derivatives formed during the test was 213.4 grams.

The weight of unreacted acetaldehyde was 18.5 grams.

The absorber water collected during the test (27 liters) contained 127.0 grams of hydrochloric acid.

Table VII

Data Sheet on Chlorination Test No. 3d

Reactor-B
Catalyst - none (7" Feldspar)
Pressure - 720 mm.

Chlorine Manometer - 7.8"
Acetaldehyde Rotameter - 39 mm.

Data:

Time	Temperature								
	Acetaldehyde		Chlorine		Reactor	Reactor	Condenser		Room
	preheat bath	into reactor	preheat bath	into reactor	preheat bath		water bath	exit gases	
(min)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
0	30.0	36.0	26.0	27.0	17.0	17.0	9.5	3.0	25.0
5	30.0	36.0	26.0	27.0	17.0	29.0	9.5	12.0	25.0
10	30.0	36.0	26.0	26.5	17.0	30.0	9.5	10.0	25.0
15	30.0	35.5	26.0	26.0	17.0	31.0	9.5	9.0	25.0
20	30.0	35.0	26.0	26.0	17.0	31.0	9.5	10.0	25.0
25	30.0	34.0	26.0	26.0	17.0	31.0	9.5	10.0	25.0
30	30.0	34.0	26.0	26.0	17.0	30.5	9.5	11.0	25.0
35	30.0	33.0	26.0	26.0	17.5	30.5	9.5	12.5	25.0
40	30.0	33.0	26.0	26.0	17.5	30.5	9.5	14.0	25.0
45	30.0	32.5	26.0	26.0	17.5	30.5	9.5	18.5	25.0
50	30.0	32.0	26.0	26.0	17.5	30.5	9.5	24.0	25.0
55	30.0	31.5	26.0	26.0	17.5	30.0	9.5	30.5	25.0
60	30.0	31.0	26.0	26.0	18.0	30.0	9.5	36.0	25.0
65	30.0	30.5	26.0	26.0	18.0	30.0	9.5	41.0	25.0
70	30.0	30.0	26.0	26.0	18.0	30.0	9.5	44.0	25.0
75	30.0	30.0	26.0	26.0	18.0	30.0	9.5	44.0	25.0
80	30.0	30.0	26.0	26.0	18.0	30.0	9.5	?	25.0

Results: The test was ended when the condensate receiver exploded just prior to the eighty minute reading.

The weight of chlorinated derivatives formed during the test was 59.5 grams.

The weight of unreacted acetaldehyde was 27.6 grams.

The absorber water collected during the test (19 liters) contained 53.6 grams of hydrochloric acid.

No flammation occurred in the reactor during the test.

Table VIII

Summary of Conditions and Results of Chlorination Tests

Test No.	Temp. (°C)	Catalyst used	Rate of flow of reactants: Chlorine (L/hr)	Rate of flow of reactants: Acetaldehyde (L/hr)	Pressure (mm)	Time of test (min)	Acetaldehyde: input (g)	Acetaldehyde: reacted (g)	Acetaldehyde: unreacted (g)	HCl formed (g)	Flammation in reactor	Explosion: trap	Explosion: cond. rec.	Actual prod. formed (g)	Calculated Related Yields: Basis: react. CH_3CHO: mono (g)	Basis: react. CH_3CHO: di (g)	Basis: react. CH_3CHO: tri (g)	Basis: HCl formed: mono (g)	Basis: HCl formed: di (g)	Basis: HCl formed: tri (g)
1a	-----	none	67	33	711	10	-----	-----	-----	-----	+	-	-	-----	---	---	---	---	---	---
2a	-----	none	75	25	723	5	-----	-----	-----	-----	+	-	-	-----	---	---	---	---	---	---
2b	34.1	none	75	25	712	110	114.5	51.5	63.0	-----	+	-	-	74.6	92	133	173	---	---	---
3a	28.8	none	80	20	706	120	66.8	31.8	35.0	-----	+	-	-	105.6	57	82	106	---	---	---
2c	30.0	none	75	25	709	120	124.9	83.2	41.7	143.5	+	-	-	279.6	148	214	279	294	211	175
3b	-----	none	80	20	712	2	-----	-----	-----	-----	-	+	-	-----	---	---	---	---	---	---
1b	-----	none	67	33	712	3	-----	-----	-----	-----	-	+	-	-----	---	---	---	---	---	---
3c	34.3	none	80	20	712	85	47.3	24.5	22.8	115.5	+	-	-	110.9	44	63	82	230	165	147
1c	30.0	none	67	33	712	120	155.1	109.4	45.7	67.4	-	-	-	164.0	194	281	367	145	105	93
2d	31.5	none	75	25	708	120	124.9	106.4	18.5	127.0	-	-	-	213.4	189	272	357	273	194	175
3d	30.5	none	80	20	720	80	44.6	17.0	27.6	53.6	-	-	+	59.5	30	44	57	115	83	74
4	240.0	C.(act)	67	33	705	10	-----	-----	-----	-----	-	-	-	-----	---	---	---	---	---	---
7	-----	$AlCl_3$	67	33	714	5	-----	-----	-----	-----	-	-	-	-----	---	---	---	---	---	---
8	-----	$AlCl_3$	75	25	704	4	-----	-----	-----	-----	-	-	-	-----	---	---	---	---	---	---
10	-----	$FeCl_3$	67	33	708	15	-----	-----	-----	-----	-	-	-	-----	---	---	---	---	---	---

No-Yield Tests With a Catalyst

Reactor-B, which contained a 7" filling of catalyst, was used during each of the below mentioned tests.

Activated Carbon. One test was attempted using anhydrous activated carbon as the catalyst and was designated as test 4. The chlorine manometer reading was 5.7", the acetaldehyde rotameter reading was 67 mm., and the pressure was 705 mm.

No flammation occurred in the reactor during the test; however, the temperature within the reactor rose to 240°C. within a period of ten minutes. Since the apparatus as constructed for the experimental tests was not capable of controlling the temperature within the reactor, the use of anhydrous activated carbon as a catalyst was discarded.

Aluminum Chloride. Tests 7 and 8 were attempted using anhydrous aluminum chloride as a catalyst. For test 7 the chlorine manometer reading was 5.7", the acetaldehyde rotameter reading was 67 mm., and the pressure reading was 712 mm. The conditions for test 8 were: chlorine manometer - 7.0", acetaldehyde rotameter - 50 mm., and the pressure was 712 mm.

No spontaneous ignitions occurred during the course of the tests. During each test it was noticed that as soon as the run was started the aluminum chloride in the vicinity of the acetaldehyde inlet started to change in color from white to brown, similar to phenomena when sublimed anhydrous aluminum chloride comes into contact with water. Within a few minutes that part of the aluminum chloride which had turned brown became an impermeable mass that prevented the passage of the reacting gases

through the reactor. An examination of the brown mass showed that the aluminum chloride also had caused a polymerization of the chloro-derivatives of acetaldehyde.

Ferric Chloride. Test 10 was conducted using anhydrous ferric chloride (sublimed), extended on feldspar, as a catalyst. The chlorine manometer reading was 5.7", the acetaldehyde rotameter reading was 67 mm., and the pressure was 708 mm.

No spontaneous ignitions occurred in the reactor during the test. At the end of fifteen minutes the flow of gases through the reactor was stopped by a plug of black polymer formation in the reactor.

IV. DISCUSSION

A. Discussion of Results

Spontaneous Ignitions in the Lower Section of Reactor-A. The flame which was propagated in the lower section of reactor-A during experimental tests 1a, 2c, and 3c was probably a result of the impinging effect produced when the reacting gases entered the reactor. The reactor was coated with black paint prior to the start of experimental test 3a to determine whether or not the flammation in the lower section of the reactor was caused by a spontaneous photochemical reaction between the entering chlorine and acetaldehyde. With the reactor "blacked out" the spontaneous flammation occurred as it did in the exposed system.

Glasstone[5] states that an increase in the velocity of gaseous molecules striking each other raises the additional energy required for reaction, known as the energy of activation, as a result of interchanges occurring in collisions.

The velocity of chlorine and acetaldehyde at the point of impact was equivalent to 4.7 feet per second. This resultant velocity of the two entering gases was evidently sufficient to increase the energy of activation of the chlorine and acetaldehyde to a level which caused spontaneous ignitions to take place in the reactor at the point of impact of the two entering reactants.

Spontaneous Ignitions in the Upper Section of Reactor-A. Two theories can be presented with respect to the cause of the spontaneous ignitions which took place in the upper section of reactor-A during experimental tests 2a, 2b, and 3a. By upper section is meant that volume at the top of the reactor not occupied by the feldspar filler.

One theory that can be used to explain the above mentioned phenomena relates to photochemistry. During the experimental tests when there was flammation in the upper section of the reactor the chlorination apparatus was located in such a position that only diffused daylight from a northeast window could have provided photochemical effects.

The reactant gases passed through the feldspar bed with a velocity of approximately 4.7 feet per second. Just as soon as the reactant gases left the feldspar bed and entered the upper section of the reactor the velocity of the gases was reduced to approximately 0.06 feet per second. This reduction in the velocity served as a means of increasing the number of collisions between the light-sensitized chlorine and the acetaldehyde at the interface between the feldspar bed and the unoccupied space of the reactor. These collisions resulted in a release of the light energy from the chlorine in the form of heat energy which was sufficient to cause ignition of the inflammable acetaldehyde.

The second theory is based on the formation of static charges. When the reactant gases met, they immediately formed minute particles of the chloro-derivatives of acetaldehyde that appeared in the top section of the reactor as a dense white fog. These particles of chloro-derivatives were heavier than either of the reactant gases; therefore,

they tended to fall towards the bottom of the reactor. However, the velocity of the gases within the feldspar bed was sufficient to carry most of the chloro-derivative particles into the upper section of the reactor where, as described in the first theory, the velocity of the gases was greatly reduced. The tendency then, in the upper section of the reactor, was for the particles of chloro-derivatives to settle towards the interface between the feldspar layer and the upper section of the reactor. As the particles approached the interface, the velocity of the gases leaving the interface was sufficient to lift the particles up and away from the interface; thereby, was initiated a vertical vibrational movement of the particles. This vibrational motion that was set up by the chloro-derivative particles caused a static charge to envelope them. The difference in potential between the slightly ionized gaseous reactants and the charged chloro-derivative particles released the charge on the particles. The release of the charge was sufficient to cause spontaneous ignition in the upper section of the reactor.

Explosions in the Reactor Trap. During experimental tests 1b and 3b the explosion that occurred in the reactor trap within a period of three minutes after the test had been started can be attributed to a photochemical reaction between chlorine and acetaldehyde. The above statement is substantiated by the fact that during experimental test 3c the reactor trap was enclosed by a black cloth bag and no explosion occurred. Furthermore, during all of the tests made subsequent to test 3c there were no explosions in the enclosed reactor trap.

Rate of Flow of the Reactants. During the experimental tests that produced yields of the chloro-derivatives of acetaldehyde; that is, experimental tests 2b, 3a, 2c, 3c, 1c, and 3d, the reaction between chlorine and acetaldehyde was not completed in the reactor. The reaction was continued in the reaction-gases condenser and/or the condensate receiver. This reaction was indicated in all tests by a rise in the temperature of the non-condensed gases leaving the condensate receiver. All of the above mentioned tests were carried out using a total rate of flow of reactants of 100 liters per hour. Due to the fact that the reaction was not completed in the reactor an increase in the rate of flow of reactants to 500 and 1000 liters per hour was not feasible.

Collection of Chloro-Derivatives of Acetaldehyde. The liquid chloro-derivatives that were formed by the reaction between acetaldehyde and chlorine were collected, to a large extent, in the acetaldehyde condensate flask. Prior to conducting experimental tests it was thought that the liquid chlorinated derivatives would be collected entirely in the product flask attached to the bottom of the reactor.

The size of the chloro-derivative particles formed was very minute, approaching colloidal size, and appeared in the system as a mist. The particles were heavier than the gaseous dispersing medium; however, the velocity of the reactant gases through the system was sufficient to eventually carry the particles out of the reactor and into the condensate receiver where a resulting mixture of liquid acetaldehyde and chloro-derivatives was collected.

Separation of Acetaldehyde and its Chloro-Derivatives by Fractionation. The only physical constant available for the three chloro-derivatives of acetaldehyde is the boiling point; therefore, a separation by fractionation was the only method by which the actual extent of chlorination could be determined for each experimental test.

Unsuccessful attempts were made to separate, by fractionation, a mixture of the chloro-derivatives and unreacted acetaldehyde collected during experimental tests 2b and 3a. In each case the separation of the acetaldehyde was accomplished without difficulty, but when the temperature of the vapors in the top of the column reached 85°C. a polymerization took place in both the distilling flask and in the column itself. The polymer was black in color, and its presence prevented further separation by fractionation.

Heilbron[8] states that the di-chloro-derivative of acetaldehyde polymerizes when heated. However, the temperature limitations required for polymerization are not given in the literature.

Interpretation of Yields. The extent to which chlorination substitution occurred in the acetaldehyde molecule during the experimental tests was empirically determined by use of the law of definite proportions. The theoretical weight of each chloro-derivative that could have been formed during an experimental test, assuming 100 per cent conversion, was calculated using the following formulae:

$$CH_3CHO + Cl_2 \longrightarrow CH_2ClCHO + HCl$$

$$CH_3CHO + 2Cl_2 \longrightarrow CHCl_2CHO + 2HCl$$

$$CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO + 3HCl$$

One series of calculations were made using as a basis for the calculations the weight of acetaldehyde that reacted during the experimental test. Another series of calculations were made, when possible, using as a basis the weight of hydrochloric acid formed during the experimental test.

The calculated yields are shown in Table VIII on page 43.

Evaluation of Yields. From the calculations that were made to interpret the yields of chloro-derivatives formed during each of the experimental tests the following postulations can be made:

Greatest yields of chlorinated derivatives were formed when a ratio of three moles of chlorine to one mole of acetaldehyde were combined. However, the composition of the product was predominately the mono-chloro-derivative of acetaldehyde.

A ratio of four moles of chlorine to one mole of acetaldehyde produced a lower yield of product, but at the same time the product that was formed had a composition which indicated that it was mostly the tri-chloro-derivative of acetaldehyde.

Corrosive Nature of the Gaseous Reactants and the Chloro-Derivatives of Acetaldehyde. During the experimental work it was found that gaseous acetaldehyde reacted with rubber tubing and caused the rubber tubing to become hard and brittle within a short period of time.

The liquid chloro-derivatives of acetaldehyde were very corrosive to rubber, cork, and tin foil.

Tygon tubing was satisfactorily used for connections on the Pyrex glass tubing carrying chlorine, gaseous acetaldehyde, liquid acetaldehyde,

and the liquid chloro-derivatives of acetaldehyde.

B. Recommendations

The following recommendations are suggested for additional research on the vapor phase chlorination of acetaldehyde:

Reactor Design. The reactor should be constructed to alleviate the removal of the heat of reaction as it forms in the reactor. One method that can be used to accomplish the removal of heat from the reactor is the injection of an inert gas, such as carbon dioxide, into the reactor.

Catalyst. Since positive catalysts caused the formation of polymers or excessive temperatures in the reactor, it is recommended that a negative catalyst be used either with or without the aid of ultraviolet light.

Separation of Chlorinated Derivatives. The use of vacuum distillation as a means of separating the three chloro-derivatives of acetaldehyde should be attempted as a possible method to prevent polymerization of the chloro-derivatives which occurred during fractionation.

V. CONCLUSIONS

The following conclusions can be enumerated as a result of this investigation:

1. When the reactant gases were allowed to strike each other directly on entering the reactor, with a resultant velocity of 4.7 feet per second, a flammation occurred in the reactor.

2. At velocities below 4.7 feet per second a flammation occurred when the reactant gases were exposed to diffused daylight.

3. The reaction between acetaldehyde and chlorine was not completed in the reactor when the rate of flow of reactants was 100 liters per hour.

4. An explosion occurred in the condensate receiver when the temperature of the exit gases from the reaction-gases condenser rose above 44°C.

5. During the fractionation the chloro-derivatives of acetaldehyde formed a black polymer at temperatures above 85°C.

6. The use of anhydrous aluminum chloride as a catalyst was unsatisfactory. The formation of a polymer in the reactor prevented the reactant gases from passing through the reactor.

7. Anhydrous ferric chloride (sublimed), extended on a feldspar filler, was unsatisfactory as a catalyst for the reaction between acetaldehyde and chlorine. The formation of a black polymer in the reactor prevented the reactant gases from passing through the reactor.

8. The use of anhydrous activated carbon as a catalyst caused the temperature in the reactor to rise to 240°C. It was not possible to

affect a removal of the heat from the reactor with the apparatus that was used.

9. At approximately 30°C. a ratio of three moles of chlorine to one mole of acetaldehyde produced the greatestyields of the chloro-derivatives of acetaldehyde, but the mono-chloro-derivative was formed in excess.

10. At approximately 30°C. a ratio of four moles of chlorine to one mole of acetaldehyde produced a lower yield of the chloro-derivatives of acetaldehyde; however, the formation of the tri-chloro-derivative of acetaldehyde was predominant.

VI. SUMMARY

The insecticide dichloro-diphenyl-trichloroethane, commonly known as DDT, is synthesized by the condensation of chlorobenzene with chloral. The chloral consumed each month now averages over 1,300,000 pounds. Chloral is produced commercially by the chlorination of ethyl alcohol which is essentially a batch process. It is also possible to produce chloral by the liquid phase chlorination of acetaldehyde. Since both acetaldehyde and chlorine are gases at room temperature the possibility of producing chloral continuously by the vapor phase chlorination of acetaldehyde warrants investigation.

The purpose of this investigation was to determine the effect of time, temperature, concentration and catalysis in the vapor phase chlorination of acetaldehyde and to find the yield and quality of the chlorinated derivatives produced.

The chlorination apparatus was constructed from glassware and metallic equipment. The chlorine gas passed through a pressure stabilizer, that smoothed out small pressure changes from the cylinder and then into a manometer where the rate of flow was measured. From the manometer the chlorine gas passed through a heat exchanger where it was preheated prior to entry into the reactor. The acetaldehyde was preheated in a water bath and then allowed to flow into a rotameter where the rate of flow was measured prior to its entry into the reactor. During the course of the experimental stage two different reactors were used. In one reactor, 51 mm in diameter and 14" long, the gases entered the system through a ring-

bulb arrangement located at the bottom of the reactor. The other reactor, 34 mm in diameter and 8" long, contained two perforated glass bulbs placed one above the other and two inches apart. The bottom of the reactor was fitted with a flask used to collect the chloro-derivatives that formed. The reaction gases, unreacted acetaldehyde and chlorine, and the hydrogen chloride formed during the reaction passed out the top of the reactor, through a trap, and into a heat exchanger which served to condense the gaseous acetaldehyde. The liquified acetaldehyde plus the chlorinated derivatives were collected in a flask placed at the outlet end of the heat exchanger. The gaseous chlorine and hydrogen chloride entered a hydrogen chloride absorber where the hydrogen chloride was absorbed by a countercurrent flow of water and the chlorine allowed to flow into the atmosphere.

A series of experimental tests were made at approximately 30°C.; chlorine to acetaldehyde ratios of 2 to 1, 3 to 1, and 4 to 1; holding constant the time of each test, the pressure, and the total rate of flow of reactants. Experimental tests were made as above with the following catalysts: activated carbon, aluminum chloride and ferric chloride.

The results of this investigation indicated that when the reactant gases were allowed to strike each other directly on entering the reactor, with a resultant velocity of 4.7 feet per second, a flammation occurred in the reactor. At velocities below 4.7 feet per second a flammation occurred when the reactant gases were exposed to diffused daylight.

The reaction between acetaldehyde and chlorine was not completed

in the reactor, but continued in the reaction-gases condenser and/or the condensate flask, when the rate of flow of reactants was 100 liters per hour. An explosion occurred in the condensate flask when the temperature of the exit gases rose above 44°C.

Attempts to separate the chloro-derivatives by fractionation were unsatisfactory as the chloro-derivatives formed a black polymer at temperatures above 85°C.

The use of anhydrous aluminum chloride and ferric chloride as catalysts was unsuccessful. In each case a polymer was formed in the reactor which prevented the reactant gases from passing through the reactor. When anhydrous activated carbon was used as a catalyst the temperature in the reactor rose to 240°C. It was not possible to remove the heat of reaction from the reactor with the apparatus that was used.

At approximately 30°C.; a ratio of three moles of chlorine to one mole of acetaldehyde produced the greatest yields of the chloro-derivatives of acetaldehyde, but the mono-chloro-derivative was formed in excess; a ratio of four moles of chlorine to one mole of acetaldehyde produced a lower yield of the chloro-derivatives of acetaldehyde; however the formation of the tri-chloro-derivative of acetaldehyde was predominant.

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