# THE DESIGN OF A PLANT FOR THE COMMERCIAL PRODUCTION OF A PESTICIDAL DERIVATIVE OF CHLORAL HYDRATE

by

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# I. INTRODUCTION

In 1874, Zeidler(37) condensed chloral with chlorobenzene to give dichloro-diphenyl-trichloro-ethane (DDT) but more than sixty years passed before the insecticidal properties of DDT were discovered by a Swiss chemist, Muller. In 1939, having been made available to the Swiss farmers to combat the Colorado potato beetle, DDT saved the crop from the insects and was hailed as a pesticide superior to any other in use at that time.

The accomplishments of DDT, used by the U. S. Army during World War II, to control flies, lice and other disease-bearing insects are well known. It is, however, by no means a universal insecticide as it has shown no particular promise against the red spider, cotton boll weevil, Mexican bean beetle and certain plant lice(30).

Since chloral is an excellent pesticide in its own right and chlorobenzene has no pesticidal qualities, it is felt that if chloral were condensed with a compound having proven insecticidal properties, the product would be an insecticide superior to DDT. The chlorinated benzene having the most outstanding pesticidal qualities is para-dichlorobenzene, which for many years has been effectively used to combat the peach tree borer, the sugar cane grub and many other agricultural pests.

The object of this study is to design a commercial plant for the production of a pesticide formed by the condensation of para-dichlorobenzene with chloral.

## II. LITERATURE REVIEW

The product to be manufactured is to be a new one on the market and there is no published information on the subject. However, it is reasonable to assume that the reaction will be similar to that for the production of DDT and that similar problems will be encountered. For that reason, a great deal of the literature reviewed dealt with the manufacture of DDT. The new product will be competitive to DDT and for that reason the production data for DDT will be used in the absence of any for 2,2 bis(2,5 dichlorophenyl)-1,1,1 trichloroethane (hereafter referred to as BDT).

Production of DDT:- DDT, abbreviated form of dichlorodiphenyl-trichloroethane, was first used on a large scale as an insecticide by the Swiss in 1939, when their potato crop was threatened by the imported Colorado potato beetle. The Geigy Co., who had been experimenting with the use of DDT as a pesticide, made sufficient quantities of the DDT available to the Swiss Government to check the beetle menace.

History:- DDT was first synthesized by O. Zeidler, a German chemistry student, in 1874. The discovery was made while doing routine experimental work in connection with a thesis he was preparing. Following Zeidler's(41) description in 1874 of its synthesis, no further mention of DDT is found in the literature until 1942. In that year a British patent was issued(15) which states that p.p-dichlorodiphenyltrichlorethane may be produced as follows(30):

"225 parts of chlorobenzene are mixed with 147 parts of chloral or the corresponding amount of chloral hydrate and then 1000 parts of sulfuric acid monohydrate are added. Whilst stirring well the temperature rises to 60°C. and then sinks slowly down to room temperature, the mass then containing solid parts. It is poured into a great deal of water, whereupon the product separates in solid form. It is well washed and crystallized from ethyl alcohol forming fine white crystals, having a weak fruit-like odour."
This patent was assigned to J. R. Geigy A.-G.

The pesticidal qualities of DDT were first discovered in 1939 by Paul Muller a research chemist for J. R. Geigy of Basle, Switzerland. Later that year, Geigy supplied a test quantity of material to Dr. R. Weismann for use in experiments designed to find an effective agent to control the Colorado potato beetle which was menacing the Swiss potato crop.

Soon after this, Geigy research workers discovered the efficiency of this product for louse control. The

DDT manufactured by the J. R. Geigy Co., was known by the trade name "Gesarol", and an extension of "Gesarol" on inert talc was marketed under the trade name "Neocide".

The history of the manufacture of DDT in the United States by the Geigy Co. is more fully explained by a report issued by their New York office. Extracts of that report follow(5);

Production Difficulties:- "The product never had been manufactured commercially in the United States, therefore a difficult production problem arose. This was solved in an amazingly short time by the Cincinnati Chemical Works at Norwood, Ohio. They began in May, 1943 to manufacture DDT without contract or letter of intent. Until the first of 1944, the Cincinnati Chemical Works was the only maker of DDT in the United States. Since January 1st, three other companies have produced DDT and have accounted for 40 percent of total production; Cincinnati alone producing 60 percent. Expediting by the War Production Board of much needed machinery aided greatly the early mass production of the product.

"Geigy, through the Cincinnati Chemical Works, was almost solely responsible for the louse powder which conquered the typhus epidemic in Naples, and the Cincinnati Chemical Works has been by far the largest producer of DDT up to this moment. Many thousands of pounds of its product have been flown and shipped to various battle fronts. Up to date, the quantity manufactured in the Cincinnati Chemical Works has been sufficient to protect over 50,000,000 individuals against typhus for one month. During last January there were in the Naples area alone several million applications, this 'Neocide' dusting procedure having since been shown in newsreels throughout the United States."

Laboratory Synthesis of DDT:- The original laboratory synthesis of DDT was made by O. Zeidler(41) in 1874. His method consists of reacting one volume of chlorobenzol with two volumes of chloral hydrate in the presence of four to five volumes of concentrated sulfuric acid as a condensing agent. This mixture is digested and agitated intermittently while warming on a water bath. When the separation of the white mass is complete, a large amount of water is added and the separating oil is washed with water and crystallized from hot ether-alcohol mixture.

In 1944, Iris and Leyva published the following method for preparation of DDT(17):

"To 16.4 grams of chloral hydrate (0.1 mole) in 50 grams of concentrated sulfuric acid (d. 1.84), is added 20 grams of fuming sulfuric acid (8-10% $SO_3$). The mixture is cooled to 2° C. by immersion in ice and is stirred constantly while adding 22.4 grams of chlorobenzene (0.2 mole) drop by drop at a rate of 15 drops per minute. A pale green-yellow emulsion forms and at the end of the addition the mixture is heated to 75° C. for 2 hours; then cooled on ice. On standing, an oily layer separates and solidifies in the form of a gummy mass, clear gray in color. This layer is separated from the lower sulfuric acid layer, and washed free of acid, allowed to solidify in air, then washed with 10% NaOH, followed by water till neutral, and dried. The product is dissolved in 96% ethyl alcohol, 3 grams of animal charcoal added, and the mixture refluxed for two hours at 75° C. and filtered. On cooling the filterate, the product separates in the form of small white needles of silky brilliance, melting point 107° C.; yield 10 grams. Dilution of the alcohol, by pouring into water, forms a white emulsion which separates with the precipitation of white DDT crystals in time; yield 20 grams."

S. F. Darling(10), in 1945, gives the following laboratory procedure:

"DDT is obtained in 50 grams yield (70% of theoretical) by adding successively 350 grams of 95% sulfuric acid, 50 grams of 20% oleum, 45 grams (0.2 mole) of chlorobenzene, and 34 grams (slightly over 0.1 mole) of chloral hydrate with constant stirring for 1.5 hours. The crude product on crystallization from 500 ml. boiling water has a melting point of 90° C., but may be recrystallized from ethyl alcohol to give the pure product with a melting point of 108° C."

Brothman Continuous Process for Production of DDT(6):- The materials used for the production of DDT are chlorbenzol, oleum, and chloral, with an excess of chlorobenzol being used. The proper amounts of the reactants are fed by metering pumps into the first reactor where a condensation reaction takes place to produce dichloro-diphenyl-trichloro-ethane, its isomers and polymers.

Condensation vessels are in series and have equal capacities. All use turbine mixer agitation and are provided with internal coils to maintain the reaction temperature. Overall yield, based on chloral, is 95% of a DDT mixture having a minimum setting point of 88° C.

When the reaction is completed, the emulsion passes into a settling tower where the oleum separates out. This is a chemical stoneware tower designed for a 1-in. per min. descent rate for the heavier particles in the feed and a hold-up time of 120 min.

DDT liquor is then scrubbed with water to remove any mechanically-entrained oleum. This scrubbing occurs in the second settling column and consists of both parallel and counter-current washing.

A third column provides for final neutralization of the entrained acid by washing with a soda ash solution in a manner similar to that used for washing with water.

A fourth settling tower gives the neutralized DDT a final water wash.

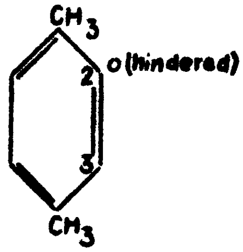
The chlorbenzol solvent is removed from the DDT by vacuum distillation in a stripping still at 35 mm. absolute pressure and 221° F. The temperature is maintained at 221° F. in order to keep the DDT mass, now stripped of its solvent, in a liquid state.

The molten DDT from the stripper still contains approximately 0.195 lb. of chlorbenzol per 5.5 lb. of DDT which is removed by distillation in an air flush still similar in design to the chlorbenzol stripper.

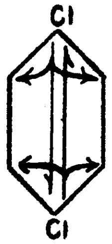
Molten DDT now free of chlorbenzol is run to a flaker, consisting of a heated trough through which a chilled drum rotates at 4.5 r.p.m. The DDT is chilled to 186° F., solidifies on the drum and is flaked off.

Production of DDT Using Chlorosulfonic Acid(31):- Technical-grade DDT in 77% yield is produced by the reaction of chlorosulfonic acid with chloral hydrate and chlorobenzene. The process is carried out with the metathetical quantity of chlorosulfonic acid on chloral hydrate and chlorobenzene. The optimum conditions are a reaction time of 14 hours at a temperature of 20° C. This process is not entirely competitive with the Brothman process but holds several advantages for the smaller manufacturer. Condensation is carried out in the presence of a minimum of acid and an almost equivalent amount of DDT per unit reactor space is produced even when inert solvents are employed.

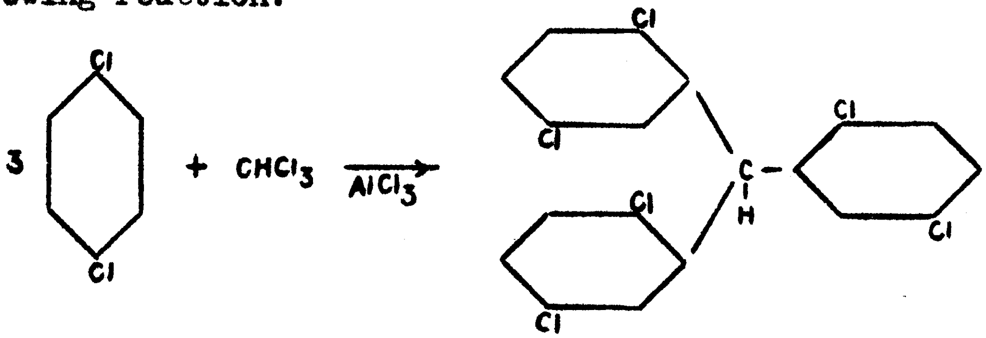
Production of BDT:- There is no reference in literature to the condensation of para-dichlorobenzene with chloral hydrate but there is evidence that such a reaction is practical. Using p-xylene as an example, Fieser$^{(12)}$ states that the position available for substitution is the number 3 carbon as the number 2, or the position ortho to the number 1 methyl group, is hindered.



The number 3-position is ortho-activated and is only moderately hindered, therefore the substitution will take place there. Fieser states there is very little difference between the methyl and halogen substitution groups so a comparison is possible. Both the methyl and chlorine groups are ortho-para directing and the directive influence would be as follows:



Since, regardless on which carbon the condensation takes place, it will still bear the same relationship to the two halogen components, there will be only one product formed and no isomers or products to complicate the reaction. Wilson and Cheng(39) condensed para-dichlorobenzene with chloroform in a Friedel-Crafts synthesis to give the following reaction:



Twenty-six grams of p-dichlorobenzene was condensed with 7 grams of chloroform in the presence of 10 grams of aluminum chloride. The temperature was kept at 55-60° C. and the reaction time was 8 hours. This reaction definitely shows that condensation will take place using para-dichlorobenzene.

The production of BDT will take place in two steps, the first of which is the production of chloral and the second is the actual production of the BDT.

<u>Production of Chloral</u>:- Chloral was first prepared in 1832 by Liebig(21) whose method is still in general use today. He prepared chloral by bubbling chlorine through an aqueous solution of ethyl alcohol. A. J. Hale(16) gives an account of the reaction as follows:

"Chloral is produced by the chlorination of alcohol in enamelled vessels. The vessel must be fitted with internal coils for heating and cooling and with chlorine distributing tubes. The operation requires about five days. The first day chlorine is passed in at 20-25° C., the second day the temperature is raised to 50° C., and during the next two or three days is gradually raised to 95° C. When the liquid has a specific gravity of 49°Be'., the maximum amount of chloral alcoholate has been formed. The mixture is cooled and an equal volume of concentrated sulfuric acid is added. Upon distillation, the chloral distills over at about 90° C."

An improvement upon this process is described by Thorpe(35):

"Chloral and its hydrate are the most volatile products of the action of chlorine on alcohol and may therefore be removed by continuous distillation. Chlorine and chlorinated alcohol are introduced into a vessel heated in a water bath from which the vapors pass into a second and then into a third heated vessel. The residual chlorine is absorbed in a cylinder provided with baffle plates. The rectifier is fed at the middle with chloral hydrate or alcoholate and at the top with 60° Be', sulfuric acid. The condensed vapor is rectified a second time with the portion coming over above 94° C. being pure chloral."

The Brothman continuous process(6) also manufactures chloral by the chlorination of ethyl alcohol, using as raw materials 95% ethyl alcohol, chlorine gas, 36% hydrochloric acid, iron, and 96% sulfuric acid. The alcohol is chlorinated to chloral alcoholate using iron chloride, prepared by dissolving the iron in the hydrochloric acid, as catalyst. The chlorinators consist of a bank of three reactors, the first two designed for a working capacity of 1395 gal. and the last for 2,140 gal. Alcohol is fed continuously to the reactors and chlorination is controlled in the first two chlorinators to yield a produce of a prescribed specific gravity. Water is added to the last unit to liberate alcohol from chloral alcoholate and to form chloral hydrate.

The flow of chlorine is countercurrent to the flow of the alcohol and agitation is attained by the use of gas-lift and draft-tube assemblies. Chlorine for the third reactor is drawn from a recycle line off the vapor section of the first reactor, the second reactor draws its chlorine from the third reactor, and the first reactor from the second. Free chlorine is fed into the last reactor and is regulated by automatic feed control. The bank is designed to give 60% yield of chloral from alcohol.

The chlorinators are vertical tanks of mild steel plate lined with a single course of 4.5-in. chemical brick backed up with a 0.375-in. Pyroflex layer. All have chemical stoneware open top draft tubes with Karbate gas-diffuser elements to produce 5 hp. gas lift agitation in the first two units and 7.5 hp. in the third. Temperature is controlled by passing steam through internal coils.

Chlorinated "oil" from the last chlorinator contains free chloral, chloral alcoholate, excess alcohol, ethylidene dichloride, ethyl chloride, trichloracetal and resinous matter. In the acidulator, this "oil" is mixed with 96% sulfuric acid which completes the freeing of chloral from chloral alcoholate. The acidulator retains 95% of the influent stream for at least one hour.

From the acidulator the liquid is sent to fractionating columns to remove side reaction impurities. The first column separates chloral from the high-boiling constituents and by using a high reflux ratio maximum mole fraction of 0.006 of "high boilers" is left in the bottoms.

Chloral mixed with trichloroacetal and resinous material is fed to the second fractionating column which, by using a comparatively low reflux ratio, makes virtually a quantitative separation of chloral. The chloral is sent to a surge tank located between the chloral and the DDT units.

The fractionating columns consist of chemical stoneware sections and are packed with 0.5 in. Berl saddles.

Chlorination produces hydrogen chloride in a theoretical 5:1 mole ratio to chloral. The hydrogen chloride is scrubbed with orthochlorbenzol to prevent carry-over of organics and is then fed to a 10-coil, internally cooled Knight absorption tower packed with saddles. The absorption of HCl is virtually quantitative and 36% muriatic acid is produced.

Conant(7) states that chloral can be prepared by treating acetaldehyde with chlorine water or by the action of chlorine on anhydrous alcohol. In the latter case, the chlorine first oxidizes the alcohol to acetaldehyde then chlorinates the aldehyde. Pinner(28) gives an account of the preparation of chloral by the chlorination of acetaldehyde but since his article there is nothing in literature about the preparation of chloral in this manner.

Chloral can also be prepared by distilling starch or sugar with hydrochloric acid and manganese dioxide(26) by distilling tetra-chloroether with sulfuric acid(26), and from the reaction of trichloroacetal and sulfuric acid at 150° C.(26). By oxidizing trichloroethane at room temperature and treating the oxide with anhydrous aluminum chloride, the oxidation product is converted into a mixture of dichloroacetyl chloride and chloral(34,8). None of these methods, however, are economically feasible for a commercial process.

Applications of BDT:- There is no record in literature of tests having ever been made to determine the effectiveness or uses of BDT as an insecticide. However, since it is similar to DDT and contains para-dichlorobenzene it is felt that by determining the use of these the applications of BDT can be predicted.

Applications of DDT:- Compositions of DDT in emulsion form have been used to impregnate clothing which retains lethal effectiveness against the typhus-bearing louse for a month or longer despite several normal launderings. Walls and ceilings covered with a DDT spray(23) remain deadly to flies for three months and cattle made nervous by flies have been quieted by sprayings of the compound(5). In ordinary domestic use, the compound has been effective against moths, fleas(22), bedbugs(25), and silver fish.

DDT is also very effective against grasshoppers(38), Japanese beetles(13), the codding moth(2), the white-fringed beetle(40), squash bugs, flea hoppers, corn leafhoppers, harlequin bugs, roaches, cowpea weevils, Colorado potato beetles(33), fruit tree borers, tortois beetles(2), cotton aphids, brown cottonbugs, mirids(32), apple blossom weevils(30), and the oriental fruit moth(11). DDT is presumed to act as a repellant, when used against the lesser grain borer(9) and against termites(18).

<u>Physiological Effect of DDT on Insects</u>(5):-

"Like the natural products, pyrethrum, rotenone and nicotine, DDT compositions are poisonous on contact, paralyzing an insect's nervous system. These natural products, pyrethrum, rotenone, and nicotine, however, lose their strength in a short time after application to the plant. Lead arsenate, Paris green and other inorganic stomach poisons hold their effectiveness indefinitely, but the insect must eat the poison if it is to be killed. Certain insects, however, like plant lice, do their feeding by sucking the sap within the plants and so do not swallow the dust or the spray residue left on the outside of the plants. For these there must be an insecticide that will kill on contact.

"'Gesarol' is both a stomach and contact poison, a unique characteristic, indeed. Claims by Geigy, Switzerland, of this double quality were at first received with some skepticism by American scientists. Their reluctance may be appreciated when it is stated that of 3,000 synthetic organic insecticides tested by the Department of Agriculture only two were found to possess both contact and stomach lethal qualities, sodium fluoride and DDT. From an economic standpoint, the savings may be understood when it is known that in the same area it has been necessary heretofore to use two poisons, stomach and contact, to combat the two types of pests. With few exceptions, 'Gesarol' takes care of both.

"Fumigation and egg destruction, which are the other general methods of insect control, are not as convenient and direct in action as the spraying and dusting with DDT compositions. DDT compositions have no ovicidal value but the effect of these compositions is so lasting that the insect is killed as it is hatched.

Applications of Para-dichlorobenzene:- Para-dichlorobenzene has very definite pesticidal qualities. It has been effectively used against mosquito larva(18), carpet beetles, cigaret beetles, sweet potato weevils(14) and peach tree borers(3). It has limited applications for use against clothes moth larvae(27) but a high concentration of vapor is necessary to get a 100% killing of the larvae. It has also been widely used to control damping-off, bed rot and downy mildew of tobacco(1) which is commonly known as blue mold. This compound has greater pesticidal qualities than those of any of the other chloro-benzenes.

# III. EXPERIMENTAL

## A. Plan of Investigation

Preparation of chloral. Using as a chlorinating tower a column of two inch inside diameter "Pyrex" tubing, six feet in height and packed with three-eights inch glass marbles, 2500 cc. of technical grade acetaldehyde will be chlorinated to chloral. The column will be so fitted that the chlorinated ethanal can be recycled while fresh ethanal is being added and a chlorinated product taken off. Chlorine will be passed in at the bottom of the tower, and the unreacted chlorine plus the hydrogen chloride formed will pass out at the top while ethanal is fed in the top and passes out the bottom of the column. No catalyst will be used.

The system will be filled with acetaldehyde at an initial temperature of 32° F. and the recycling pump started. As the chlorination proceeds the temperature will be raised to 100° F., and the chlorine will be slowly bubbled through the column, countercurrent to the flow of acetaldehyde which will be recycled at a rate of one gallon per minute. At one hour intervals, samples of the recycled liquid will be taken to determine the boiling points and specific gravities. When the boiling point of the reaction mixture has risen above 110° F., 1000 cc. of acetaldehyde will be added to the recycling liquid at such a rate as to keep the boiling point of mixture at 110° F. As the acetaldehyde is being added, an equal volume of chlorinated acetaldehyde will be withdrawn from the system.

The chlorinated product obtained from the above system will be collected and used as a raw material for a similar reaction. The system will be filled and brought to equilibrium as described, except the equilibrium temperature will be 114° F. and chlorinated acetaldehyde will be used instead of acetaldehyde. The per cent of chloral in the chlorinated product will be determined.

The following points will be determined:

(1) Equilibrium conditions and yield.

(2) Whether the acetaldehyde is miscible with the recycled solution.

(3) Whether the boiling point of acetaldehyde and recycled solution at equilibrium will be above 100° F. If below 100° F., the temperature will be determined and the experiment re-run using this as initial temperature.

(4) The feasible time required for the reaction under the above conditions.

**Production of 2,2 bis(2,5 dichlorophenyl) 1,1,1 trichloroethane.** The preparation of 2,2 bis(2,5 dichlorophenyl) 1,1,1 trichloroethane will be made on a mole basis. In a 1000 cc. Wolff flask equipped with an agitator, 294 grams (two moles) of para-dichlorobenzene, 117 grams of 95.5% sulfuric acid (sp.gr. 1.84), and 147 grams (one mole) of chloral will be mixed. The mixture will be rapidly agitated throughout the reaction. At the end of the reaction time, the precipitant will be separated by filtering. To remove excess acid, the precipitant will first be washed with a saturated sodium carbonate solution, then with water.

The following points will be determined:

(1) Equilibrium conditions and side reactions.
(2) The feasible length of reaction.
(3) Yield of condensation product.
(4) Physical constants of product.

**Design of the Insecticide Plant.** Consideration will be given to the following preliminary engineering studies:

(1) Comprehensive market surveys or locations.
(2) Plant sites.
(3) Fuel and water sources.
(4) Transportation facilities.
(5) Material supplies.
(6) Labor supply.

(7) Laws and codes.

(8) Working up of process flow sheets.

(9) Working up design flow sheets.

(10) Temtative specifications of machinery

(11) Tentative specifications of materials.

(12) Power systems.

(13) Calculation of heat balances.

(14) Calculation of material balances.

(15) Preliminary sizing and designing of vessels, exchanges and process units.

(16) Drawing of preliminary plant layout.

(17) Drawing of preliminary equipment layout.

(18) Preparation of preliminary cost estimates.

## B. Materials

The following materials were used in the investigation:

### Raw Materials

Acetaldehyde, technical. Obtained from Eimer and Amend, New York, N. Y.

Benzene Dichloride, para, technical. Obtained from Eimer and Amend, New York, N. Y.

Chloral Hydrate, U. S. P. (crystal). Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J.

Chlorine. Obtained from Matheson Co., East Rutherford, N. J.

### Catalysts

Aluminum Chloride, Anhydrous sublimated, reagent grade, Code 1230. Obtained from General Chemical Co., New York, N. Y.

Zinc Chloride, C. P., granular. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J.

### Carriers

Acid Sulfuric, technical, 20% fuming. J. T. Baker Chemical Co., Phillipsburg, N. J.

Sulfuric Acid, C. P., special, 95.5% (Sp. Gr. 1.84). Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J.

## Solvents

Alcohol, Methyl, absolute refined. Obtained from Phipps and Bird, Inc., Richmond, Va.

Benzol, technical. Obtained from Phipps and Bird, Inc., Richmond, Va.

Petroleum Ether, reagent grade, C. P. Obtained from Phipps and Bird, Inc., Richmond, Va.

## Acid Neutralizer

Sodium Carbonate. Obtained from Diamond Alkali Co., Pittsburgh, Pa.

## C. Apparatus

Tube, Pyrex glass, 2 in. inside dia. 6 ft. long. Obtained from Chemical Engineering Stock Room. Used as a chlorinating column.

Pump, Eco single impeller ½ in. gearless, bronze. Obtained from Eco Engineering Co., Neward, N. J. Used to recycle the chlorinated acetaldehyde.

Motor, ¼ h.p. Craftsman. Obtained from Chemical Engineering Supply Room. Used to drive Eco pump.

Flask, Wolff. 1000 cc., Pyrex. Obtained from Chemical Engineering Stock Room. Used for condensation reaction vessal.

Flask, Wolff. 150 cc., Pyrex. Obtained from Chemical Engineering Stock Room. Used for boiling point determinations.

Tubing glass, 10 mm. Obtained from Chemistry Supply Room. Used to recirculate the chlorinated acetaldehyde.

Two thermometers, mercury bulb, immersion type, 0-300° F. Obtained from Chemical Engineering Stock Room.

Motor, Fultork. Obtained from Chemical Engineering Stock Room. Used to power agitator for condensation reaction.

Agitator, glass. Made in Chemical Engineering Department from glass rod. Used to agitate reactants in condensation reaction.

Jugs, glass, one-gallon. Obtained from Chemical Engineering Stock Room. Used for reaction between gaseous acetaldehyde and chlorine.

Two heaters, electric, Chromalox, 360 w., 120 v. Obtained from Edwin L. Wiegand Co., Pittsburgh, Pa. Used for heating reaction mixtures.

Condensers, Liebig, 400 mm. Obtained from Chemical Engineering Stock Room. Used to condense acetaldehyde vapors from chlorinating column.

Ring stands with clamps. Obtained from Chemical Engineering Stock Room. Used to support reaction apparatus.

Funnel, glass separatory, 500 cc. Obtained from Chemical Engineering Stock Room. Used to separate chloral from sulfuric acid.

Marbles, glass, 3/8-in., 25-lb. Obtained from Chemical Engineering Stock Room. Used as packing for chlorinating column.

Assorted beakers and flasks. Obtained from Chemical Engineering Stock Room.

Bucket, one-gallon iron. Obtained from Chemical Engineering Stock Room. Used as a constant temperature bath.

## D. Method of Procedure

### 1. Chloral Production Studies

**Determination of the Length of Time of the Reaction.** Two experimental runs were made for the primary purpose of determining the most feasible time of reaction for the run. The preparation of chloral by chlorination of acetaldehyde was broken down into two phases, the first of which was the chlorination of technical grade acetaldehyde to an intermediate chlorinated compound (specific gravity 1.15-1.20) and the second of which was the addition of chlorine to form the saturated compound, trichloroacetal (specific gravity 1.5121). Samples of the reaction mixture were taken at the end of each hour of operation and the specific gravities and boiling points determined. From the results obtained, the length of reaction for maximum production of chloral was determined and a third run, similar to the preceding, was made to correlate the results.

**Determination of the Temperature at which the Reaction Should be Carried Out.** Two experimental runs were made, each using 1500 cc. of technical grade acetaldehyde and an excess of chlorine, varying the temperature of the recycled mixture. One run was made with the reaction mixture in the first phase being heated to 110° F. and the mixture in the second phase heated to 120° F. The second run was made with the reaction mixture in the first phase being heated to 89° F. and the mixture in the second phase heated to 114° F. Samples were taken at the end of each hour of operation and specific gravities and boiling points of the reaction mixtures were determined. From the results obtained, the temperature giving the least amount of polymerization and the highest yield of chloral was determined and a third run, similar to the preceding, was made to correlate the results.

Determination of the Effect of Sunlight on the Reaction. Approximately 100 cc. of acetaldehyde were put into each of two one-gallon jugs and allowed to vaporize, then sufficient chlorine gas was added to each jug to give an orange color to the vapor space within. One jar was placed in a dark locker and left for 24 hours; the other was placed in the sunlight for a short period (less than 10 seconds). The reaction products were compared and the results noted.

Methods of Analysis of Reaction Mixture.

(1) Boiling point. Fifty cc. of the reaction mixture were placed in a 150 cc. Wolff flask, which was left open to the atmosphere. A thermometer was placed in the flask through one of the openings and extended down until

the mercury bulb was one-quarter inch below the surface of the liquid. The flask was then placed in a water bath and the water was slowly heated until the reaction mixture began to boil, at which point a temperature reading was taken.

(2) Specific gravity. Specific gravity determinations were made by use of a Westphal balance. Samples of the reaction mixture were placed in a constant temperature (40° F.) bath together with a water sample and left overnight. The specific gravity of the water sample was determined first and then readings were made on the mixture samples. The readings were converted to 20° C. (68° F.) based on water at 4° C. (39.2° F.).

(3) Per cent of chloral. A 100 cc. sample of the reaction product was taken and 50 cc. of water added. The mixture was thoroughly shaken and allowed to stand for thirty minutes, after which the liquid was poured into four 12.5 cm. evaporating dishes and evaporated at 194° F. until dry. The crystals remaining in the evaporating dishes were

collected and weighed. The weight thus determined was of chloral hydrate and was corrected to chloral. The specific gravity of the initial mixture was known and, from the data obtained, the per cent of chloral was calculated.

## 2. Condensation Reaction Studies

Determination of Catalyst to be Used. Three samples were prepared, each containing 240 cc. of chlorinated acetaldehyde and 294 grams of para-dichlorobenzene. To one solution was added 64 cc. of 98% sulfuric acid (sp. gr. 1.84) after which the temperature of the mixture was brought up to 130° F. and held constant for four and one-half hours. Another solution was mixed with 44.45 grams of anhydrous aluminum chloride and the temperature held at 130° F. for seven hours. The third solution was mixed with 45.43 grams of anhydrous zinc chloride, prepared by heating zinc chloride for 18 hours at 266° F., and reacted for eight hours at a temperature of 130° F. The data obtained from the above experiments were evaluated for further work.

Determination of Product Yield. Two samples were prepared, each containing 170 grams of chloral hydrate, 294 grams of para-dichlorobenzene, 100 cc. of 98% sulfuric acid (sp. gr. 1.84), and 300 cc. of oleum (20% $SO_3$). One solution was reacted at room temperature for five hours and the other solution reacted under the same conditions for 24 hours. Upon completion of the reactions, the product crystals were separated from the unreacted materials, dried and weighed. The results were evaluated for further work.

## E. Data and Results

The experimental data and results are presented in the following tables.

Table I presents the data and results obtained in the chlorination of acetaldehyde using an excess of chlorine gas.

Table II presents the data and results obtained in the condensation of the chlorinated acetaldehyde product containing chloral with para-dichlorobenzene.

Table III presents the data and results obtained in the condensation of para-dichlorobenzene with chloral hydrate in a mixture of 98% sulfuric acid (sp. gr. 1.84) and oleum (20% $SO_3$).

## Table I

## Chlorination of Acetaldehyde

| Run No. | $CH_3CHO$ ml. | Reaction Time hrs. | Temp. Phase 1 °F. | Temp. Phase 2 °F. | Sp. Gr. Product | B. P. Product °F. | Remarks |
|---|---|---|---|---|---|---|---|
| 1 | 1000 | 4 | 96 | 114 | 1.2343 | 135 | Pump developed a leak and run had to be stopped. |
| 2 | 1500 | 5 | 100 | 120 | 1.2702 | 144 | Tarry material formed in product. |
| 3 | 1500 | 5 | 96 | 114 | 1.3000 | 150 | Analysis indicated 53.45% chloral. |
| 4 | 1500 | 5 | 96 | 114 | 1.2959 | 148 | Analysis indicated 53.45% chloral. |

Table II

Condensation of Chlorinated Acetaldehyde with Para-dichlorobenzene

| Run No. | Chlor. Acetal ml. | $C_6H_4Cl_2$ gms. | Catalyst | Catalyst gms. | Temp. °F. | Time Run hrs. | Remarks |
|---|---|---|---|---|---|---|---|
| 1A | 240 | 294 | 98% $H_2SO_4$ | 118 | 150 | 1½ | Plastic material formed. |
| 2A | 240 | 294 | None | - | 130 | 7 | No reaction |
| 3A | 240 | 294 | None | - | 130 | 24 | No reaction |
| 4A | 240 | 294 | 98% $H_2SO_4$ | 118 | 130 | 4 | Tarry product formed. |
| 5A | 240 | 294 | $AlCl_3$ | 44.5 | 130 | 7 | Cubic crystals formed. |
| 6A | 240 | 294 | $ZnCl_2$ | 45.4 | 130 | 8 | Cubic crystals formed. |

### Table III

Condensation of 170 grams of Chloral Hydrate with 294 grams of Para-dichlorobenzene Using a Mixture of 100 cc. of 98% Sulfuric Acid and 300 cc. of Oleum (20% $SO_3$) as Carrier.

| Run No. | Temp. °F. | Time hrs. | BDT Formed gms. |
|---|---|---|---|
| 1B | 80 | 5 | 25.6 |
| 2B | 80 | 24 | 36.2 |

## The Design of a BDT Plant

The following section contains the design of the BDT plant. The design has been arranged as follows:

A. Theoretical Calculations

B. Material Balance

C. Selection of Equipment

D. Raw Material Cost Calculations

E. Building and Land Costs

F. Equipment Cost Calculations

G. Labor Costs

H. Summaries

I. Plant Location

J. Plant Layout and Elevation

K. Schedule of Operation

L. Preconstruction Cost Summary

## A. Theoretical Calculations

The proposed plant is to produce 1000 tons of BDT per year. The production of DDT for the first three months of 1946 was 10,091,822 pounds and as the preliminary data indicates that the cost of BDT will be higher than that of DDT, the use of BDT will be limited to cases in which DDT is not effective. The BDT plant will be designed to produce five percent of the annual production of DDT.

### Plant Specifications

Annual Output: 1000 tons BDT.

Production Capacity: 25% excess.

Operation: 3 shifts (8 hour) per day.

40 hour week.

10 day vacation, unitized.

250 days total working time per year.

6000 hours of production, overall.

5800 hours of production, actual.

432 lb./hr. BDT production.

450 lb./hr. to take care of slowdown.

## Laboratory and Semiworks Data

Composition of condensation reaction product:

| | |
|---|---|
| BDT, per cent | 5.8 |
| Chloral, per cent | 31.4 |
| Para-dichlorobenzene, per cent | 37.2 |

Specific gravities of reactants:

| | |
|---|---|
| Chloral Hydrate, at 68° F. | 1.908 |
| Para-dichlorobenzene, at 68° F. | 1.458 |
| Sulfuric Acid (98%), at 68° F. | 1.840 |
| Oleum (20% $SO_3$), at 68° F. | 1.916 |

## Reaction Calculations

Basis: 6-hour cycle.

Production: 2700 pounds per 6-hour cycle.

Condensation reaction:

$$CCl_3CHO.H_2O + 2\ C_6H_4Cl_2 \longrightarrow CCl_3CHO(C_6H_4Cl_2) + H_2O$$

$$165.42 \quad + 2(147.01) = \quad 441.44 \quad + \ 18$$

Chloral Hydrate needed:

$$\frac{165.42}{441.44} \times 2700 = 1008 \text{ lb.}$$

Chloral necessary for recycle:

$$\frac{1008}{0.058} \times \frac{147.42}{165.42} \times 0.942 = 14600 \text{ lb.}$$

Chloral hydrate added for decomposition by $H_2SO_4$:

$$(14600 + 1008 \times \frac{147.42}{165.42}) \times 0.0483 \times \frac{165.42}{147.42} = 838 \text{ lb.}$$

Total chloral hydrate added per 6-hour cycle:

$$1008 + 838 = 1846 \text{ lb.}$$

Para-dichlorobenzene needed:

$$\frac{2 \times 147.01}{441.44} \times \frac{2700}{0.98} = 1836 \text{ lb.}$$

Para-dichlorobenzene recycled:

$$\frac{1836}{0.058} \times 0.942 \doteq 29200 \text{ lb.}$$

Amount 98% sulfuric acid required:

$$100 \times 1.84 \times \frac{1008}{165.42} = 3546 \text{ lb.}$$

## B. Material Balance

Basis: Pounds per 6-hour cycle

**Storage.**

| Entering @ 68° F. | | Leaving @ 68° F. | |
|---|---|---|---|
| $CCl_3CHO.H_2O$ | 1846 lb. | $CCl_3CHO.H_2O$ | 1846 lb. |
| $C_6H_4Cl_2$ | 1836 | $C_6H_4Cl_2$ | 1836 |
| $H_2SO_4$ (98%) | 1122 | $H_2SO_4$ (98%) | 1122 |
| Oleum | 3546 | Oleum | 3546 |
| Total | 8350 lb. | Total | 8350 lb. |

**Reactor.**

| Entering @ 68° F. | | Leaving @ 68° F. | |
|---|---|---|---|
| $CCl_3CHO.H_2O$ | 1846 lb. | $CCl_3CHO$..(recycle) | 14600 lb. |
| $CCl_3CHO$ (recycle). | 14600 | $C_6H_4Cl_2$ | 29236 |
| $C_6H_4Cl_2$ (feed) | 1836 | BDT | 2700 |
| $C_6H_4Cl_2$ (recycle). | 29200 | $CCl_3COOH$ | 36 |
| $H_2SO_4$ (98%) (feed) | 1122 | $H_2SO_4$ (98%) | 4753 |
| $H_2SO_4$ (98% recycle) | 45 | $H_2SO_4$ (mono-hyd.). | 152 |
| $H_2SO_4$ (mono-hyd.). | 1 | Total | 52196 lb. |
| Oleum | 3546 | | |
| Total | 52196 lb. | | |

## Rotary Vacuum Filter No. 1.

| Entering @ 68° F. | |
|---|---|
| **As crystals** | |
| $C_6H_4Cl_2$ | 29236 lb. |
| BDT | 2700 |
| $CCl_3COOH$ | 33 |
| Total | 31969 lb. |
| **As solution** | |
| $CCl_3CHO$ | 14600 lb. |
| $CCl_3COOH$ | 3 |
| $H_2SO_4$ (98%) | 4753 |
| $H_2SO_4$ (mono-hyd) | 152 |
| Total | 19508 lb. |
| Grand total | 51477 lb. |

| Leaving @ 68° F. | |
|---|---|
| **As filter cake** | |
| $C_6H_4Cl_2$ | 29200 lb. |
| $H_2SO_4$ (98%) | 174 |
| $H_2SO_4$ (mono-hyd) | 6 |
| Total | 29380 lb. |
| **As filtrate** | |
| BDT | 2700 lb. |
| $CCl_3COOH$ | 36 |
| $CCl_3CHO$ | 14600 |
| $H_2SO_4$ (98%) | 4579 |
| $C_6H_4Cl_2$ | 36 |
| Total | 22097 lb. |
| Grand Total | 51477 lb. |

## Rotary Vacuum Filter No. 2.

| Entering @ 68° F. | |
|---|---|
| **As crystals** | |
| BDT | 2700 lb. |
| $CCl_3COOH$ | 33 |
| $C_6H_4Cl_2$ | 36 |
| Total | 2769 lb. |
| **As solution** | |
| $CCl_3COOH$ | 3 lb. |
| $CCl_3CHO$ | 14600 |
| $H_2SO_4$ (98%) | 4579 |
| $H_2SO_4$ (mono-hyd) | 146 |
| Total | 19328 lb. |
| **As wash solution** | |
| $H_2O$ | 1000 lb. |
| $Na_2CO_3$ | 106 |
| Total | 1106 |
| Grand total | 23203 lb. |

| Leaving @ 68° F. | |
|---|---|
| **As filter cake** | |
| BDT | 2700 lb. |
| $C_6H_4Cl_2$ | 36 |
| $H_2O$ | 41 |
| Total | 2777 lb. |
| **As filtrate** | |
| $CCl_3CHO$ | 14600 lb. |
| $H_2SO_4$ (98%) | 4525 |
| $H_2SO_4$ (mono-hyd) | 145 |
| Total | 19270 lb. |
| **As waste wash solution** | |
| $H_2O$ | 971 lb. |
| $Na_2SO_4$ | 79 |
| $CCl_3COONa$ | 41 |
| $Na_2CO_3$ | 36 |
| Total | 1127 lb. |
| **Lost as gas** | |
| $CO_2$ | 29 lb. |
| Grand total | 23203 lb. |

### Centrifuge.

Entering @ 68°

| As liquor | |
|---|---|
| $CCl_3CHO$ | 14600 lb. |
| $CCl_3COOH$ | 3 |
| $H_2SO_4$ (98%) | 4525 |
| $H_2SO_4$ (mono-hyd) | 145 |
| Total | 19273 lb. |

Leaving @ 68° F.

| Light fraction | |
|---|---|
| $CCl_3CHO$ | 14600 lb. |
| $H_2SO_4$ (98%) | 45 |
| $H_2SO_4$ (mono-hyd) | 1 |
| Total | 14646 lb. |
| **Heavy fraction** | |
| $CCl_3COOH$ | 3 lb. |
| $H_2SO_4$ (98%) | 4480 |
| $H_2SO_4$ (mono-hyd) | 144 |
| Total | 4627 lb. |
| Grand Total | 19273 lb. |

## C. Selection of Equipment

### Chloral Hydrate Storage.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| $CCl_3CHO.H_2O$.... 1846 lb. | $CCl_3CHO.H_2O$.... 1846 lb. |

Requirements:

Minimum supply on hand: 4-weeks.

Replenishment period: 4-weeks.

Capacity of storage area: 10-weeks supply.

Containers: 100-lb. drums.

Requirement per 6-hour cycle: 18.5 drums.

Requirement per day: 18.5 x 4 = 74 drums.

Working days per week: 5-days.

Requirements for 10-weeks: 74 x 5 x 10 = 3700 drums.

Height of drum storage pile: 3-drums.

Dimensions of drums: 12-in. dia. x 20-in. ht.

Floor area required: 1 x 3700/3 = 1233 sq. ft.

Height of ceiling: 9-ft.

Type of floor: Concrete.

## Para-dichlorobenzene Storage.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| $C_6H_4Cl_2$........ 1836 lb. | $C_6H_4Cl_2$........ 1836 lb. |

Requirements:

Minimum supply on hand: 4-weeks.

Replenishment period: 4- weeks.

Capacity of storage area: 10-weeks supply.

Containers: 100-lb. drums.

Requirement per 6-hour cycle: 18.4 drums.

Reaction cycles per day: 4.

Requirement per day: 18.4 x 4 = 73.6 drums.

Working days per week: 5-days

Requirements for 10-weeks: 73.6 x 5 x 10 = 3680 drums.

Height of drum storage pile: 3 drums.

Dimensions of drums: 12-in. dia. x 20-in. ht.

Floor area required: 1 x 3680/3 = 1227 sq. ft.

Height of ceiling: 9-ft.

Type of floor: Concrete.

## Soda Ash Storage.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | | Leaving | |
|---|---|---|---|
| Soda ash....... | 106 lb. | Soda ash....... | 106 lb. |

Requirements:

Minimum supply on hand: 4-weeks.

Replenishment period: 4-weeks.

Capacity of storage area: 10-weeks supply.

Containers: 500-lb. barrels.

Requirement per 6-hour cycle: 0.212 drums.

Cycles per day: 4.

Requirement per day: 0.212 x 4 = 0.848 drums.

Working days per week: 5-days.

Requirements for 10-weeks: 0.848 x 5 x 10 = 42.4 drums.

Height of drum storage pile: 1-drum.

Dimensions of drums: 30-in. dia. x 36-in. ht.

Floor area required: 2.5 x 2.5 x 43 = 312 sq. ft.

## Sulfuric Acid Storage.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| $H_2SO_4$ (98%).... 1267 lb. | Reactor feed |
| | $H_2SO_4$ (98%).... 1122 lb. |
| | Acid regenerator |
| | $H_2SO_4$ (98%).... 145 lb. |
| | Total............ 1267 lb. |

Requirements:

Minimum supply on hand: 2-weeks.

Replenishment period: 6-weeks.

Capacity of storage area: 8-weeks supply.

Containers: 10,000-gal. tank car.

Capacity of tank car:

$10,000 \times 8.345 \times 1.84 = 153,548$-lb.

Requirements per day: $1267 \times 4 = 5068$-lb.

Working days per week: 5-days.

Requirements for 8-weeks: $5068 \times 5 \times 8 = 202,720$ lb.

Necessary volume of tank:

$202,720/(62.4 \times 1.84) = 1770$ cu. ft.

Safety allowance, 10% = $\underline{177}$

Actual volume....... 1947 cu. ft.

Capacity of tank: $1947 \times 7.48 = 14,550$-gal.

Selection of sulfuric acid storage tank: Available as standard, a Lancaster hydro-pneumatic storage tank, mild steel, 15,000-gal. capacity(20).

Tank dimensions: O.D., 96-in.
Length, 41-ft. 2-in.
Shell thickness, 0.540-in.
Capacity, 15,000-gal.

## Oleum Storage.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| Oleum.......... 3546 lb. | Oleum......... 3546 lb. |

Requirements:

The oleum necessary for the reaction will be obtained from the sulfuric acid reclamation unit.

Minimum supply on hand: 1-week.

Replenished: Daily.

Cycles per day: 4.

Working days per week: 5-days.

Capacity of tank: 3546 x 4 x 5 = 70,920 lb.

Necessary volume of tank:

70,920/(62.4 x 1.916) = 594 cu. ft.
Safety allowance, 10% = 60
Actual volume...... 654 cu. ft.

Tank capacity: 654 x 7.48 = 4880 gal.

Selection of tank: Available as standard, a Lancaster hydro-pneumatic storage tank, mild steel, 5000-gal. capacity(20).

Tank dimensions: O.D., 72-in.
Length, 24-ft. 5-in.
Shell thickness, 0.405-in.
Capacity, 5000-gal.

## Acid Air Pump.

Requirements:

Volume acid flow: 29.7 cu. ft./6-hour cycle.

Time acid flows: 20-min./6-hour cycle.

Acid head: 20-ft.

Pressure required to move acid: 16.7 psig.

Volume air required:

$$(29.7)\ (36.4/14.7)/20 = 3.2 \text{ cu. ft./min.}$$

Selection of pump: Available as standard, a Nash Hytor Compressor, AL 571, complete.

Specifications:

Pressure: 20 psig.

Volume: 4.0 cu. ft./min.

RPM: 1750

Motor: 1½ HP, 220-440v., 3-phase, 60-cycle, AC.

Power Requirements:

1.5 HP x 0.33 hr. x 0.746 x 4 = 1.49 kw.hr.

<u>Drum Elevator.</u>

To lift 100-lb. drums of chloral hydrate and paradichlorobenzene from storage area to feed hopper level.

Requirements:

Capacity: 60 100-lb. drums per hour.

Height: 20-ft., pulley to pulley.

Drum dimensions: 12-in. dia. x 20-in. ht.

Selection of elevator: Available as standard, a Link-Belt Standard Barrel Elevator, Style A, Chain No. 83, wheel diameter 16.75-in., and arm radii 11-in. and 6-in.(24).

Motor: 1 HP, 220-440v., 3-phase, 60-cycles, A.C.

## Chloral Hydrate Feed Hopper.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| $CCl_3CHO.H_2O$..... 1846 lb. | $CCl_3CHO.H_2O$..... 1846 lb. |

Requirements:

Approximate volume: 23 cu. ft.

Cone shaped.

Outlet diameter: 8-in.

Dimensions: 2½-ft. dia. x 3½-ft. deep.

Material of construction: 3/16-in. mild steel plate.

### Para-dichlorobenzene Feed Hopper.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| $C_6H_4Cl_2$........ 1836 lb. | $C_6H_4Cl_2$....... 1836 lb. |

Requirements:

Approximate volume: 1836/(62.4 x 1.3) = 23 cu. ft.

Cone shaped.

Outlet diameter: 8-in.

Dimensions: 2½-ft. dia. x 3½-ft. deep.

Material of construction: 3/16-in. mild steel plate.

## Soda Ash Solution Storage Tank.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | | Leaving | |
|---|---|---|---|
| Total.......... | 1106 lb. | Total......... | 1106 lb. |

Requirements:

Capacity of tank: 24-hr. supply.

Volume required: 480-gal.

Selection of tank: Available as standard, a Lancaster hydro-pneumatic storage tank, mild steel, 550-gal. capacity(20).

Tank dimensions: O.D., 36-in.
Length, 11-ft.
Capacity, 550-gal.

Selection of mixer: Available as standard, a Lightin agitator, 1 HP, mild steel shaft and blade.

Motor: 1 HP, 220-440 v., 3-phase, 60-cycle, a.c.

## Wash Solution Pump.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | | Leaving | |
|---|---|---|---|
| Total.......... | 1106 lb. | Total....... | 1106 lb. |
| Volume....... | 120 gal. | | |

Requirements:

Time operated per cycle: 20-min.

Volume per cycle: 120-gal.

Capacity: 120/20 = 6-gpm.

Head: 15-ft.

Type: Gear Pump.

RPM: 1750.

Suction: 1-in.

Discharge: 1-in.

Material of construction: Mild Steel.

Motor: 0.5 HP, 220-440 v., 3-phase, 60-cycle, a.c.

Power Requirements:

o.5 HP x 0.33-hr. x 0.746 x 4 = 0.498 kw. hr.

## Reactor.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| Total.......... 52196 lb. | Total........ 52196 lb. |
| Volume....... 566.6 cu. ft. | |

Requirements:

Safety factor: 100%.

Necessary volume of tank: 566.6 cu. ft.

Actual volume of tank: 1134 cu. ft.

Type: Closed, cylinderical, vertical.

Type bottom: Cone shaped.

Type top: Standard dished head.

One 6-in. opening in bottom for drain; quick-opening valve.

Two 8-in. openings in top for solid reactants feed hoppers.

Two 2½-in. openings in top for sulfuric acid feed lines.

One 2-in. opening in top for chloral feed line.

Opening for agitator shaft (fabrication).

Tank equipped with agitator.

Material of construction: Mild steel.

## Reactor Agitator.

Selection of equipment: Available as standard, a Lightin angular off-center agitator, 5 HP, mild steel shaft and blade(4).

Motor: 5 HP, 220-440 v., 3-phase, 60-cycle, a.c.

Power Requirements:

5 HP x 5-hr. x 0.746 x 4 = 74.6 kw. hr.

## Reactor Pump.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| Total.......... 51441 lb. | Total........ 51441 lb. |

Volume....... 567 cu. ft. or 4240 gal.

Requirements:

Time operated per cycle: 20 min.

Volume per cycle : 4240 gal.

Capacity: 4240 x 3 = 12720 gal. per hr.

12720/60 = 220 gpm.

Head: 15-ft.

Type: Open impeller centrifugal pump.

RPM: 1750.

Suction: 6-in.

Discharge: 6-in.

Material of construction: Mild steel.

Motor driven, single stage.

Motor: 10 HP, 220-440 v., 3-phase, 60-cycle, a.c.

Power Requirements:

10 HP x 0.33-hr. x 0.746 x 4 = 9.85 kw. hr.

## Rotary Vacuum Filter No. 1.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | | Leaving | |
|---|---|---|---|
| Total.......... | 51477 lb. | Filter cake... | 29380 lb. |
| | | Filterate..... | 22097 |
| | | Total........ | 51477 lb. |

Requirements:

Operating time per cycle: 20-min.

Capacity: 51477 x 3 = 154,000-lb. slurry per hr.

29380 x 3 = 97,000-lb. solids per hr.

Material of construction: Mild steel.

Filter medium: Woven mild steel wire of open texture.

Selection of filter: Available as standard, an Oliver Continuous Top-feed Filter(28).

Specifications:

Diameter: 5.25-ft.

Length: 10-ft.

Area: 165 sq. ft.

Construction: Mild steel.

Capacity: 49.5 tons of solids per hour.

Motor: 2 HP, 220-440 v., 3-phase, 60-cycle a.c.

Power Requirements:

2 HP x 0.33-hr. x 0.746 x 4 = 2.07 kw. hr.

**Bucket Elevator.**

To lift from the bottom of rotary vacuum filter no. 1 into para-dichlorobenzene feed hopper.

Requirements:

Capacity: 22-tons per hour.

Height: 20-ft., pulley to pulley.

Weight of material: 82-lb. per cu. ft.

Selection of Elevator: Available as standard, a Link-Belt Vertical Continuous Bucket Elevator, Type No. 7(24).

Specifications:

Elevator No.: 766.

Size of buckets: 8x5x7.75-in.

Capacity: 25-tons per hour.

Motor: 1 HP, 220-440 v., 3-phase, 60-cycle, a.c.

Power Requirements:

1 HP x 0.33-hr. x 0.746 x 4 = 0.985 kw. hr.

Filtrate Pump No. 1.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| Total.......... 22,097 lb. | Total....... 22,097 lb. |
| Volume....... 1,760 gal. | |

Requirements:

Type: Centrifugal, open impeller.

Capacity: 1760/20 = 88-gpm.

Head: 5-ft.

RPM: 1750.

Suction: 2-in.

Discharge: 2-in.

Material of construction: Mild steel.

Motor: 5 HP, 220-440 v., 3-phase, 60-cycles, a.c.

Power Requirements:

5 HP x 0.33-hr. x 0.746 x 4 = 4.93 kw.-hr.

## Rotary Vacuum Filter No. 2.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | Leaving |
|---|---|
| Total.......... 23309 lb. | Filtrate..... 19270 lb. |
| | Filter cake.. 2777 |
| | Wash Solution. 1233 |
| | Lost as gas... 29 |
| | Total........23309 lb. |

Requirements:

Operating time per cycle: 20-min.

Capacity: 23,309 x 3 = 70,000-lb. slurry per hr.

2777 x 3 = 8400-lb. solids per hour.

Materials of construction: Mild steel.

Filter medium: Woven mild steel wire cloth of close-texture.

Separation of wash solution from filtrate type.

Selection of filter: Available as standard, an Oliver Continuous Filter(28).

Specifications:

Diameter: 3-ft.

Length: 2-ft.

Area: 18 sq. ft.

Construction: Mild steel.

Capacity: 5.4-tons of solids per hour.

Motor: 0.5 HP, 220-440 v., 3-phase, 60-cycle, a.c.

**Power Requirements:**

0.5 HP x 0.33-hr. x 0.746 x 4 = 0.49 kw. hr.

## Filtrate Pump No. 2.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | | Leaving | |
|---|---|---|---|
| Total.......... | 19270 lb. | Total....... | 19270 lb. |
| Volume....... | 1540 gal. | | |

Requirements:

Type: Gear, motor driven.

Capacity: 1540/20 = 77-gpm.

Head: 5-ft.

RPM: 1750

Suction: 2-in.

Discharge: 2-in.

Material of construction: Mild steel.

Motor: 3 HP, 220-440 v., 3-phase, 60-cycles, a.c.

Power Requirements:

3 HP x 0.33-hr. x 0.746 x 4 = 2.955 kw. hr.

**Centrifuge.**

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | | Leaving | |
|---|---|---|---|
| Liquid.......... | 19273 lb. | Light fraction.. | 14646 lb. |
| | | Heavy fraction.. | 4627 |
| | | Total........... | 19273 lb. |

Requirements:

Type: Super-centrifuge, continuous.

Separation: 99%.

Time operated per cycle: 20-min.

Capacity: 19,273 x 3 = 57,813-lb. per hour.

Volume capacity: 74 gpm.

Material of construction: Mild steel.

Motor: 5 HP, 220-440 v., 3-phase, 60-cycles, a.c.

Power Requirements:

5 HP x 0.33-hr. x 0.746 x 4 = 4.93 kw. hr.

Chloral Pump.

Material Balance: Basis, pounds per 6-hour cycle.

| Entering | | Leaving | |
|---|---|---|---|
| Total.......... | 14646 lb. | Total........... | 14600 lb. |

Requirements:

Pump will be used 20-min. once every six hours. At this time it will handle 14,646-lb. or 1170-gal. of chloral and sulfuric acid.

Specifications:

Type: Gear pump, motor driven.

Capacity: 58-gpm.

Head: 20-ft.

RPM: 1750.

Suction: 2-in.

Discharge: 2-in.

Material of construction: Mild steel.

Motor: 2 HP, 220-440 v., 3-phase, 60-cycles, a.c.

Power Requirements:

2 HP x 0.33-hr. x 0.746 x 4 = 1.97 kw. hr.

## D. Raw Material Cost Calculations

Basis: Pounds per 24-hour day of operation

**Chloral Hydrate.**

| | | |
|---|---|---|
| Cost of 7384-lb. @ $0.90/lb. | $6745.60 | |
| Freight @ $0.79/100-lb. | 58.50 | |
| Total | | $6804.10 |

**Para-dichlorobenzene.**

| | | |
|---|---|---|
| Cost of 7344-lb. @ $0.11/lb. | $ 807.84 | |
| Freight @ $0.79/100-lb. | 58.50 | |
| Total | | $ 866.34 |

**Sulfuric Acid (98%).**

| | | |
|---|---|---|
| Cost of 5068-lb. @ $16.50/ton | $ 41.81 | |
| Freight @ $0.79/100-lb. | 40.29 | |
| Total | | $ 82.10 |

**Soda Ash.**

| | | |
|---|---|---|
| Cost of 424-lb. @ $0.0105/lb. | $ 4.45 | |
| Freight @ $0.79/100-lb. | 3.35 | |
| Total | | $ 7.80 |

**Water.**

| | | |
|---|---|---|
| Cost of 480-gal. process water @ $0.35/1000-gal. | $ 0.17 | |
| Cost of 800-gal. sanitary water @ $0.35/1000-gal. | $ 0.28 | |
| Total | | $ 0.45 |

|  |  |  |
|---|---|---|
| **Electric Power.** |  |  |
| Operational, 96.4 x \$0.0208(36) | \$ 2.00 |  |
| Lighting, 65.0 x \$0.0208(36) | 1.35 |  |
| Total |  | \$ 3.35 |
| **Phone.** |  |  |
| Cost at \$0.125/day | \$ 0.13 |  |
| Total |  | \$ 0.13 |
| Total cost per day of operation |  | \$7764.24 |
| Annual cost (250 working days) |  | \$1,941,060.00 |

## E. Building and Land Costs

### Storage Building.

Description:

Single-story warehouse, 3660 sq. ft. of floor area, unheated, equipped with lighting fixtures.

Cost:

Total at $1.50 per sq. ft.(36)..........$ 5490.00

### Main Building.

Description:

Two-story building for light manufacturing, 1200 sq. ft. of floor area, heated, equipped with lighting and heating fixtures.

Cost:

Total at $2.00 per sq. ft.(36)..........$ 2400.00

### Land.

Description:

Lot, 120 x 180 ft., with 150-ft. frontage on railroad.

Cost:

Total....................................$ 150.00

### Railroad Siding.

Cost:

| | |
|---|---|
| Total at $5.00 per ft., 150-ft. | $ 750.00 |

### Fencing.

Description:

Lot to be fenced on three sides not on railroad with one 15-ft. gate.

Cost:

| | | |
|---|---|---|
| Fencing at $3.00 per ft.(36) | $ 1005.00 | |
| Gate | 60.00 | |
| Total | | $ 1065.00 |

| | |
|---|---|
| Grand Total | $ 9855.00 |

## F. Equipment Cost Calculations

**Sulfuric Acid Storage Tank:**

| | | |
|---|---|---|
| Tank cost(4) | $ 1800.00 | |
| Installation, 5%(36) | 90.00 | |
| Freight, 1-RR car, 150 miles | 97.10 | |
| Total | | $ 1987.10 |

**Oleum Storage Tank:**

| | | |
|---|---|---|
| Tank cost(4) | $ 360.00 | |
| Installation(36) | 18.00 | |
| Freight, $0.79/100-lb. x 36.00 x 0.79 | 28.40 | |
| Total | | $ 406.40 |

**Acid Air Pump:**

| | | |
|---|---|---|
| Total cost(4) | $ 335.00 | |
| Installation, 10%(36) | 33.50 | |
| Freight, 334-lb. at $0.79/100-lb. | 2.65 | |
| Total | | $ 371.15 |

**Chloral Hydrate Feed Hopper.**

| | | |
|---|---|---|
| Cost, 625-lb. x $0.17/lb.(4) | $ 106.00 | |
| Installation, 10%(36) | 10.60 | |
| Freight, $0.79/100-lb | 4.95 | |
| Total | | $ 121.55 |

### Drum Elevator:

| | | |
|---|---|---|
| Elevator Cost(36) | $ 350.00 | |
| Installation, 30%(36) | 105.00 | |
| Motor(36) | 37.00 | |
| Motor Installation(36) | 2.50 | |
| Freight, 1000-lb. at $0.79/100 | 7.90 | |
| Total | | $ 502.40 |

### Para-dichlorobenzene Feed Hopper.

| | | |
|---|---|---|
| Cost, 625-lb. x $0.17/lb.(4) | $ 106.00 | |
| Installation, 10%(36) | 10.60 | |
| Freight, 0.79/100-lb. | 4.95 | |
| Total | | $ 121.55 |

### Bucket Elevator.

| | | |
|---|---|---|
| Elevator cost(36) | $ 350.00 | |
| Installation, 30%(36) | 105.00 | |
| Motor(36) | 37.00 | |
| Motor Installation(36) | 2.50 | |
| Freight, 1000-lb. at $0.79/100-lb. | 7.90 | |
| Total | | $ 502.40 |

### Centrifuge.

| | | |
|---|---|---|
| Cost(36) | $ 3500.00 | |
| Installation costs, 10% | 350.00 | |
| Freight, 2000-lb. at $0.79/100-lb. | 15.80 | |
| Total | | $ 3865. 80 |

**Reactor.**

| | | |
|---|---|---|
| Cost(4) | $1260.00 | |
| Installation costs, 5%(36) | 63.00 | |
| Freight, 1 RR car, 150-miles | 97.10 | |
| Total | | $1420.10 |

**Reactor Agitator.**

| | | |
|---|---|---|
| List cost(4) | $ 320.00 | |
| Installation cost, 10%(36) | 32.00 | |
| Freight, 400-lb. at $0.79/100-lb. | 3.16 | |
| Total | | $ 355.16 |

**Reactor Pump.**

| | | |
|---|---|---|
| List cost(36) | $ 100.00 | |
| Installation cost, 10%(36) | 10.00 | |
| Motor cost(36) | 180.00 | |
| Motor installation cost(36) | 8.00 | |
| Freight, 2000-lb. at $0.79/100lb. | 15.80 | |
| Total | | $ 313.80 |

**Rotary Vacuum Filter No. 1.**

| | | |
|---|---|---|
| List cost(4) | $4950.00 | |
| Installation cost, 25%(36) | 1240.00 | |
| Motor cost(36) | 130.00 | |
| Motor Installation cost(36) | 3.50 | |
| Freight, 2000-lb. at $0.79/100-lb. | 15.80 | |
| Total | | $6339.30 |

### Filter Pump No. 1.

| | | |
|---|---|---|
| Pump cost(36) | $ 75.00 | |
| Installation, 10%(36) | 7.50 | |
| Motor cost(36) | 180.00 | |
| Motor installation(36) | 5.00 | |
| Freight, 1000-lb. at $0.79/100-lb. | 7.90 | |
| Total | | $ 275.40 |

### Chloral Pump.

| | | |
|---|---|---|
| List cost(36) | $ 25.00 | |
| Installation, 10%(36) | 2.50 | |
| Motor cost(36) | 37.00 | |
| Motor installation costs(36) | 2.50 | |
| Freight, 400-lb. at $0.79/100-lb. | 3.16 | |
| Total | | $ 70.16 |

### Rotary Vacuum Filter No. 2.

| | | |
|---|---|---|
| List cost(4) | $ 1400.00 | |
| Installation costs(4) | 366.67 | |
| Motor cost(36) | 23.00 | |
| Motor installation cost(36) | 3.50 | |
| Freight, 1000-lb. at $0.79/100-lb. | 7.90 | |
| Total | | $1801.07 |

**Filter Pump No. 2.**

| | | |
|---|---|---|
| Pump cost(36) | $ 50.00 | |
| Installation, 10%(36) | 5.00 | |
| Motor cost(36) | 130.00 | |
| Motor installation(36) | 3.50 | |
| Freight, 800-lb. at $0.79/100-lb. | 6.30 | |
| Total | | $ 194.80 |

**Wash Solution Tank.**

| | | |
|---|---|---|
| List cost(4) | $ 110.00 | |
| Installation cost, 5%(36) | 5.50 | |
| Freight, 1000-lb. at $0.79/100-lb. | 7.90 | |
| Total | | $ 123.40 |

**Wash Solution Pump.**

| | | |
|---|---|---|
| List cost(36) | $ 25.00 | |
| Installation cost, 10%(36) | 2.50 | |
| Motor cost(36) | 37.00 | |
| Motor installation cost(36) | 2.50 | |
| Freight, 400-lb. at $0.79/100-lb. | 3.16 | |
| Total | | $ 70.16 |
| Equipment total | | $ 841.70 |

**Process Piping.**

| | |
|---|---|
| Cost, 25% of equipment cost(37) | $4710.30 |
| **Grand Total** | $23552.00 |

## G. Labor Costs

| Name | Number | Section | Hr./day | Rate | Pay/yr. |
|---|---|---|---|---|---|
| Superintendent | 1 | Supervision | - | $4800/yr. | $4800.00 |
| Ass't. Sup't. | 1 | Supervision | 8 | 3600/yr. | 3600.00 |
| Supervisor | 2 | Supervision | 8 | 3000/yr. | 6000.00 |
| Operator | 3 | Reactor | 8 | 0.75/hr. | 4680.00 |
| Operator | 3 | Separatory | 8 | 0.75/hr. | 4680.00 |
| Laborer | 2 | Warehouse | 8 | 0.50/hr. | 2080.00 |
| Mechanic | 1 | Maintenance | 8 | 1.00/hr. | 2080.00 |
| Total labor costs per year............... | | | | | $32600.00 |

Note: Basis, 250 working days and 10 days vacation with pay per year.

## H. Summaries

### Raw Material Cost Summary

Basis: Pounds per 24-hour day of operation.

| | |
|---|---|
| Chloral hydrate | $ 6804.10 |
| Para-dichlorobenzene | 866.34 |
| Sulfuric acid (98%) | 82.10 |
| Soda Ash | 7.80 |
| Water | 0.45 |
| Electric power | 3.35 |
| Phone | 0.13 |
| Total cost per day | $ 7764.24 |

Annual cost of raw materials..........$ 1,941,060.00

Note: 250 working days per year.

## Building and Land Costs Summary

| | |
|---|---|
| Storage building | $ 5490.00 |
| Main building | 2400.00 |
| Land | 150.00 |
| Railroad siding | 750.00 |
| Fencing | 1065.00 |
| Total | $ 9855.00 |

## Equipment Cost Summary

| | |
|---|---|
| Sulfuric acid storage tank | $ 1987.10 |
| Oleum storage tank | 406.40 |
| Acid air pump | 371.15 |
| Wash solution storage tank | 123.40 |
| Wash solution pump | 70.16 |
| Drum elevator | 502.40 |
| Chloral hydrate feed hopper | 121.55 |
| Para-dichlorobenzene feed hopper | 121.55 |
| Reactor | 1420.10 |
| Reactor agitator | 355.16 |
| Reactor pump | 313.80 |
| Rotary vacuum filter no. 1 | 6339.30 |
| Filter pump no. 1 | 275.40 |
| Bucket elevator | 502.40 |
| Rotary vacuum filter no. 2 | 1801.07 |
| Filter pump no. 2 | 194.80 |
| Centrifuge | 3865.80 |
| Chloral pump | 70.16 |
| Process piping | 4310.30 |
| Total | $23552.00 |

## Labor Costs Summary

Basis: 250 working days and 10 days vacation with pay per year.

| | |
|---|---|
| Superintendent (1) | $ 4800.00 |
| Assistant superintendent (1) | 3600.00 |
| Supervisors (2) | 6000.00 |
| Reactor operators (3) | 4680.00 |
| Separator operators (3) | 4680.00 |
| Elevator operators (3) | 4680.00 |
| Warehouse laborers (2) | 2080.00 |
| Mechanic (1) | 2080.00 |
| Total labor costs per year | $32600.00 |

## I. Plant Location

In determining the best location for the BDT plant, the following factors were considered and evaluated:

1. Availability of raw materials. The raw materials are available in the Niagara Falls and the St. Louis areas. Total, 300 points.

2. Transportation. Transportation is available to nearly all parts of the country where the product will be needed. Since the product is to be less bulky than the raw materials, proximity to the raw material source will have the advantage over proximity to market. Total. 200 points.

3. Labor. Relatively small amount of both skilled and unskilled labor required. therefore labor should be equally available in both areas. Total, 50 points.

4. Water supply. No special chemical properties of water are required and the quantity requirements can be satisfied in either of the industrial areas, Total, 50 points.

5. Waste disposal. All of the plant wastes are liquids and non-corrosive in the concentrations discarded. There will be no health hazard or stream

pollution. Total, 100 points.

6. Power. Power requirements are low and can be equally satisfied in either location. The difference in rates between the two areas is small. Total, 50 points.

7. Market. Since the finished product will be less bulky than the raw materials required, it is of advantage for the plant to be located close to the raw material supply rather than to the market. Total, 100 points.

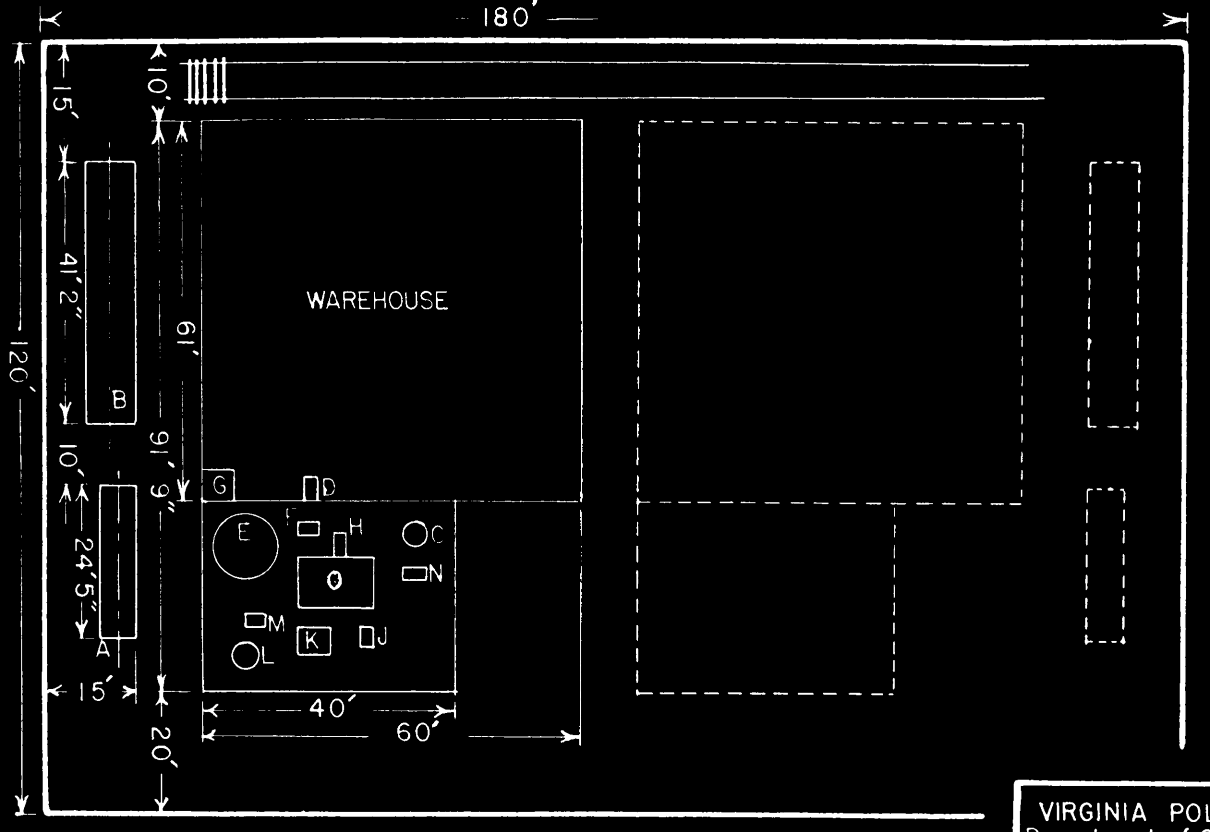
8. Climate. Climatic conditions will not affect the production and the costs of buildings will be affected but slightly in either area. Total, 50 points.

| Factor | Relat. Wt. | Niagara Falls | St. Louis |
|---|---|---|---|
| 1. Raw mat'ls | 300 | 300 | 290 |
| 2. Transport. | 200 | 175 | 150 |
| 3. Labor | 50 | 45 | 50 |
| 4. Water | 50 | 50 | 50 |
| 5. Waste Disp. | 200 | 190 | 200 |
| 6. Power | 50 | 45 | 50 |
| 7. Market | 100 | 90 | 50 |
| 8. Climate | 50 | 40 | 45 |
| Total | 1000 | 935 | 885 |

By an evaluation of the above factors, it was found that the best location of the BDT plant is in Up-state New York.

## J. Plant Layout and Elevation

Scale models of all the equipment were made in order to select the most efficient plant layout. The models were made to the scale of 1-in. = 1-ft. The units were set up so as to give the most compact arrangement possible and retain easy accessibility of equipment. Since no information is available as to the sulfuric acid recovery plant, no provisions were made for its location.

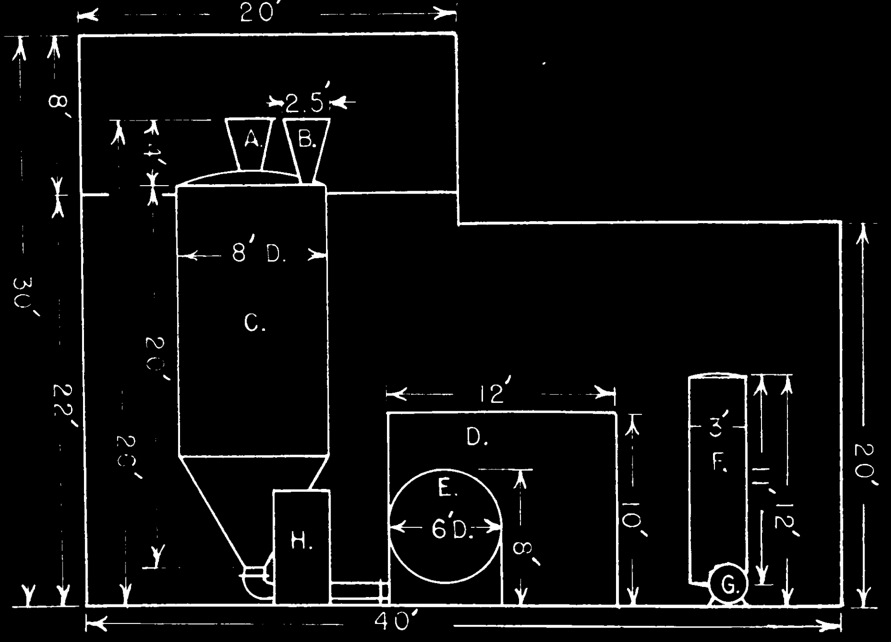


LEGEND
A. Oleum Storage
B. $H_2SO_4$ Storage
C. Soda Ash Tank
D. Keg Elevator
E. Reactor
F. Reactor Pump
G. Air Pump
H. Elevator
J. Filter Pump
K. Filter
L. Centrifuge
M. Chloral Pump
N. Wash Pump
O. Filter

VIRGINIA POLYTECHNIC INSTITUTE
Department of Chemical Engineering Lab.
Blacksburg, Virginia

PLAN VIEW OF BDT PLANT

Drawn By: J.H.G. Date: 8/29/46
Approved By: Date: 8/30/46
Scale: 1"= 30' Drawing No. 1



LEGEND:
- A. Chloral Feed Hopper
- B. $C_6H_4Cl_2$ Feed Hopper
- C. Reactor
- D. Filter No 1
- E. Filter No 2
- F. Soda Ash Tank
- G. Soda Ash Pump
- H. Centrifuge

VIRGINIA POLYTECHNIC INSTITUTE
Department of Chemical Engineering
Blacksburg, Virginia

ELEVATION VIEW OF BDT PLANT

Drawn By: J H G Date: 8/30/46
Checked By: Date: 9/1/46
Approved By: Date: 9/2/46
Scale: 1"=10' Drawing No. 2

## K. Schedule of Operation

Basis: One 6-hour cycle.

| Hours | 1-5 | 5.33 | 5.67 | 6.0 |
|---|---|---|---|---|
| Reactor, filling | | | ↔ | ↔ |
| Reactor, reaction | ↔ | | | |
| Reactor, emptying<br>Reactor pump | | ↔ | | |
| Filter No. 1 | | ↔ | ↔ | |
| Bucket elevator | | ↔ | ↔ | |
| Filter No. 2 | | ↔ | ↔ | |
| Wash solution pump | | ↔ | ↔ | |
| Centrifuge | | | ↔ | |
| Chloral pump | | | ↔ | ↔ |

## L. Preconstruction Cost Summary

| | | |
|---|---|---|
| 1. Raw Materials | | $1,941,060.00 |
| 2. Equipment | | 23,552.00 |
| 3. Buildings and Land | | 9,855.00 |
| 4. Labor and Supervision | | 32,600.00 |
| 5. Fixed Charges.(36) | | |
| Taxes at 2% on 60% of evaluation of L-2 and L-3 | $ 388.80 | |
| Insurance, 0.75%(L-2 - L-3) | 243.00 | |
| Depreciation: | | |
| Buildings and land, 5% | 492.75 | |
| Equipment, 33.3% | 7500.00 | |
| Social security: | | |
| 1½% on wages under $2500 per year ($18,200) | 273.00 | |
| Total fixed charges | $ | 8,897.55 |
| 6. Working Capital.(36) | | |
| Raw material costs | $ 1,941,060.00 | |
| Labor and supervision | 32,600.00 | |
| Fixed charges | 8,897.55 | |
| Incidentals | 2,000.00 | |
| Total working capital | | $1,984,557.55 |

## Capital Investment.

| | | |
|---|---|---|
| Land and building costs. | $ 9,855.00 | |
| Equipment costs.......... | 23,552.00 | |
| Working capital.......... | 1,984,557.55 | |
| Total............... | | $ 2,017,964.55 |

## Gross Income.

Annual production BDT... 1000 tons.

| | |
|---|---|
| Annual value at $1.98/lb........... | 3,960,000.00 |

## Annual Costs.

| | | |
|---|---|---|
| Annual operating costs: | | |
| Raw materials..... | $ 1,941,060.00 | |
| Labor............. | 32,600.00 | |
| Fixed charges, management and distribution, 25% on gross income.... | 990,000.00 | |
| Total............... | | $ 2,963,660.00 |

## Net Income.

| | | |
|---|---|---|
| Annual value product... | $ 3,960,000.00 | |
| Annual costs............ | 2,963,660.00 | |
| Net income........ | | $ 996,340 .00 |

## Break-even Price.

| | |
|---|---|
| At 6% on capital investment, price per pound............. | $ 1.55 |

# IV. DISCUSSION

## A. Discussion of Results

Effect of the Length of Time on the Chloral Reaction. Using an excess of chlorine, 1500 cc. of acetaldehyde was chlorinated to chloral by recycling the acetaldehyde through a chlorinating column for five hours and bubbling chlorine through the acetaldehyde counter-current to its flow. No fresh acetaldehyde was added during the first hour of chlorination but after that time and for the duration of the run, 250 cc. per hour of fresh acetaldehyde was added as feed. By the determination of the boiling points and specific gravities of the hourly samples taken, it was found that the chlorination of acetaldehyde proceeded vigorously during the first hour of the run and the heat of reaction caused the reaction mixture temperature to increase from 32° F. to 104° F. After the first hour, chlorination proceeded slowly and was accompanied by the formation of tarry materials. At the end of five hours of chlorination, the product was a black, viscous liquid which contained no filterable solids. The reaction mixture was circulated during the chlorination by a bronze gearless pump. The copper in the bronze reacted with the hydrogen chloride formed by the reaction to give cupric chloride which deposited on the glass beads in the column. There was an appreciable erosion of the pump during the reaction runs. The specific gravity of the chlorinated product increased from 0.783 to 1.1076 in the first hour of chlorination and from 1.1076 to 1.2959 in the next four hours of chlorination. Part of the latter increase was probably due to polymerization. The boiling point of the mixture increased from 68° F. to 113° F. during the first hour of reaction and to 148° F. after five hours. Upon analysis, it was found that 53.45% of the chlorinated product was chloral.

Effect of Temperature on the Chloral Reaction. By making two runs at various temperatures, it was found that for best results the temperature in the first phase of the reaction should not exceed 96° F. and the temperature in the second phase should not exceed 114° F. In the first phase of the reaction in which fresh acetaldehyde was added as feed, it was found that if the temperature of the reacting mixture was above 96° F., the pressure developed by the boiling of the added acetaldehyde was so great that it stopped the circulation of the reaction mixture. In the second phase of the reaction, tarry products were produced by increasing the temperature from 114° F. to 120° F.

Investigation of the Catalyst to be Used in the Condensation Reaction. Four solutions were made up, in each of which was 240 cc. of chlorinated acetaldehyde product containing chloral, 294 grams of para-dichlorobenzene, and 400 cc. of methanol. The methanol was used as a solvent for the para-dichlorobenzene. To one solution was added 64 cc. of 98% sulfuric acid (sp. gr. 1.84) as catalyst and the mixture reacted for four and one-half hours at 130° F. The reaction had to be stopped at the end of four and one-half hours because the viscosity of the reacting materials became so great that it would have been impossible to remove the plastic product from the reaction vessel if the reaction had continued for the remainder of the seven hours. Polymerization of the reacting materials occurred and a plastic material resulted upon cooling to 85° F. Forty-four and forty-five one-hundredths grams of anhydrous aluminum chloride, reagent grade, Code 1230, was added to the second solution as catalyst and the mixture reacted at 130° F. for seven hours; a crystalline condensation product resulted but could not be separated from the needle-like crystals of para-dichlorobenzene by use of selective solvents. The solvents used were methanol, benzol, carbon tetrachloride, petroleum ether, methanol and benzol, carbon tetrachloride and benzol, and petroleum ether and methanol. When 45.43 grams of anhydrous zinc chloride, prepared by heating zinc chloride for 18 hours at 266° F., was reacted with the third solution for eight hours at a temperature of 130° F., a similar unseparable condensation product was formed. This reaction was continued one hour beyond the seven hours because other work made it impractical to stop it at the end of seven hours. The fourth solution was held at a temperature of 130° F. for seven hours without a catalyst and as no appreciable reaction had taken place, the time of reaction was extended to 24 hours without any appreciable reaction taking place.

Per Cent of Condensation Reaction Product. Since it was impossible, in reactions in which the chlorinated acetaldehyde product was used to supply the chloral needed for the reaction, to separate the condensation product from the unreacted para-dichlorobenzene in order to make a quantitative determination, two runs were made using chloral hydrate to supply the necessary chloral. The conditions used were the optimum determined for the production of DDT by J. E. Bryan(4), except that para-dichlorobenzene was substituted for chlorobenzene in equivalent molar quantities. One run was made for a period of five hours (optimum time as given by Bryan) and a second made for 24 hours in order to get an indication of the effect of time on the reaction. No solvent was added for the para-dichlorobenzene and the unreacted portion remained in lump form. The condensation reaction product, 2,2 bis(2,5 dichlorophenyl) 1,1,1 trichloroethane, was in cubic crystalline form and had a melting point of 112° F. It was easily separated from the larger para-dichlorobenzene lumps by washing with water. It was found that processing for five hours on a one mole basis produced 25.6 grams of condensation product and processing for 24 hours produced 36.2 grams.

### The Effect of Sunlight on the Chloral Reaction.

By putting 100 cc. of acetaldehyde in a one-gallon glass jug and allowing it to vaporize, then adding sufficient chlorine gas to give the gaseous mixture an orange color, it was found that chlorine and acetaldehyde react with explosive violence when sunlight is present. The reactants were put into the jug in a room lighted by indirect daylight and no appreciable reaction occurred in the time required for the filling but immediately the jug was placed in direct sunlight, an exothermic reaction took place with sufficient violence to blow the top off the jug. The products formed by the reaction were carbon and tarry materials. Another one-gallon jug was similarly filled with acetaldehyde and chlorine and placed in a dark locker for 24 hours. This reaction produced a straw colored liquid which showed no evidence of carbonization.

## B.. Recommendations

It is recommended that further study be made on the following problems:

1. The chlorination of acetaldehyde in the vapor phase should be attempted because of the difficulty of controlling acetaldehyde in the liquid phase. The heat of reaction of the chlorination of acetaldehyde is sufficient to vaporize the acetaldehyde and make it difficult to recycle it in order to obtain uniform results.

2. In the initial phase of chlorination of liquid acetaldehyde to chloral, samples should be taken at fifteen minute intervals and the per cent of chloral determined as well as the specific gravities and boiling points of the solution in order to get an accurate log of the progress of the reaction.

3. Effect of catalysts, such as iron chloride, anhydrous aluminum chloride and others, on the rate of chlorination of acetaldehyde and on the per cent of chloral formed in the chlorinated product requires further attention.

4. Effect of temperature, from 32° F. to 68° F., on the condensation of chloral and para-dichlorobenzene in the presence of 98% sulfuric acid for reaction periods of eight hours and under has not been determined.

When these materials are reacted for a period greater than eight hours, excessive polymerization results and a plastic product is formed.

5. The separation of 2,2 bis(2,5 dichlorophenyl) 1,1,1 trichloroethane from the unreacted para-dichlorobenzene should be attempted by use of selective solvents such as chlorinated naphthalenes and benzenes. The structural characteristics of the chlorinated naphthalenes and benzenes are similar to those of para-dichlorobenzene and dissimilar to those of 2,2 bis(2,5 dichlorophenyl) 1,1,1 trichloroethane; therefore these liquids should show a selective solvent action towards para-dichlorobenzene.

6. A complete chemical analysis of the products of the condensation reaction is necessary in order to obtain a complete understanding of the progress of the reaction. Since the purpose of this investigation was to obtain data for the design of a commercial plant for the production of BDT, no analyses of the products of reaction were required.

7. Bronze was recommended as a material of construction(28) for use where chlorine and hydrogen chloride are to be handled but it did not stand up under those chemicals in the chlorination of acetaldehyde.

A wiping action was present and the bronze pump contaminated the product. An aluminum rotor used in the pump during the final runs showed no signs of erosion and it is suggested that experiments be made to determine the feasibility of using aluminum or any other practicable metal as a material of construction.

## V. CONCLUSIONS

From the results of the investigation the following conclusions were drawn:

1. By chlorinating 1500 cc. of acetaldehyde at 96° F. with an excess of chlorine gas, it was found that the specific gravity of the chlorinated product increased from 0.783 to 1.1076 in the first hour of chlorination and from 1.1076 to 1.2959 in the next four hours of chlorination. The boiling point of the mixture increased from 68° F. to 113° F. during the first hour of reaction and to 148° F. after five hours.

2. By chlorinating 1500 cc. of acetaldehyde with an excess of chlorine gas for five hours at a temperature of 96° F., analysis indicated that 53.45% of the chlorinated product was chloral.

3. By making two five-hour runs, each using 1500 cc. of acetaldehyde and an excess of chlorine gas but having reaction temperatures of 96° F. and 100° F., respectively, in the first phase and reactiontemperatures of 114° F. and 120° F., respectively, in the second phase, it was found that if the reaction temperature in the first phase was above 96° F., fresh acetaldehyde added as feed boiled with sufficient vigor to stop the flow of feed. If the temperature in the

second phase of the reaction was above 114° F., tarry products were formed.

4. The condensation of 294 grams of para-dichlorobenzene with 240 cc. of the chlorinated acetaldehyde product containing chloral at 130° F. for eight hours was catalyzed by 44.45 grams of anhydrous aluminum, sublimated, and 45.43 grams of anhydrous zinc chloride and a crystalline product resulted. The product crystals could not be separated from the unreacted para-dichlorobenzene crystals by the use of methanol, benzol, carbon tetrachloride, petroleum ether, methanol, and benzol, carbon tetrachloride and benzol, and petroleum ether and methanol as selective solvents.

5. When the condensation of para-dichlorobenzene with the chlorinated acetaldehyde product containing chloral was catalyzed with 64 cc. of 98% sulfuric acid (sp. gr. 1.84) and reacted for four and one-half hours at 130° F., polymerization of the reacting materials occurred and a plastic material resulted.

6. When no catalyst was used in the condensation of para-dichlorobenzene with the chlorinated acetaldehyde product containing chloral at a reaction temperature of 130° F., no appreciable reaction had occurred after 24 hours.

7. By condensing 294 grams of para-dichlorobenzene with 170 grams of chloral hydrate in the presence of 100 cc. of 98% sulfuric acid (sp. gr. 1.84) and 300 cc. of oleum (20% $SO_3$) at room temperature, it was found that five hours of reaction produced 25.6 grams of BDT and 24 hours of reaction produced 36.2 grams.

8. By putting 100 cc. of acetaldehyde in a one-gallon glass jug and allowing it to vaporize, then adding sufficient chlorine gas to give the gaseous mixture an orange color, it was found by placing the jug in direct sunlight that acetaldehyde and chlorine react with explosive violence when catalyzed by sunlight.

9. The designed plant has a capacity of 2700 pounds of BDT per day and requires a capital investment of $2,017,964.55, an annual cost of $2,963,660.00 and a profit of $996,340.00 per year.

10. The break-even selling price of the product producing six per cent return on the capital investment is $1.55 per pound.

## VI. SUMMARY

The discovery of the insecticidal properties of DDT by Mueller of Switzerland(5) started a wave of research on the pesticidal properties of similar materials in the hope of finding a compound with superior properties to those of DDT. To date no published work has been done on 2,2 bis(2,5 dichlorophenyl) 1,1,1 trichloroethane but its structural characteristics indicate that it has superior pesticidal qualities to those of DDT.

The purpose of this investigation was to design a plant for the commercial production of 1000 tons of BDT per year. Research was conducted to determine operating conditions for the production of chloral from acetaldehyde and chlorine gas, for the production of BDT from the chlorinated acetaldehyde product and para-dichlorobenzene, and for the production of BDT from chloral hydrate and para-dichlorobenzene using 98% sulfuric acid and oleum (20% $SO_3$) as dehydrating agents and carriers.

The studies of the manufacture of chloral by chlorination of acetaldehyde showed that the best tested conditions for the chlorination of 1500 cc. of acetaldehyde when using an excess of chlorine gas and a reaction period of five hours were temperatures of 96° F. and 114° F. in the first two and last three hours of the reaction, respectively.

The investigation of the production of BDT by condensing 294 grams of para-dichlorobenzene with 240 cc. of chlorinated acetaldehyde product for eight hours at a temperature of 130° F. indicated that greatest yield of BDT occurred when 44.45 grams of anhydrous sublimated aluminum chloride or 45.43 grams of anhydrous zinc chloride was used as catalyst. The BDT produced could not be separated from the unreacted para-dichlorobenzene crystals by use of methanol, benzol, carbon tetrachloride, petroleum ether, methanol and benzol, carbon tetrachloride and benzol, and petroleum ether and methanol as selective solvents.

The studies of the production of BDT by reacting 294 grams of para-dichlorobenzene and 170 grams of chloral hydrate in the presence of a mixture of 100 cc. of 98% sulfuric acid and 300 cc. of oleum (20% $SO_3$) at a temperature of 80° F. showed that five hours of reaction produced 25.6 grams of BDT and that 24 hours of reaction produced 36.2 grams of BDT.

The plant for the commercial production of BDT was designed using the data obtained from the condensation of para-dichlorobenzene with chloral hydrate as indicated above.

Preconstruction cost accounting of the designed plant indicates an annual cost of $2,017,964.55 and a surplus of $996,340.00 per year. This is based on a selling price of $1.98 per pound for the BDT.

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