W. G. KRUMMRICH PLANT

A RECONSTRUCTION OF PROCESS DEVELOPMENT FOR PRODUCTION OF ESTERS OF 2,4,5-TRICHLOROPHENOXYACETIC ACID (2,4,5-T ACID ESTERS)

In 1960, production of the butyl, isobutyl and isooctyl esters of 2,4,5-T acid was initiated in Dept. 268 of the Krummrich plant.

Dept. 268 was also the site for the production of other esters.

In 1965 and 1969, revised Standard Manufacture Processes were issued for the butyl and isobutyl esters, which incorporated minor cost saving process changes. Copies of the 1965 processes were not located. No revised process incorporating these changes in the isooctyl ester manufacture was issued. This may imply that production of this ester ceased prior to 1969. However, production of all three esters had definitely stopped by 1970 according to our "Sources of Product Information" book.

Over the years, the basic chemistry for the production of these esters did not change. The 2,4,5-T acid was reacted with the appropriate alcohol using a small amount of sulfuric acid as catalyst. The reaction was originally driven to completion by removing the binary alcohol/water azeotrop and, on cooling and separating, recyling the alcohol. The 1969 processes for the butyl and isobutyl esters used toluene as a solvent for increased efficiency in driving the reaction to completion and in the water/alcohol separation. When the reaction was complete, the toluene and excess alcohol were stripped off and the sulfuric acid in the product neutralized by cyclohexylamine. Specific details and flow charts representative of the processes are attached.

Dept. 268 - Process Description

ISOOCTYL 2,4,5-T

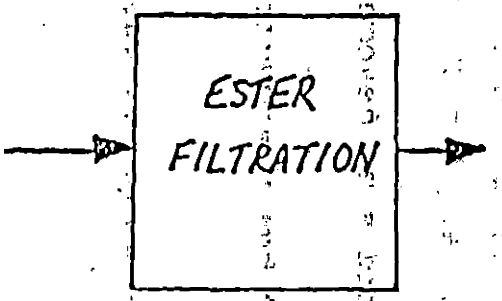
SYNOPSIS OF PROCESS

2,4,5-Trichlorophenoxyacetic acid is esterified with Isooctyl alcohol in the presence of sulfuric acid catalyst. The reaction is carried out at 200 mm. pressure and 135 to 140°C.

The water of reaction is removed as a binary azeotrope with the alcohol. The column is not used for isooctyl esters. Condensed azeotrope is separated continuously and the alcohol layer returned to the reactor.

Exact quantities of raw materials are used as any excess alcohol is difficult to strip off.

At the completion of the reaction the batch is pumped to the neutralizer, neutralized with cyclohexylamine, filtered and pumped to a steel storage tank, tank cars, tank trucks or 55 gallon drums.



(145 FT.^{2} HORIZONTAL TANK, VERTICAL LEAF FILTER)

FLOW SHEET
Iso Octyl 2,4,5-T

Dept. 268 - Process Description

ESTERS

SYNOPSIS OF PROCESS

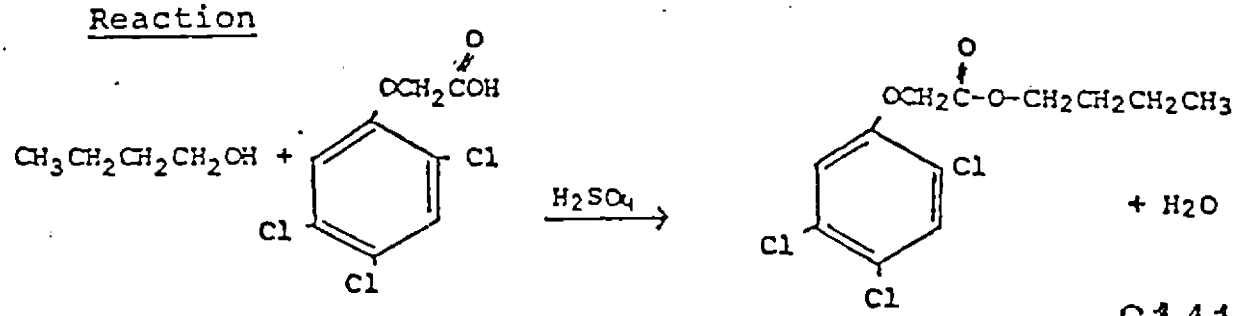
A. General

2,4,5-Trichlorophenoxyacetic Acid is esterified with butyl alcohol or isobutyl alcohol in the presence of sulfuric acid and toluene. The sulfuric acid functions as a catalyst and toluene as a solvent for increased efficiency in water-alcohol separation. The reaction is carried out at 580 mm Hg. abs. pressure and 130°C - 140°C.

Complete reaction occurs through use of excess alcohol and constant removal of water. The alcohol, toluene and water vapors are condensed and separated, and the alcohol - toluene mixture refluxed back to the reactor. Prior to the reaction step, the particular acid, alcohol and toluene are premixed (at atmospheric pressure and 70°C). At the completion of the reaction, excess alcohol and toluene are stripped from the batch by maintaining the reactor at 50 mm Hg. abs. pressure and 140 - 150°C for two hours. Cyclohexylamine is then added to neutralize the H_2SO_4 and stabilize the batch. After filtration, the batch is pumped to storage, tank cars, tank trucks, or 55 gallon drums.

B. Butyl 2,4,5-T Ester

Reaction



Butyl Alcohol	2,4,5-T	Butyl 2,4,5-T Ester	Water
Mol. Wt. 74.12	Mol. Wt. 255.45	Mol. Wt. 311.56	Mol. Wt. 18.01

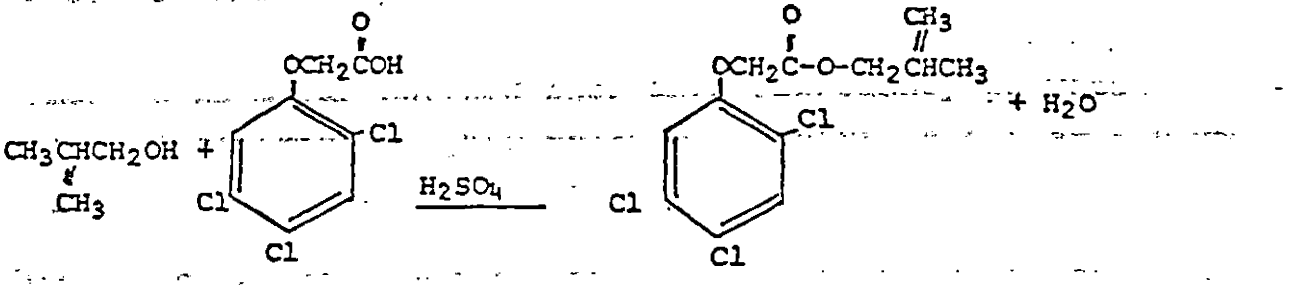
Dept. 268 - Process Description

ESTERS

SYNOPSIS OF PROCESS

C. Isobutyl 2,4,5-T Ester

Reaction



Isobutyl Alcohol	2,4,5-T	Isobutyl 2,4,5-T Ester	Water
Mol. Wt. 74.12	Mol. Wt. 255.45	Mol. Wt. 311.56	Mol. Wt. 18.01

FLOW SHEETS

A. Slurry (Pre-Mix)

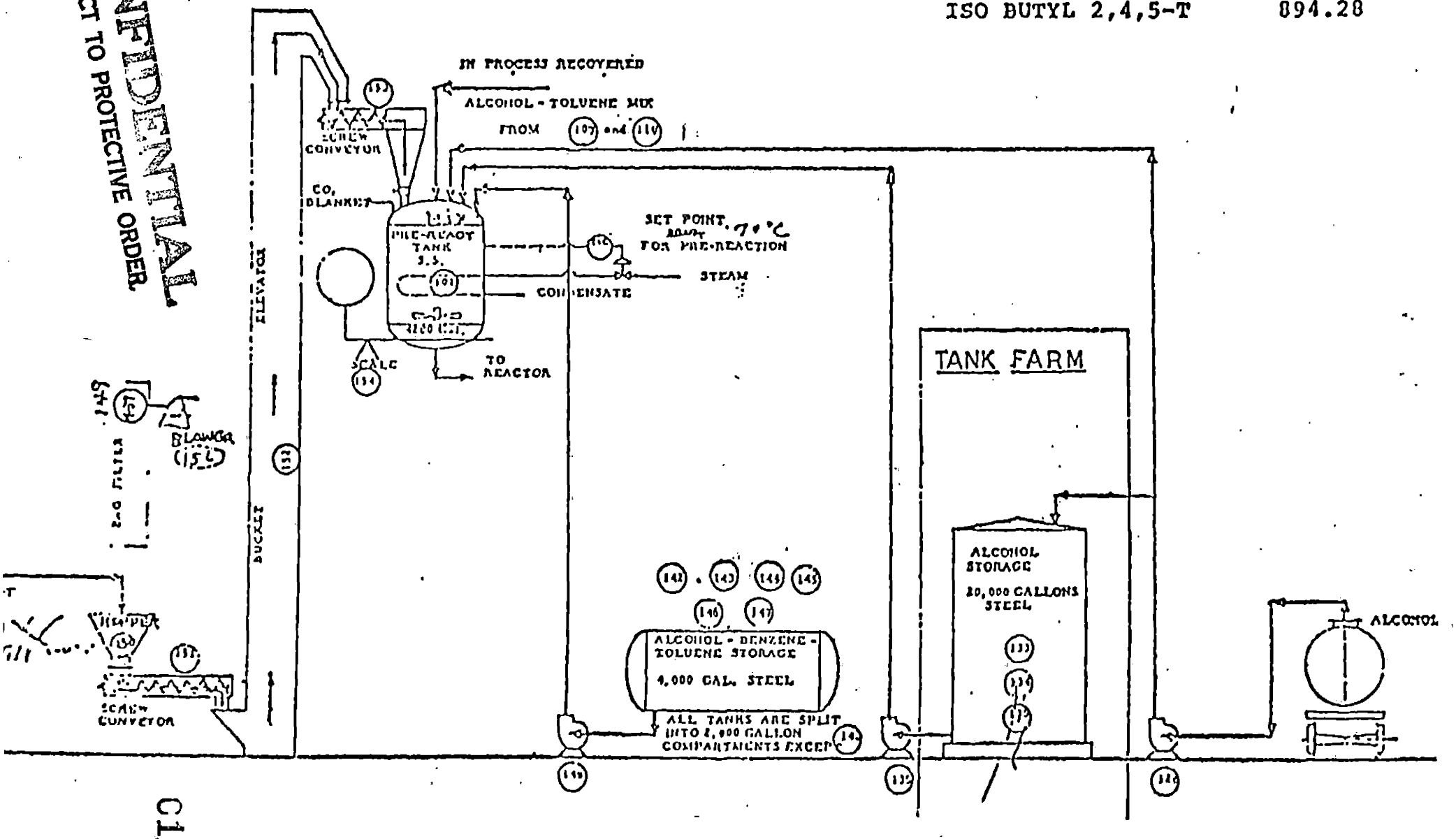
B. Reaction

C. Neutralization and Filtration

A. PRE-MIX (SLURRY)

DEPT.268

BUTYL 2,4,5-T	894.12
ISO BUTYL 2,4,5-T	894.28

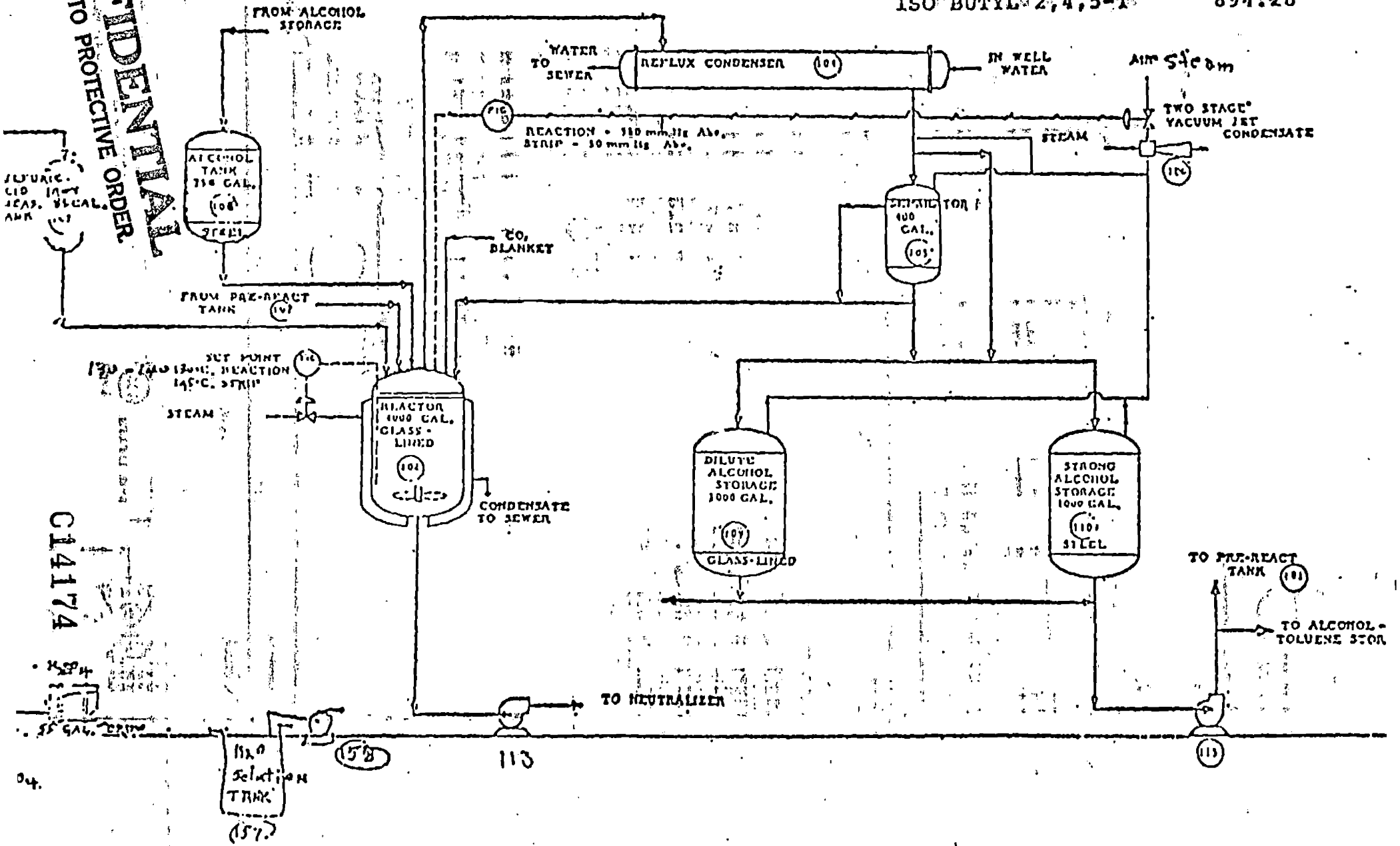


B. REACTION

DEPT. 268

BUTYL 2,4,5-T 894.12

ISO BUTYL 2,4,5-T 894.28



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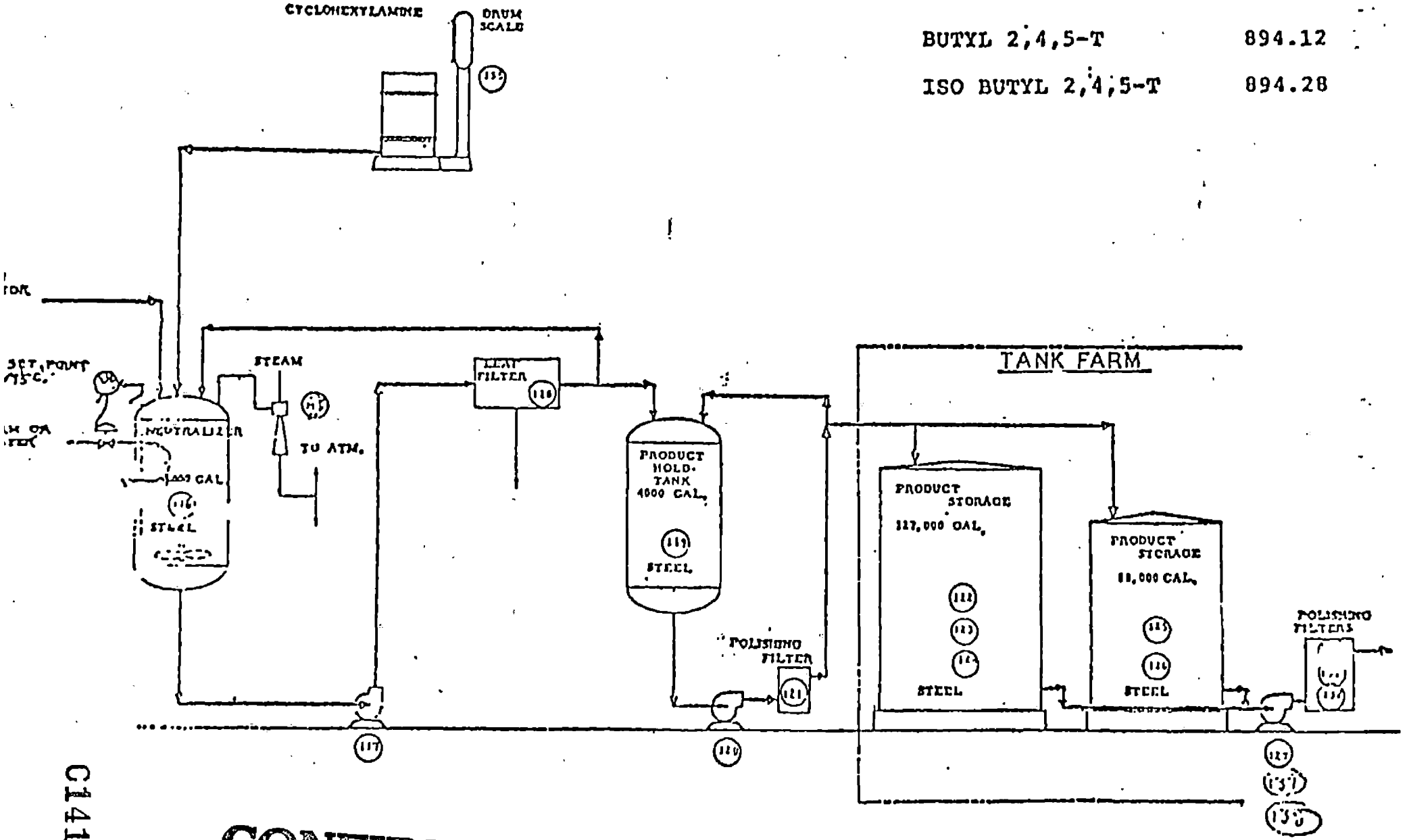
C. NEUTRALIZATION & FILTRATIO
DEPT. 268

BUTYL 2,4,5-T	894.12
ISO BUTYL 2,4,5-T	894.28



Dept. 268 - Proces Description

ESTERS

PROCESS IN DETAIL

A. Pre-Mix (Slurry Tank)

General

Butyl alcohol or Isobutyl alcohol and 2,4,5-Trichlorophenoxyacetic acid are charged by weight according to the scale on which the slurry tank is mounted. The slurry tank is 316 S.C. 4000 gallons, with heating coils and agitator. The temperature is controlled at 70°C.

The alcohol and toluene charge is made up by pumping recovered alcohol and toluene from the strong tank. This material is analyzed for alcohol and toluene composition. The appropriate amount of fresh alcohol and toluene are added to complete the charge. Then 2,4,5-T is charged via the conveying system. When the proper amount of 2,4,5-T has been added, as determined by the scale setting, the conveying system will automatically shut off. At this time the knife valve on the slurry tank is closed to prevent vapors from entering the conveying system. A constant CO_2 gas purge is maintained on the slurry tank.

B. Reaction

The slurry tank is dropped to the reactor by gravity and vacuum on the reactor. After the weigh tank mix is charged to the 4,000 gallon glass-lined reactor, 20 lbs. of sulfuric acid (6 inches on gage) are added. The vacuum controller is set at 580 mm Hg. abs. pressure and the reactor heated to 130 - 140°C. Vapors from the reactor are condensed in a Karbate condenser, and separated in a 400 gallon stainless steel tank. The top layer of alcohol and toluene is refluxed back to the reactor. The water layer, containing the water of reaction and some alcohol and toluene, is periodically

Dept. 268 - Process Description

ESTERS

PROCESS IN DETAIL

B. Reaction (continued)

drained to the 1,000 gallon glass lined, dilute alcohol tank to prevent the water from accumulating in the separator and being refluxed back to the reactor.

The reaction takes place at 580 mmg Hg. abs. pressure and 130 - 140°C. in the presence of 0.2 mole H_2SO_4 catalyst. Vapors of alcohol, toluene, and water are condensed, separated, and the alcohol - toluene mix refluxed back to the reactor.

Following reaction, excess alcohol and toluene are stripped from the batch, condensed, and collected in the 1,000 gallon steel, strong alcohol tank. The temperature controller is adjusted to 145°C and the pressure controller set at 50 mm Hg. abs. pressure. During the 2 hour strip period, total reflu is stopped and both the separator and weak alcohol tank are by-passed. At the end of the strip period, the vacuum is released by addition of CO_2 to the reactor.

If at the end of two hours there is an appreciable flow of condensed alcohol and toluene from the condensor the strip period should be extended.

The bottom (water) collected in the weak alcohol tank during refluxing is drained. The remaining alcohol and toluene are used to charge the weigh tank. The alcohol and toluene collected in the strong alcohol tank during stripping operations are also recharged to the weigh tank. These two sources of alcohol and toluene comprise the recovered alcohol which was previously discussed.

ESTERS

PROCESS IN DETAIL

C. Neutralization and Filtration

Catalyst and other acidic compounds are neutralized by the addition of cyclohexylamine to the 4,000 gallon, steel, neutralizer. The batch is agitated for 30 minutes and sampled. The analyses are performed in the laboratory. If excess cyclohexylamine is less than 0.01% additional lbs. of cyclohexylamine are added. The batch is again agitated for 30 minutes and resampled. This continues until the batch is within specifications for excess cyclohexylamine.

The batch is circulated through the filter until the forward flowing stream from the filter is clear. Complete analysis of the finished, filtered ester is determined by the laboratory. The filter is a Shriver horizontal tank, vertical leaf pressure filter. The screens are 304 S.S. 24 x 110 mesh. No precoat is necessary.

The batch is then pumped to the 4,000 gallon, steel, product hold tank, drummed, pumped to tank trucks, tank cars, or to either 127,000 gallon or 88,000 gallon steel storage tanks. The ester is passed through a 25 micron cartridge polishing filter before being shipped by drum, tank car or tank truck, or stored in the storage tanks.

A RECONSTRUCTION OF PROCESS DEVELOPMENT FOR PRODUCTION OF PENTACHLOROPHENOL AND SODIUM PENTACHLOROPHENATE

Pentachlorophenol and its Variants

The production of pentachlorophenol apparently began in 1938 in the W Building pilot plant at the Queeny plant to provide sales development quantities. At that time, pentachlorophenol was called Santophen 20. The sodium salt, called Santophen 20S, and a pine oil/alcohol/pentachlorophenol mixture, called Santophen 20 P.A., were also made. Within a year, full production was started at the Krummrich plant.

It appears that pentachlorophenol (later called Penta) was marketed in flake form from 1939 until the late 1950s or early 1960s. Then Penta as well as Penta 60 (so called because it contained around 60% pentachlorophenol) were offered in prilled form and the flaking operation discontinued. From 1970, Penta was also offered in 2000 lb. blocks as well as the prilled form. The sodium salt of Penta (later called Santobrite) was produced in powder, briquette and 30% aqueous solution forms throughout its history. Apparently, Santophen 20 P.A. was only offered for a few years. The production of Santobrite was discontinued in 1975; Penta and Penta 60 in 1978.

Over the years, the chemistry for the production of Penta and Santobrite remained essentially the same. Phenol, or chlorophenol fractions from the production of o- and p-chlorophenol or 2,4-dichlorophenol was progressively chlorinated with subsequent increases in reaction temperature until the appropriate crystallization point was reached (for Penta, 174-182°C; for Penta 60, 145°C). Iron powder was first used as catalyst; later, aluminum. Santobrite was simply the neutralization of Penta with sodium hydroxide.

In 1972, sublimation of the prilled Penta was reduced by addition of Provalent 4A oil and more effectively by Humble NU50-38 oil.

The evolution of the pentachlorophenol and sodium pentachlorophenate processes follows.

Record of J.F. Queeny Pilot Plant (W Building) Demonstration of the Pentachlorophenol Process (1938)

309 batches of pentachlorophenol and seven of tetrachlorophenol were made on this job. 57,851 lbs. of phenol, 87,903 lbs. of Plant B dichlor fractions and 441,141 lbs. of trichlorophenol were used as crude material to be chlorinated and 774,545 lbs. of pentachlorophenol and tetrachlorophenol were produced.

The quality of the pentachlorophenol was consistently better than that previously produced in the laboratory. A crystallizing point (C.P.) within about 1°C of that desired was consistently obtained. This was not achieved in laboratory work.

Alkali insoluble content was consistently much lower than that obtained in the laboratory ranging from 1-2% compared to 10-12% in the laboratory.

General Outline of Pentachlorophenol Process Demonstration at the W.G. Krummrich Plant (1938-39)

Phenol is chlorinated in a monel chlorinator, iron powder being used as a catalyst. Temperature is maintained at 60-65°C during chlorination to trichlorophenol, 65-70° from trichlor to tetrachlor and slowly raised to 190° during chlorination to pentachlorophenol, keeping 10-15° above the C.P.

The HCl evolved is purified by passing through phenol to remove free chlorine, through a system of coolers and H_2SO_4 scrubber to remove phenol.

The pentachlorophenol is flaked into containers or run molten into a lye solution to form sodium pentachlorophenate. The alkalinity of this solution is adjusted as required, the solution filtered and evaporated to dryness on a double drum dryer. The dry material is packed directly or briquetted and then packed.

Chlorinations were started on October 11, 1938. When the second chlorinator was installed it was made with a hemispherical downward dish and central drain so that it would drain clean. The plan was to chlorinate to trichlorophenol in the first chlorinator, in the absence of iron, and complete the chlorination in the second chlorinator. This was done in five batches and the color somewhat improved. Failure of the stirrer in the first chlorinator necessitated complete chlorination in the second chlorinator and it was found that the same improved color was maintained in a single step chlorination in this chlorinator as were observed in the two step chlorination.

Following installation of the second chlorinator the scrubber phenol from each batch was incorporated in the charge for the succeeding batch without difficulty. Flaking of the product offered no particular problem.

The neutralization of pentachlorophenol with NaOH to form the sodium salt offered no particular problem other than control of the alkalinity. Use of a control test involving titration to the phenolphthalein endpoint proved unreliable and equipment for plant control by means of potentiometric titration was developed.

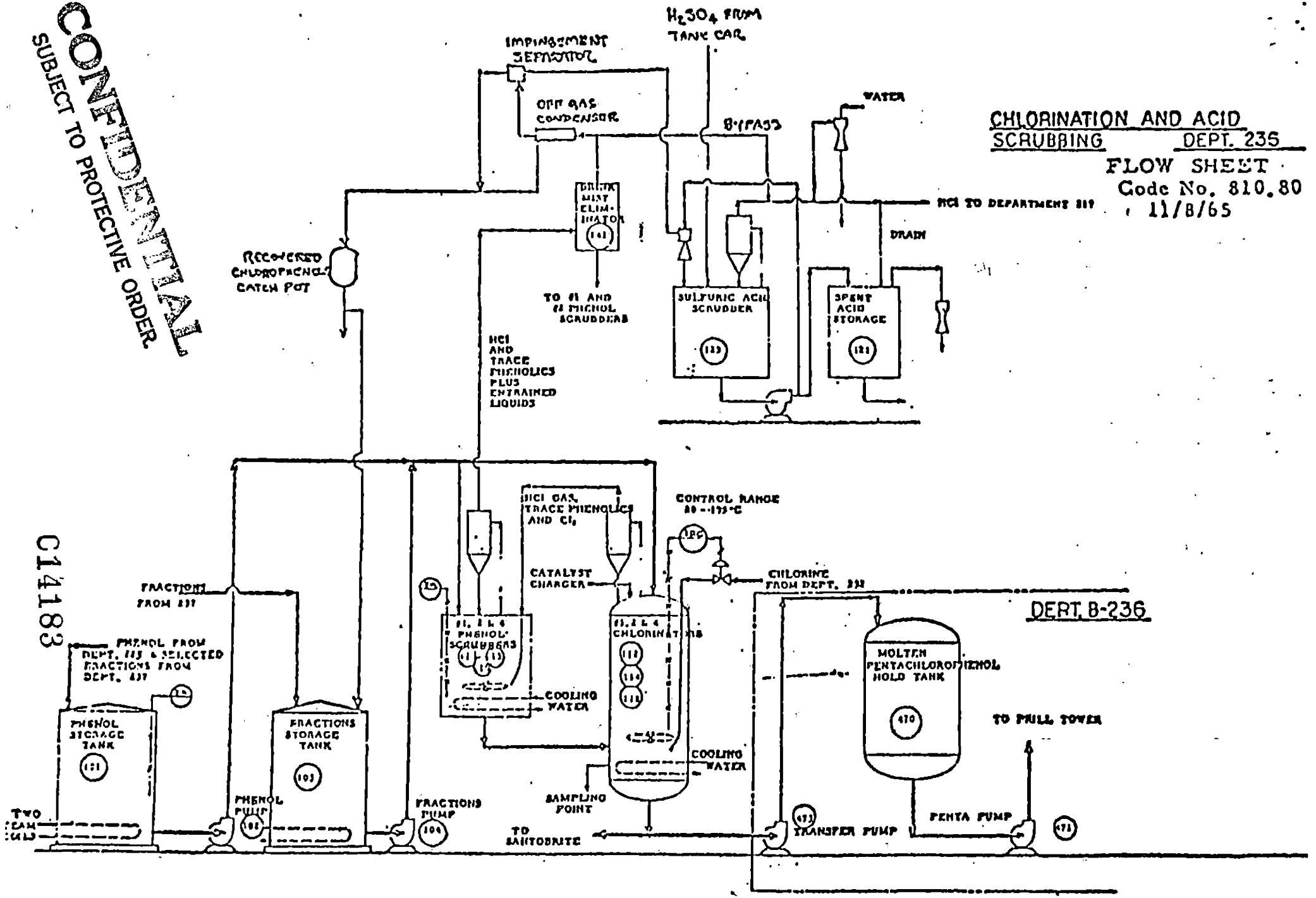
PROCESS FLOW SHEETS (1965) FOR:

Pentachlorophenol Molten

Pentachlorophenol Prilling & Packaging

CONFIDENTIAL
SUBJECT TO PROTECTIVE ORDER

C14183



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SUBJECT TO PROTECTIVE ORDER.

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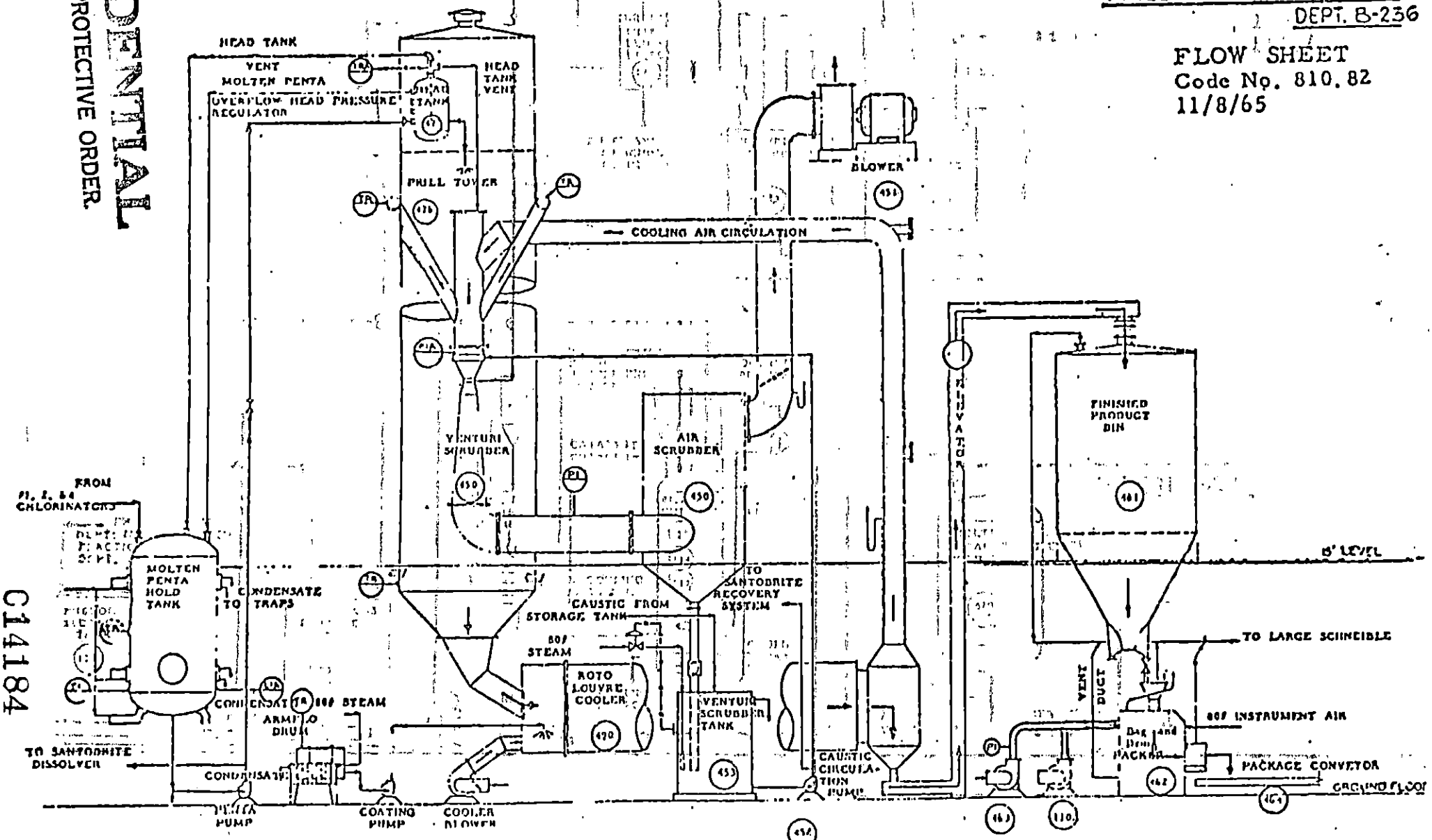
PRILLING AND PACKAGING

DEPT. B-236

FLOW SHEET
Code No. 810.82
11/8/65

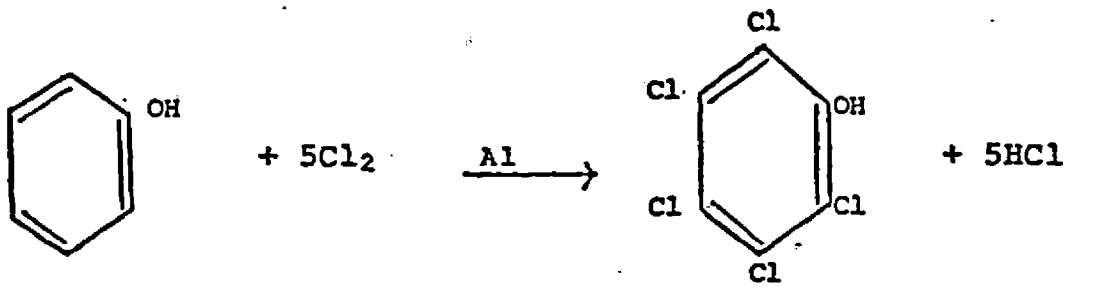


SYNOPSIS OF PROCESS

Dept. 236 (Molten Penta)

Molten Pentachlorophenol is produced by the batchwise chlorination of phenol or chlorophenol fractions from the refined chlorophenols operation. Aluminum catalyst is added at the dichlor stage. When the crystallizing point reaches the range 174° - 182°C, the chlorination is stopped.

The basic reaction for the process is:



Phenol (Liquid) (94.05) | Chlorine (Gas) | Pentachlorophenol (Molten) (266.29) | Hydrogen Chloride (Gas) (36.46)

The molten Penta is then transferred to the hold tank for use in Santobrite Solution, Prill Penta or cast into blocks.

The by-product HCl produced in the chlorination reaction is scrubbed in successive phenol and sulfuric acid scrubbers.

Dept. 226 (Prilled Penta)

Prilled Pentachlorophenol is produced by dispersing molten Penta into fine streams using a "shower head" type prill plate, and causing the molten streams to solidify by cooling with ambient air. The cooling chamber is an 8' diameter x 40' high prill tower. As the prills fall through the tower, they solidify and then pass from the tower into a Roto-Louvre cooler for further cooling.

The prills are then conveyed in a bucket elevator to a storage hopper to await packaging. The prills are packaged into bags or fibre paks using a St. Regis pneumatic packer.

The air used for cooling in the prill tower and cooler passes through a Venturi scrubber where it is scrubbed with a dilute caustic solution.

Dept. 236 (Penta 60)

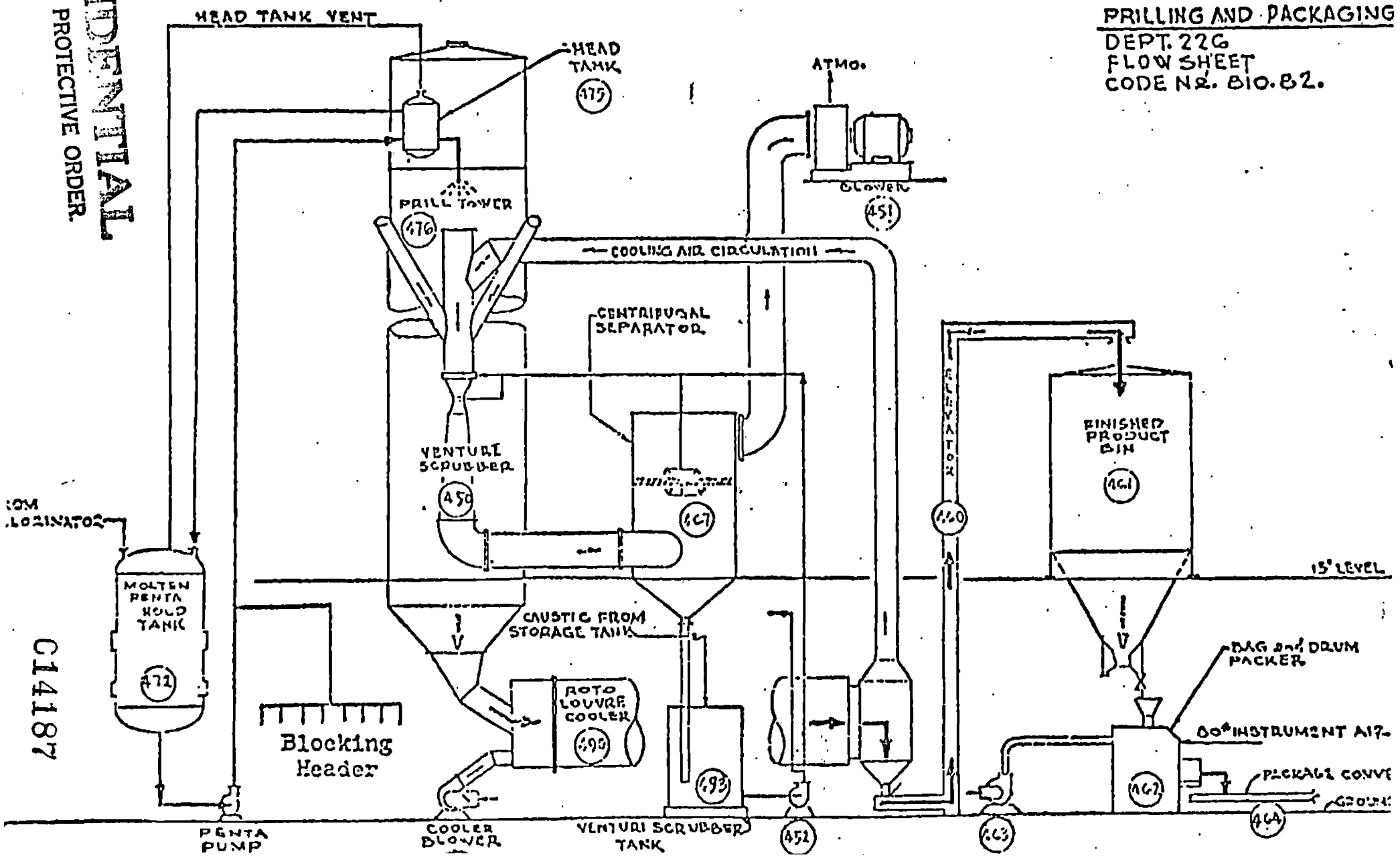
Penta 60 is a mixture of about 60% Penta and 35% Tetrachlorophenol. This product is produced essentially the same as Molten Penta, except that the chlorination is terminated earlier. The reaction is terminated when the batch temperature reaches 153-157°C (145°C crystallizing point). This material prilled in the same manner is Molten Penta.

CONFIDENTIAL

SUBJECT TO PROTECTIVE ORDER.

C14187

PRILLING AND PACKAGING
DEPT. 226
FLOW SHEET
CODE NO. 810.82.



AUG 23 1982 Bob Borsdt Law Dept,

School of Public Health
UNIVERSITY OF ILLINOIS AT THE MEDICAL CENTER, CHICAGO

Area Code 312, Telephone 996-6620
Mailing Address: P.O. Box 6998 · Chicago, Illinois 60680

June 16, 1982 JUN 21 1982

Mr. Garth Fort
Regulatory Management Director, State
Monsanto Company
800 N. Lindbergh
St. Louis, Mo. 63166

Dear Mr. Fort:

We are requesting your cooperation in a study being conducted by the University of Illinois School of Public Health under contract with the Illinois Institute for Energy and Natural Resources entitled "Identification of Potential Sources of Environmental Contamination with Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans in the State of Illinois."

The purpose of this study is to collect existing data on sources of PCDDs and PCDFs in Illinois and to propose epidemiologic study designs to assess the degree of hazard, if any, associated with these sources. Our strategy is summarized in the following tasks:

1. Identify and contact Illinois producers of organic chemicals and pesticides, the production of which may lead to the inadvertant production of trace amounts of PCDDs or PCDFs.

2. Identify hazardous waste disposal sites in Illinois which may be contaminated with trace amounts of PCDDs or PCDFs.

3. Identify all municipal and industrial incinerators in Illinois.

4. Identify past usage of PCDD/PCDF contaminated pesticides in Illinois.

5. Identify industries with potential occupational exposure to PCDDs or PCDFs.

6. Design epidemiologic studies to assess the degree of hazard associated with PCDD and PCDF sources.

Please note that we are relying entirely on existing data and will not be undertaking any sampling as part of this project. Also, we will be examining the feasibility of various epidemiologic study designs; we are not carrying out an actual epidemiologic study.

School of Public Health
UNIVERSITY OF ILLINOIS AT THE MEDICAL CENTER, CHICAGO

Area Code 312, Telephone 996-6620
Mailing Address: P.O. Box 6998 · Chicago, Illinois 60680

The completed study will be published as an ENR Report entitled Identification of Potential Sources of Environmental Contamination with Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans in the State of Illinois and will be generally available as a scientific document. The report will contain a literature review which will emphasize the wide range of toxicity among the various PCDD and PCDF isomers and the importance of isomer specific analysis. The data which your company provides will be carefully referenced. If data from a specific company is not available, we will rely on the list of potential sources compiled by Esposito, Tiernan, and Dryden in Dioxins, Publ. No. 600/2-80-197, USEPA, 1980.

I have attached a list of questions which we are sending to all chemical producers identified through the Stanford Research Institute's Directory of Chemical Manufacturers as producers of pesticides and chemicals which may have been contaminated with PCDDs or PCDFs. The SRI Directory lists your Sauget plant as having produced 2,4-dichlorophenol, o-chlorophenol, o-dichlorobenzene, p-dichlorobenzene, O-nitrophenol, chlorobenzene, 1-chloro-2-nitrobenzene, 1-chloro-4-nitrobenzene, 3,4-dichloroaniline, 1,2-dichloro-4-nitrobenzene, o-nitroanisole, p-chlorophenol, and polychlorinated biphenyls.

I understand that your company has considerable technical expertise in this area and welcome any assistance which you may be able to provide. We have allocated funds for out-of-state travel and would gladly meet with your scientific staff if you believe this will expedite our request. I was very encouraged by our phone conversation and look forward to your reply.

Sincerely,

Daniel Hryhorczuk

Daniel Hryhorczuk, M.D., M.P.H.
Assistant Professor
312-996-2597

School of Public Health
UNIVERSITY OF ILLINOIS AT THE MEDICAL CENTER, CHICAGO

Area Code 312, Telephone 996-6620
Mailing Address: P.O. Box 6998 · Chicago, Illinois 60680

U of Ill/ENR Contract: Sources of PCDDs and PCDFs in Illinois

CHEMICAL/PESTICIDE PRODUCER QUESTIONNAIRE

1. Is your company currently, or has your company ever, produced or used as an intermediate any of the chemicals or pesticides listed in Appendix A (List modified from Esposito, M.P.; Tiernan, T.O.; and Dryden, F.E. 1980. Dioxins, Publ. No. 600/2-80-197. Cincinnati, OH: USEPA)?

2. If yes, can you furnish us with present and past production statistics for these chemicals or pesticides for your Illinois facilities?

3. What were or are the major uses for these products?

4. Which processes does or did your company use for the synthesis of these chemicals or pesticides?

5. In the opinion of your chemists, can your processes lead to the inadvertant production of trace amounts of PCDDs or PCDFs? Why or why not?

6. Have you ever sampled your product, byproducts, or process wastes for PCDDs or PCDFs? If yes, what were the results of those analyses?

7. How do or did you dispose of wastes from these processes (such as still bottoms)? If you dispose of your own wastes, do you monitor your disposal sites for environmental release of trace amounts of PCDDs or PCDFs? What are the results of such monitoring?

8. How many employees were or are involved in the production of these chemicals or pesticides? Has your medical surveillance detected any abnormalities suggestive of PCDD or PCDF exposure? Are you conducting any epidemiologic studies regarding potential employee exposure to PCDDs or PCDFs?

9. What precautions does your company take to reduce occupational and environmental exposure to PCDDs and PCDFs?

10. Do you wish to inform us of any other studies which your company is conducting in this area?

C14190

Daniel Hryhorczuk, MD, MPH
Principal Investigator
312-996-2597

Douglas Hoffman
Research Associate
312-633-5310

APPENDIX A

In addition to the organic chemicals and pesticides listed below, we are requesting information on

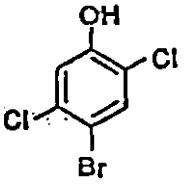
CHLORINATED BENZENES

POLYCHLORINATED BIPHENYLS

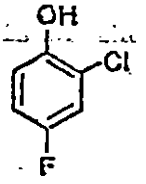
TABLE 7. ORGANIC CHEMICALS RELATED TO DIOXIN FORMATION

Class I

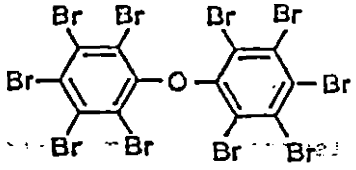
4-BROMO-2,5-DICHLOROPHENOL



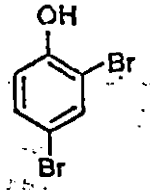
2-CHLORO-4-FLUOROPHENOL



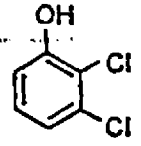
DECABROMOPHENOXYBENZENE



2,4-DIBROMOPHENOL



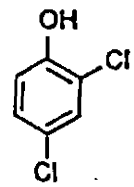
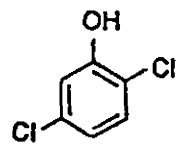
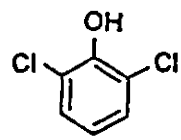
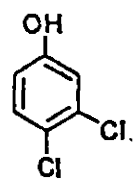
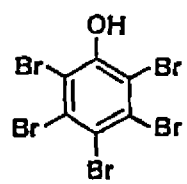
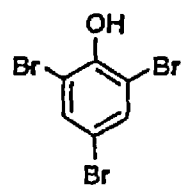
2,3-DICHLOROPHENOL



(continued)

TABLE 7 (continued)

Class I (continued)

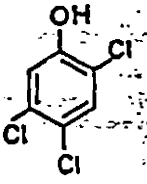
2,4-DICHLOROPHENOL	
2,5-DICHLOROPHENOL	
2,6-DICHLOROPHENOL	
3,4-DICHLOROPHENOL	
PENTABROMOPHENOL	
2,4,6-TRIBROMOPHENOL	

(continued)

TABLE 7 (continued)

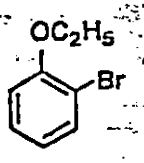
Class I (continued)

2,4,5-TRICHLOROPHENOL

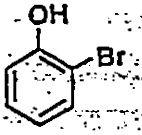


Class II

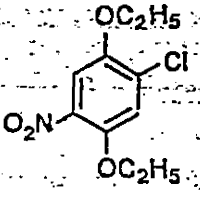
BROMOPHENETOLE



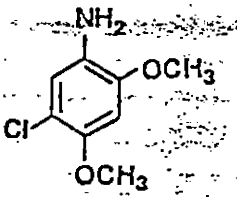
O-BROMOPHENOL



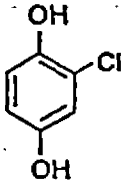
2-CHLORO-1,4-DIETHOXY-5-NITROBENZENE



5-CHLORO-2,4-DIMETHOXY-ANILINE



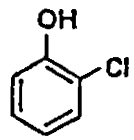
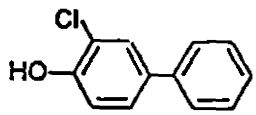
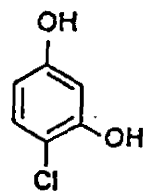
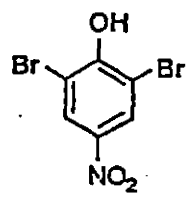
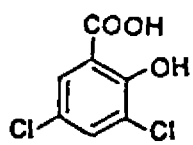
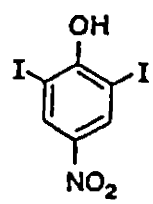
CHLOROHYDROQUINONE



(continued)

TABLE 7 (continued)

Class II (continued)

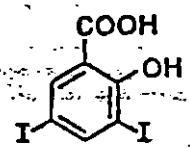
O-CHLOROPHENOL	
2-CHLORO-4-PHENYLPHENOL	
4-CHLORORESORCINOL	
2,6-DIBROMO-4-NITROPHENOL	
3,5-DICHLOROSALICYLIC ACID	
2,6-DIIODO-4-NITROPHENOL	

(continued)

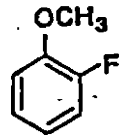
TABLE 7 (continued)

Class II (continued)

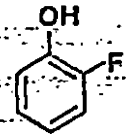
3,5-DIIODOSALICYLIC ACID



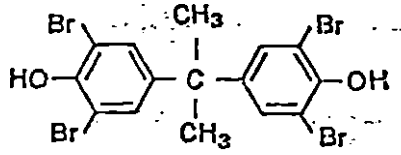
O-FLUOROANISOLE



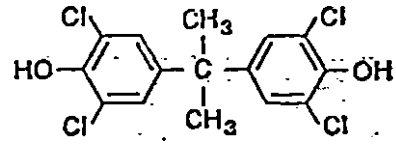
O-FLUOROPHENOL



TETRABROMOBISPHENOL-A



TETRACHLOROBISPHENOL-A



Class III

3-Amino-5-chloro-2-hydroxybenzenesulfonic acid
2-Amino-4-chloro-6-nitrophenol
o-Anisidine
Benzaldehyde
Bromobenzene
o-Bromofluorobenzene

(continued)

TABLE 7 (continued)

Class III (continued)
o-Chlorofluorobenzene
3-Chloro-4-fluoro-nitrobenzene
3-Chloro-4-fluorophenol
4-Chloro-2-nitrophenol
Chloropentafluorobenzene
2,4-Dibromofluorobenzene
3,4-Dichloroaniline
o-Dichlorobenzene
3,4-Dichlorobenzaldehyde
3,4-Dichlorobenzotrichloride
3,4-Dichlorobenzotrifluoride
1,2-Dichloro-4-nitrobenzene
3,4-Dichlorophenylisocyanate
3,4-Difluoroaniline
o-Difluorobenzene
1,2-Dihydroxybenzene-3,5-disulfonic acid, disodium salt
2,5-Dihydroxybenzenesulfonic acid
2,5-Dihydroxybenzenesulfonic acid, potassium salt
2,4-Dinitrophenol
2,4-Dinitrophenoxyethanol
3,5-Dinitrosalicylic acid
Fumaric acid
Hexabromobenzene
Hexachlorobenzene
Hexafluorobenzene
Maleic acid
Maleic anhydride
o-Nitroanisole
2-Nitro-*p*-cresol
o-Nitrophenol
Pentabromochlorocyclohexane
Pentabromoethylebenzene
Pentabromotoluene
Pentachloroaniline
Pentafluoroaniline
o-Phenetidine
Phenol (from chlorobenzene)
1-Phenol-2-sulfonic acid, formaldehyde condensate
Phenyl ether
Phthalic anhydride
Picric acid
Sodium picrate
Tetrabromophthalic anhydride
1,2,4,5-Tetrachlorobenzene
Tetrachlorophthalic anhydride
Tetrafluoro-*m*-phenylenediamine
Tribromobenzene
1,2,4-Trichlorobenzene
2,4,6-Trinitroresorcinol

PESTICIDE CHEMICALS

Pesticides are the most significant group of organic chemicals in relation to dioxin occurrence. This statement is based on the structure and reaction mechanism analogy, reaction conditions, detected presence of dioxins in a number of commercial pesticide products, and a history of environmental contamination problems, particularly with trichlorophenol and 2,4,5-T.

Chlorinated dibenzo-*p*-dioxins are known to be present in at least trace amounts in a number of pesticide chemicals. These include 2,4,5-T, silvex, 2,4-D, erbon, sesone, DMPA, ronnel, tetradifon, and the various chlorophenols (Fishbein 1973). In addition, the chemical structures, reactions, and process conditions for a number of others indicate dioxin content potential.

This study deals with production of the basic pesticide chemicals. Thus it does not address problems of dioxin formation possibly resulting from formulation, storage, distribution, and utilization of the pesticides. If exposure to alkaline formation media or elevated temperatures is encountered in any of the diverse procedures for handling and use of these pesticides, dioxin formation could be a significant problem.

Selection and Classification

The pesticide chemicals were selected for evaluation in this study on the basis of molecular structure, from those listed as commercial pesticides in the Farm Chemicals Handbook. The primary criterion was an ortho-halophenolic structure, or the derivative esters and salts thereof. Also considered were ortho dihalo aromatic structures, which conceivably could convert to phenols upon exposure to alkaline conditions.

A second criterion was a minimum commercial production level of 1000 pounds or $1000 value per year. These correspond to the minimum levels required for inclusion in the Stanford Research Institute Directory of Chemical Producers, which was a primary reference. The lists are based on production during the past 10 years.

The pesticide chemicals considered in this study are listed in Table 8. They are grouped into classes representing likelihood of dioxin formation, as follows:

Class I—Highly likely to be associated with the presence of halogenated dibenzo-*p*-dioxins because of the presence of an ortho-halogenated phenol in the reaction sequence, with subjection to elevated temperature ($\geq$145° C+) plus either alkalinity or the presence of free halogen.

Class II—Reasonable but lesser probability of such dioxin association because of the presence of phenolic or aromatic structures related to dioxins; although not directly involving dioxin precursive conditions, such chemicals might form dioxins under irregular operating conditions.

TABLE 8.—LIST OF PESTICIDE CHEMICALS

General name	Chemical name
Class I	
Bifenox	Methyl-5-[2,4-dichloroephenoxy]-2-nitrobenzoate
Chloranil	2,3,5,6-Tetrachloro-2,5-cyclorhexadiene-1,4-dione

(continued)

TABLE 8. (continued)

General name	Chemical name
2,4-D and esters and salts	(2,4-Dichlorophenoxy) acetic acid and esters and salts
2,4-DB and salts	2,4-Dichlorophenoxybutyric acid and salts
Dicamba	3,6-Dichloro-2-methoxybenzoic acid
Dicamba, dimethylamine salt	3,6-Dichloro-2-methoxybenzoic acid, dimethylamine salt
Dicapthon	Phosphorothioic acid *o*-(2-chloro-4-nitrophenyl) *o,o*-dimethyl ester
Dichlofenthion	Phosphorothioic acid *o*-2,4-dichlorophenyl *o,o*-diakyl ester
Disul sodium (sesone)	2,4-Dichlorophenoxyethyl sulfate, sodium salt
2,4-DP	2-(2,4-Dichlorophenoxy) propionic acid
Erbon	2,2-Dichloropropanoic acid 2-(2,4,5-trichlorophenoxy) ethyl ester
Hexachlorophene	2,2'-Methylene bis (3,4,6-trichlorophenol)
Isobac 20	2,2'-Methylene bis (3,4,6-trichlorophenol), monosodium salt
Nitrofen	2,4-Dichlorophenyl-*p*-nitrophenyl ether
Pentachlorophenol (PCP) and salts	Pentachlorophenol and salts
Ronnel	Phosphorothioic acid, *o,o*-dimethyl O-(2,4,5-trichlorophenyl) ester
Silvex and esters and salts	2-(2,4,5-Trichlorophenoxy) propionic acid and esters and salts
2,4,5-T and esters and salts	(2,4,5-Trichlorophenoxy) acetic acid
—	2,3,4,6-Tetrachlorophenol
—	2,4,5-Trichlorophenol
Class II	
—	*o*-Benzyl-*p*-chlorophenol
Bromoxynil and esters	3,5-Dibromo-4-hydroxybenzonitrile

(continued)

TABLE 8. (continued)

General name	Chemical name
Carbonphenothion	Phosphorodithioic acid *s*-[[(4-chlorophenyl)thio]methyl] *o,o*-diethyl ester
DCPA	2,3,5,6-Tetrachloro-1,4-benzenedicarboxylic acid dimethyl ester
Dichlone	2,3-Dichloro-1,4-naphthalenedione
Dinitrobutylphenol, ammonium salt	2,4-Dinitro-6-sec-butyl phenol, ammonium salt
Loxynil	3,5-Diiodo-4-hydroxybenzonitrile
Lindane	1,2,3,4,5,6-Hexachlorocyclohexane, gamma isomer
MCPA	(4-Chloro-*o*-toloxy) acetic acid
MCPB	4-(2-Methyl-4-chlorophenoxy) butyric acid
Mecoprop	2-(4-Chloro-2-methylphenoxy) propionic acid
Parathion	Phosphorothioic acid *o,o*-diethyl *o*-(4-nitrophenyl) ester
PCNP	Pentachloronitrobenzene
—	Pipecolinopropyl-3,4-dichlorobenzoate
Piperalin	3-(2-Methylpiperidino)propyl-3,4-dichlorobenzoate
Propanil	3,4-Dichloropropionanilide
Tetradifon	1,2,4-Trichloro-5-[(4-chlorophenyl)-sulfonyl] benzene
—	2,3,6-Trichlorobenzoic acid
—	2,3,6-Trichlorophenylacetic acid and sodium salt
—	Triiodobenzoic acid

Chemical Reactions

Higher chlorinated dioxins have been detected in samples of a number of pesticides produced from 1950 to 1970. Data from these analyses were summarized by Fishbein (1973), as shown in Table 9.