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NIOSH Dioxin Registry Site Visit Report

of

Rhone-Poulenc, Incorporated
Portland, Oregon

Site Visit Dates
January 19-25, 1982

Report Written by
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16. Abstract (Limit: 200 words)

Worker exposures to 2,3,7,8-tetrachlorodibenzo-p-dioxin (1746016) were assessed at Rhone Poulenc, Incorporated (SIC-2869), Portland, Oregon in January 1982. The survey was conducted to evaluate the feasibility of including workers involved with the synthesis of 2,4,5-trichlorophenoxyacetic-acid (93765) (2,4,5-T) in the dioxin (828002) registry. Complete personnel records were kept for all workers beginning in 1960. Limited medical information was available. Processes in the production of 2,4,5-T, its isooctyl and isobutyl esters, the formulation and packaging of its esters, and the production of its triethylamine salt were assessed. Formulation included blending the completed acids and esters and mixing the solutions to the proper strengths. Synthesis, dilution, and addition of additives and filtering were part of the formulation operation for amines. The same equipment was used for processing 2,4,5-T and 2,4-dichlorophenoxyacetic-acid (94757). No pressure releases or blow outs occurred during processing. No industrial hygiene data on worker exposures to process materials was available. No analysis for dioxin contamination or process contamination was available. The authors conclude that potential exposures to 2,4,5-T or other products derived from 2,4,5-trichlorophenol (95954) exist among the workers. The cohort of workers should be included in the dioxin registry.

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PURPOSE OF SURVEY:	To evaluate the feasibility of including in the Dioxin Registry Rhone-Poulenc workers who were involved with the synthesis of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) formerly produced at this site, to discuss the details of synthesis and formulation processes for 2,4,5-T and related compounds, and to microfilm all pertinent records.
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EMPLOYEE REPRESENTATIVE CONTACTED:	Dennis Fletcher, Business Manager, International Union of Operating Engineers Local 87 (503) 286-1609
STANDARD INDUSTRIAL CLASSIFICATION:	2869 - Industrial Organic Chemicals

Abstract

A site visit was conducted at Rhone-Poulenc, Incorporated, Portland, Oregon, on January 19-25, 1982. This plant produced 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and related compounds from February 1961 to December 1962. Meetings were held to discuss the pertinent production processes. A tour was made of the facilities where 2,4,5-T and related compounds were formerly produced. During this tour an explanation was given about the current use and location of equipment used for the 2,4,5-T products. The personnel records were reviewed, and appropriate personnel files were collected and microfilmed.

Workers assigned to Cost Center 602 had potential exposure to 2,4,5-T or other TCP-derived products during the periods when they were being synthesized. Therefore, the cohort of workers employed in Cost Center 602 by Chipman Chemical during the following periods should be included in the Dioxin Registry:

February 1961 through May 1961
October 1961 through May 1962
October 1962 through December 1962.

Introduction

The National Institute for Occupational Safety and Health (NIOSH) is currently conducting an investigation of health effects resulting from occupational exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). This study, initiated in 1979, was prompted by animal studies showing TCDD to be acutely toxic and a chloracnegen, as well as a carcinogen and teratogen. TCDD is a contaminant of 2,4,5-trichlorophenol (TCP) and materials synthesized from it such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T).

Because of the widespread production and use of 2,4,5-T as a commerical herbicide since the 1940's, a registry of all workers from 2,4,5-T synthesis sites in the United States is being compiled. This registry contains data from the personnel and medical records of these workers, in addition to process information to define exposure. A retrospective cohort mortality study is planned and morbidity surveys may be conducted.

History of the Plant

In 1943, Chipman Chemical Company began the manufacture of various railroad herbicides on the site in Portland now occupied by Rhone-Poulenc, Incorporated; in 1956, the production of phenoxyalkanoic acids was initiated, and 2,4-dichlorophenoxyacetic acid (2,4-D) was the first of these produced. Portland was Chipman's only technical manufacturing site, but other locations in which "formulating" (the mixing and packaging of marketable products) was conducted were maintained across the country. At the formulating sites, a wide variety of Chipman products were handled. In 1965, Chipman was purchased by Rhone-Poulenc, Incorporated, a French company. All of Rhone-Poulenc's operations in the United States used the name Rhodia, Incorporated, until 1977, when they began to use the parent company's name. Currently, all technical manufacturing of herbicides by Rhone-Poulenc in the United States occurs at the Portland plant.

The products and their dates of production and/or formulation, as determined from limited records, are listed here.

Synthesis and formulation:

2,4-Dichlorophenol (2,4-DCP)	1956 to July 1982
2,4-Dichlorophenoxyacetic acid (2,4-D)	1956 to July 1982
N-Butyl ester of 2,4-D	1956 to present
Isobutyl ester of 2,4-D	1956 to present
Isooctyl ester of 2,4-D	1956 to present
Isopropyl ester of 2,4-D	1956 to 1960

2,4-Dichlorophenoxybutyric acid (2,4-DB)	1964 to July 1982
2(2,4-Dichlorophenoxy)propionic acid (2,4-DP)	1973 to 1976
2-Methyl-4-chlorophenoxyacetic acid (MCPA)	March 1961 to 1976
4-(2-Methyl-4-chlorophenoxy)butyric acid (MCPB)	1972 to Jan. 1973
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	Feb. 1961* to Dec. 1962**
Isooctyl ester of 2,4,5-T	Feb. 1961* to Dec. 1970**
Isobutyl ester of 2,4,5-T	Feb. 1961* to April 1966**
3,5-Dibromo-4-octanoyloxybenzonitrile (Bromoxynil octanoate)	1971 to present

* Test batches were run in July or August 1960.

**Little or no activity occurred during June, July, August, or September of 1961 or 1962.

Formulation only

2,4,5-T amines	Feb. 1961 to March 1970
Isooctyl ester of 2,4,5-T	Dec. 1970 to Nov. 1975
2(2,4,5-trichlorophenoxy)propionic acid (Silvex) and its esters	Late 1950's to March 1975

No 2,4,5-trichlorophenol (TCP) was ever synthesized by Chipman, Rhodia, or Rhone-Poulenc in any location in the United States. There are no production records dating back to the period from 1960 to June 1968, but laboratory and other auxiliary records indicate that the synthesis of 2,4,5-T acid and esters occurred predominantly from February 1961 to December 1962. However, little or no activity occurred during June, July, August, or September of these years. Test batches were run in July or August 1960. After 1962, only small amounts of 2,4,5-T esters and amines were occasionally produced from purchased T-acid and esters. These activities occurred in the ester unit of the 2,4-D Building and in the smaller Specialty Ester Building.

Purchases were made of an aqueous solution of the sodium salt of TCP from Monsanto Company in July 1960 and from Diamond Alkali Company after December 1960. Available records indicate that assays of content were made of the following: 2,4,5-T acid from Monsanto in 1962 and 1964 and from Dow

Chemical Company in 1964 and 1969; 2,4,5-T isooctyl ester from Diamond Alkali in 1960 and Thompson-Hayward Chemical Company in 1964; and Silvex ester from Thompson-Hayward in 1975. The records do not state whether these substances were actually purchased. However, company officials believe that the 2,4,5-T isooctyl ester was indeed purchased from Diamond Alkali in 1960 and Thompson-Hayward in 1964.

Annual production summaries dating back to July 1968 indicate that formulation of 2,4,5-T esters and amines ceased in 1970. The formulation of Silvex and the inclusion of 2,4,5-T in herbicide mixtures ended in 1975. During the 1968-75 period, only small amounts of products containing 2,4,5-T or other TCP-derived products were made: 1500 gal. of 2,4,5-T esters, 3500 gal. of 2,4,5-T amines, 250,000 gal. of herbicide mixtures containing 2,4,5-T esters, 75,000 gal. of liquid formulations containing Silvex and its esters, and 55,000 lbs of solid formulations containing Silvex. As a point of comparison, the company estimates that 90 million lbs of 2,4-D were produced during this time. Since 1971, bromoxynil octanoate has been produced by the company.

From the 1950's until 1971, Chipman formulated a variety of insecticides, arsenicals and mercury compounds, but the company did not synthesize any of them. These products were formulated in the Insecticide Building, and included DDT, aldrin, endrin, Malathion, Toxaphene, parathion, hexachlorobenzene, arsenicals, mercury compounds, and mixtures of sodium chlorate and sodium borate.

Department Operations and Personnel

Between mid-1960 and the end of 1962, the phenoxyalkanoic acid herbicide activities were funded from cost center 602 and were located in the same buildings in use today plus one small building, no longer present, which housed the MCPA production. A plant layout diagram (see Figure 1) is provided for reference. Four shifts worked on production and formulation of 2,4-D and its esters and amines, 2,4,5-T and its esters and amines, various blends of these products, and, after March 1961, the production of MCPA. The work was seasonal, and there was frequent shifting of workers from one to another of the jobs within the cost center 602 ; each job had specific assigned duties, such as packaging or operating certain kettles. The synthesis of 2,4,5-T took place in the Ester Room of the 2,4-D Building and also in the rear area of the 2,4-D building. Synthesis of T-esters occurred in two locations, the Ester Room of the 2,4-D Building and also in the Specialty Ester Building. Formulations of the T-acid, esters and amines were made in two locations, the Formulations Building and the Specialty Ester Building. The production of MCPA was initiated in March 1961 and was located at the site labeled "New MCPA Plant" in the plant layout diagram. After March 1961, therefore, MCPA exposure was involved for cost center 602 employees who were transferred or hired for the MCPA plant startup. Individuals working in the MCPA Building cannot be separately identified. Mr. Briggs estimated that MCPA production utilized perhaps 4 persons per shift out of a total of perhaps 25 production and formulation workers per shift. (No existing records provide actual figures.)

The walk-through tour of the current facility allowed the NIOSH personnel to make the following observations: the job locations of the personnel in areas formerly housing both 2,4,5-T and 2,4-D production operations were in close physical proximity to one another; also, there was manual handling of some of the materials in these areas. Therefore, a worker doing any job in the herbicide production buildings, except in the MCPA plant, had a reasonable likelihood of exposure to the 2,4,5-T and related products. After March 1961, the transfer of cost center 602 workers occurred regularly among the 2,4,5-T, 2,4-D, and MCPA jobs, so it is very probable that all workers employed in the cost center 602 from February 1961 to December 1962 were exposed to 2,4,5-T acid, esters and amines.

The Insecticide Building was at the opposite end of the plant site from the buildings in which the phenoxyalkanoic acid herbicides were handled; it is currently used as a warehouse (see Figure 1). The review of the personnel record system and discussions with Mr. Henshaw and Mr. Gitchlag indicate that the insecticide workers can be distinquished from the phenoxyalkanoic acid herbicide workers in the personnel records for the July 1960 to December 1962 period, because the cost centers for the two operations were distinct. Additionally, there was little transfer from one cost center to the other at that time. Therefore, it is possible to exclude the insecticide workers from the Dioxin Registry.

It is probable that any individual who worked at the site after 1962 may have never been exposed to 2,4,5-T or other TCP-derived products, because of the small amounts of 2,4,5-T and related TCP-derived products handled at this site after 1962 compared with 2,4-D and other products (as noted in the <u>History of the Plant</u> section of this report), because the 2,4,5-T related products were handled only intermittently, and because only a few workers were assigned to the processes involving these products.

<u>Description of the Personnel Records</u>

A perpetual seniority list of all workers employed even for one day was prepared by Chipman in 1960 and has been updated since then. This was used to identify exposed individuals. The personnel records of all persons who worked at any time between July 1960 and December 1962 were collected and microfilmed.

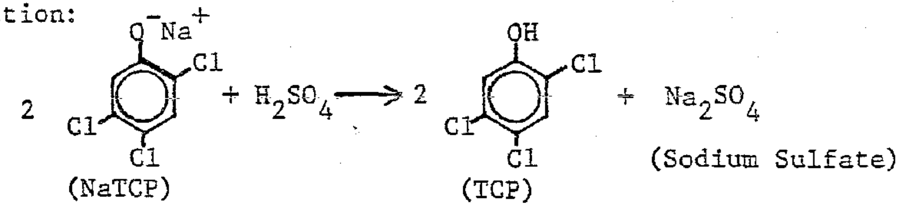
The personnel files are quite complete. They contain application forms, personnel sheets detailing rate and job changes, accident reports, Workers' Compensation claims, and medical insurance forms. Cost center notation is written on many personnel sheets, so that the cost center 602 (phenoxy-alkanoic acid herbicide) workers can be selected from the total group. From these records, it is possible to identify those hourly workers and salaried workers who worked in the cost center 602 during this period of time. Maintenance workers, who were also exposed to the insecticide formulations, can be identified. There is no way to separate formulators from operators because the union contract of the 1960-62 period identified all of the cost center 602 production workers as operators. It is also impossible to identify the particular tasks performed by each of the workers in synthesis or formulation. Additionally, for the period after 1962 the records do not identify the workers assigned to jobs involving 2,4,5-T or other TCP-derived products; however, as noted in the preceding section, these individuals composed a small percentage of the workforce.

Limited medical information is available for the workers. The medical insurance records which are in the files are not useful because they contain only monetary information and do not describe the medical condition involved. Neither Chipman, Rhodia, nor Rhone-Poulenc ever had a medical office, so there are no dispensary records. The services of local physicians were utilized.

Description of the Process for Production of 2,4,5-T Acid

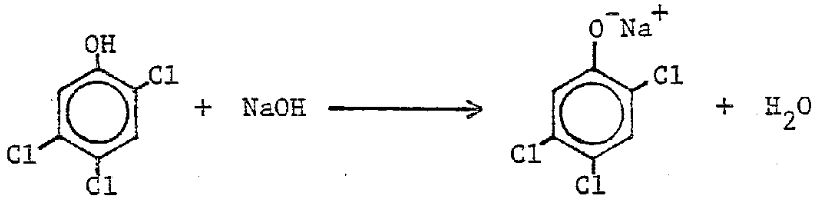
Chipman Chemical Company produced 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) using the following raw materials: sodium 2,4,5-trichlorophenate (NaTCP) (aqueous solution), sulfuric acid (H_2SO_4), flake caustic soda (NaOH), sodium carbonate (Na_2CO_3), isopropyl alcohol (IPA), and monochloroacetic acid (MCA). Other materials used in the process include benzene and water, each of which were solvents at various points in the process. The following description applies to the production of 2,4,5-T acid during each of the three years of manufacture; there were no significant changes during that time. A flow diagram is provided for this process (Figure 2); also, an equipment location diagram is included (Figure 3). Equipment numbers used in the text correspond to the numbers used in the figures. A plant layout diagram is provided for the entire Portland site (Figure 1).

The first step in the process is known as "TCP (2,4,5-Trichlorophenol) Acidification," and occurs in the agitated, 1000-gal., stainless-steel Ester Kettle (EK) 6. Here, NaTCP in aqueous solution is pumped in from tank cars and reacted with an excess of H_2SO_4 to form TCP by the following exothermic reaction:



This reaction occurs at 100°C and near-atmospheric pressure and proceeds until the pH reaches 1. At that time, the reaction is considered complete; a phase separation occurs, in which the TCP forms an organic layer at the bottom of the tank, and an aqueous layer of relatively lower density forms at the top. The aqueous layer, containing the Na_2SO_4 by-product, the unreacted excess H_2SO_4, and the water soluble impurities from the original NaTCP solution, is decanted from the top and drained to the sewer, while the TCP is drained from the bottom into EK 5. This step is included to remove the water and aqueous impurities from the NaTCP.

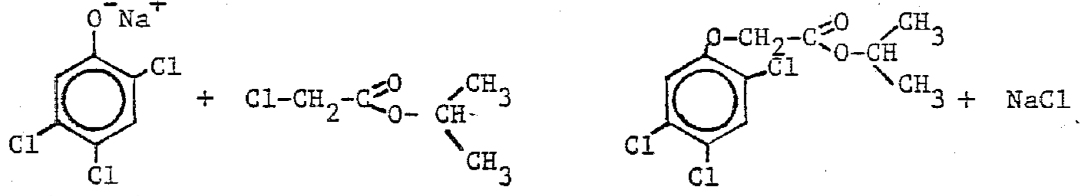
The next step in the process, known as the "TCP Dehydration," occurs in EK 5, an agitated, jacketed, 1700-gal., stainless-steel tank. After the TCP is transferred to the vessel, isopropyl alcohol (IPA) is pumped in from Recovery Tank (RT) 1, the "Dry IPA" tank. Flake caustic (NaOH), in a quantity equimolar to the quantity of TCP, is manually dumped into the vessel through a manway, and dissolves; IPA is the solvent for the NaOH. An exothermic reaction occurs at near-atmospheric pressure between the TCP and NaOH to form NaTCP and water via the following mechanism:



(TCP) (NaTCP)

The temperature at which this reaction occurs is unknown, but it is well below the mixture's reflux point of 115-119°C. The temperature does rise during the exothermic reaction; however, it does not reach the reflux point. After the addition of the NaOH is complete, the manway is closed and jacket heat is applied. The temperature of the mixture rises to the 115-119°C reflux point, and a vapor phase containing water and IPA boils off. Simultaneously, more IPA is pumped in, again from RT 1, until the mixture in EK 5 contains NaTCP, IPA, and no water. The IPA-H_2O mixture boiled off is condensed and drained to RT 2, the "Wet IPA" tank, for later recovery of the IPA (to be described later in this section); the NaTCP in IPA solution remaining in EK 5 is then ready to be pumped to EK 4 for further processing.

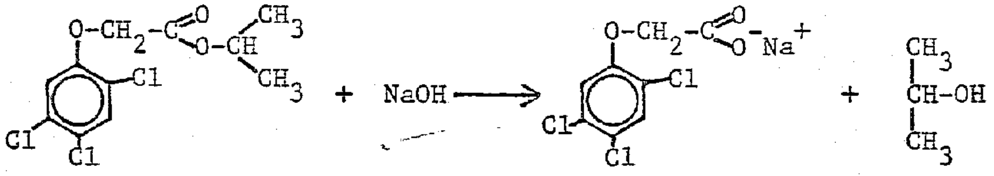
The next step in the process, known as "2,4,5-T (2,4,5-Trichlorophenoxyacetic Acid) Condensation," occurs in EK 4, which, like EK 5, is a 1700-gal., stainless-steel, agitated reactor. A solution of the isopropyl ester of monchloroacetic acid (IPE-MCA) in benzene solvent is pumped from EK 1, where it is synthesized (see description later in this section), and charged to the reactor; then the temperature is raised to 96°C, which is the boiling or reflux point for the mixture. Next, the solution of NaTCP in IPA solvent from EK 5 is introduced during a feed period of 1 hour and 20 minutes. The molar quantity of IPE-MCA charged is in excess of that of the NaTCP by a factor of 1.5-2. These two compounds react at near-atmospheric pressure to form the isopropyl ester of 2,4,5-T (IPE-2,4,5-T) and salt, via the following reaction:



(NaTCP) (IPE-MCA) (IPE-2,4,5-T)

After the feed period is completed, this reaction is taken to virtual completion by cooking the mixture at 112°C for 1 hour. When the cooking period is completed, 0.1 mole of Na_2CO_3 per mole of product is manually dumped into the reactor vessel; however, the company is unsure why this addition is included in the process. Finally, the mixture is boiled to 150°C, and a vacuum of 29 in.Hg is applied. This operation removes a vapor phase consisting of the unreacted excess IPE-MCA, the benzene, and the IPA; the vapor is condensed, and routed to RT 3, the "IPE-MCA" tank, for later reuse. The remaining mixture in EK 4, consisting of IPE-2,4,5-T with dissolved NaCl and Na_2CO_3, is pumped to EK 2, a 1000-gal., glass-lined, agitated tank, for the step labed "2,4,5-T Hold," and is stored awaiting further processing. A 96% yield of IPE-2,4,5-T, based on the charge of NaTCP to EK 4, is obtained in the process.

Water is pumped to EK 7, a 3000-gal, steel reactor; then an aqueous solution of 50% NaOH is added in a quantity sufficient to provide an amount of NaOH equimolar to the amount of the isopropyl ester of 2,4,5-T contained in EK 2. The mixture is heated to 100-110°C, which is the boiling point of the mixture. The contents of EK 2 are then pumped into the reactor, followed by more water; heat is applied to the vessel to keep the contents boiling during the addition of these materials. The resulting mixture is cooked for 5 hours at near-atmospheric pressure and a temperature which is not known (but which is probably in the 100-110°C range). This promotes a reaction between IPE-2,4,5-T and NaOH, forming sodium 2,4,5,-Trichlorophenoxyacetate (Na-2,4,5-T), via the following mechanism:



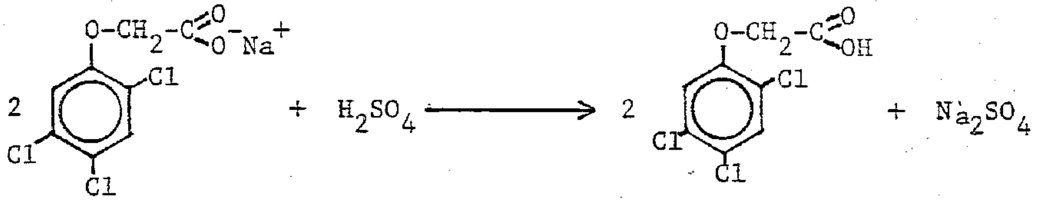
(IPA-2,4,5-T) (Na-2,4,5-T) (IPA)

Water and IPA vapor boiled off of the mixture during and after the reaction are condensed and drained to RT 4, the "H_2O - IPA" tank, for later recovery of the IPA.

The resulting aqueous solution of Na-2,4,5-T, with NaCl, Na_2CO_3, and IPA as impurities, is then pumped through a spray cooler to reduce its temperature. If the temperature is above 40°C after cooling, the solution is directed to EK 8, an agitated holding tank labelled "Na-2,4,5-T Hold", from where it can be recycled through the spray cooler. At a temperature of 40°C, the Na-2,4,5-T precipitates out of solution and a slurry is created. The slurry can be routed to EK 8 for temporary storage and agitation or can be sent directly to the closed, continuous centrifuge.

The centrifuge removes most of the liquid from the Na-2,4,5-T, leaving a cake of Na-2,4,5-T with a moisture content of approximately 50%. The moisture retains water-soluble impurities, especially NaCl and Na_2CO_3, in the cake. The cake drops out to fiber drums which are positioned and filled manually. The liquid also contains water-soluble compounds such as the NaCl and Na_2CO_3 impurities. This liquid is routed to either the drain or RT 4; the company is not certain which of these alternatives is normal for this process.

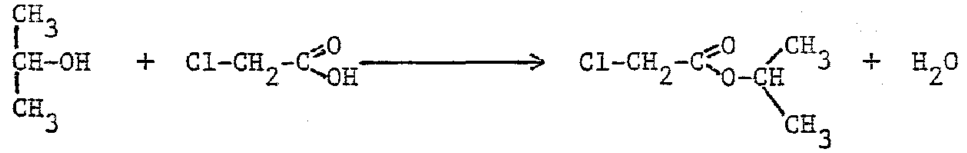
The next step in the process occurs in reactor Q2, a 3000-gal., acid-proof, brick-lined, agitated vessel. Water is added to Q2; then fiber drums containing Na-2,4,5-T cake are manually dumped into this vessel using a barrel dumper. H_2SO_4 is then added in excess to the vessel to react with Na-2,4,5-T, producing 2,4,5-T via the following reaction:



(Na-2,4,5-T) (2,4,5-T)

This reaction occurs at a temperature slightly above ambient and at near-atmospheric pressure. When the pH of the reactor contents stabilizes at 1, the reaction is considered complete. The resulting slurry of 2,4,5-T acid in water, with the unreacted excess H_2SO_4 and the Na_2SO_4, NaCl, and Na_2CO_3 by-products, is then pumped to the "Bird-Young Filter" for the final step of the process. This rotary vacuum filter removes most of the aqueous solution from the 2,4,5-T, leaving a wet cake with a 20% moisture content. The filter is continuous, and the solid automatically drops out to the drumming operation; the positioning and filling of the drums is performed manually. The aqueous solution is collected in a small tank and then drained to the "Seal Tank." From there, it is either recycled to Q2, for reuse of its acid content in another batch, or dumped to the drain when the salt (Na_2SO_4) content gets too high to dissolve more salt.

As noted previously in this section, the isopropyl ester of monochloroacetic acid (IPE-MCA) used in the reaction at EK 4 is synthesized at reactor EK 1. A solution of IPE-MCA, benzene, and IPA is pumped from RT 3 to this vessel. A sufficient quantity of benzene is added to make up for any losses in the system and to insure sufficient solvent at EK 4; also added is the amount of MCA required to make up for both the amount reacted in EK 4 in the previous batch and the amount of any losses in the system. The IPE-MCA synthesis reaction is:



(IPA) (MCA) (IPE-MCA)

Sufficient excess IPA is present in the recycled solution from RT 3 so that no IPA feed is needed here for this reaction. Losses of IPA throughout the system are made up by adding virgin IPA from storage directly to the recovered IPA in RT 1. The water by-product of the IPE-MCA synthesis reaction is continuously boiled off the mixture in EK 1, condensed, separated from the IPA and benzene by decantation in the splitter vessel, and sent to the drain.

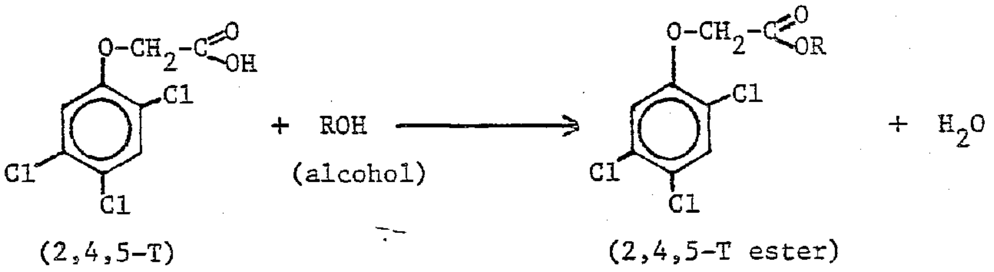
A system of distillations is used to recover the isopropyl alcohol from the two different strengths of water-IPA mixtures held in RT 4 and RT 2, which were noted previously in this section. Purified, recovered isopropyl alcohol is pumped to RT 1 for reuse, and aqueous waste is sent to the drain.

Description of the Process for Production of the Isooctyl and Isobutyl Esters of 2,4,5-T

Chipman Chemical Company produced the isooctyl and isobutyl esters of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) using isooctyl or isobutyl alcohol, as appropriate, and the 2,4,5-T product of the process described in the previous section. The isooctyl ester of 2,4,5-T is abbreviated as IOET; the isobutyl ester of 2,4,5-T, also called simply the butyl ester of T, is abbreviated as BET. The production processes for each of these esters are virtually identical except for the alcohol used, and the same equipment was used by Chipman to produce either one, on a time-sharing basis. The following description applies to the synthesis of 2,4,5-T esters during all years of manufacture; there were no significant changes during that time. Except as specifically noted, the operating pressure was near atmospheric. A flow diagram (Figure 4) is provided for this process; the equipment location diagram (Figure 3) and plant layout diagram (Figure 1) also apply to this process. As in the preceding section, the equipment numbers used in the text correspond to the numbers used in the figures.

The first step in this process is the dissolving of 2,4,5-T into a water-alcohol mixture. The appropriate alcohol is introduced into the agitated "Esterification Kettle" (EK 3) by pumping in "dry alcohol" from storage and "wet alcohol," an alcohol-water mixture, which is recycled from the "Wet Alcohol Rundown Tank" described later in this section. After the liquid is introduced to the vessel, the temperature is raised to approximately 80°C, and the wet 2,4,5-T acid cake is manually dumped into the vessel and dissolved into the mixture.

The next step in the process, the formation reaction and the purification of the ester, also occurs in EK 3. The kettle temperature is increased from 80°C, and the 2,4,5-T reacts with the alcohol, which is present in excess, to form the ester via the following endothermic reaction:



(where R is an isobutyl group or an isooctyl group, or any group of the formula C_8H_{17}-.)

As the temperature increases, a water-alcohol mixture boils off. The vapors are routed through a condenser, and the resulting water-alcohol liquid mixture is piped to the "Splitter Vessel." This vessel is a tank in which a phase separation occurs between the water and the alcohol. The bottom layer of water with some dissolved alcohol is drained to the sewer, while the top layer of alcohol with some dissolved water is returned to EK 3. As the reaction nears completion, insufficient water is produced to allow phase separation in the "Splitter Vessel." At this point, the temperature in EK 3 is 115°C. The alcohol phase from the splitter is then diverted to the "Wet Alcohol Rundown Tank" rather than back to EK 3. This continues until the temperature in EK 3 reaches 135°C. At this point, an additional charge of dry alcohol is pumped from storage into EK 3, and alcohol removal (boil-off) continues until the temperature in EK 3 again rises to 135°C. The entire system (EK 3, "Splitter Vessel," and "Wet Alcohol Rundown Tank") is then put under a vacuum of 28-29 in. Hg, and alcohol removal continues until the temperature in EK 3 reaches 150°C. The 2,4,5-T ester product in EK 3 is then ready for the next step in the process, while the alcohol with dissolved water (wet alcohol) in the "Wet Alcohol Rundown Tank" is ready for recycling for the next batch in EK 3 (as described in the first step of this process).

The final step in the process is the filtration of the 2,4,5-T ester product. This step is necessary for removal of "dirt" from the ester to provide a clear product; this is known as "polishing." The 2,4,5-T ester product is drained from the bottom of EK 3, and is pumped through the filter. A horizontal filter press is used for polishing; changing filter paper is a manual operation.

After filtration, the 2,4,5-T ester is pumped to storage tank T-22 to await formulation and packaging.

Description of the Process for the Formulation and Packaging of the Esters of 2,4,5-T

Chipman Chemical Company and Rhodia, Incorporated, formulated and packaged 2,4,5-T ester formulations using the 2,4,5-T ester produced in the process described in the previous section, Diesiline solvent (kerosene) and Triton X131 and X171 or Emcol 714 and 710 emulsifiers. After production of 2,4,5-T ester was discontinued by Rhodia in 1970, purchased material was formulated. The formulation process occurred in a single vessel, and was a simple mixing operation.

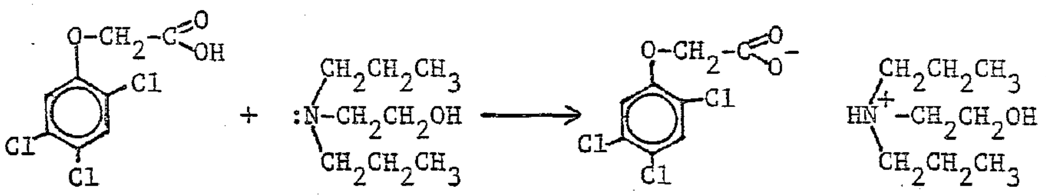
The 2,4,5-T ester is pumped into the formulation vessel (from storage tank T-22) along with the solvent and emulsifiers. These are mixed, and the formulation is pumped to the packaging area adjoining the 2,4-D building (see Figure 1).

Ester formulations are packaged in 1-, 5-, 30-, and 55-gallon containers. The 1-gallon cans are filled on a 4-spout filling machine which has an automatic shutoff. The other sizes of containers are filled manually to a specific weight. This is done by manually placing the containers on platform scales prior to filling, and manually controlling the flow.

Description of the Process for Production of the Triethylamine Salt of 2,4,5-T

Chipman Chemical Company and Rhodia, Incorporated, produced the triethylamine salt of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T triethylamine), using triethylamine and the 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) from the 2,4,5-T production process as raw materials. Other materials used in the process included: water, which is the solvent; a sequestering agent "crystal inhibitor," which prevents crystal formation by the product if the solution is mixed with "hard" water by the user; and a silicone antifoam agent. The method used to produce this amine salt is very similar to the method currently used by Rhone-Poulenc, Incorporated, to synthesize and formulate 2,4-dichlorophenoxyacetic acid (2,4-D) amine salt. The major difference between the two processes is the use of the 2,4-D and dimethylamine in the current process in place of the 2,4,5-T and triethylamine. The process for 2,4,5-T amine salt production was not significantly changed during the years in which it operated. It was a batch process utilizing a single vessel and a filter, it was conducted in the "Formulation Area" (see Figure 1). This site has not produced any other amines of 2,4,5-T besides the triethylamine salt.

The process consists of several steps. The first step is addition of water to the vessel, T-19. Then 2,4,5-T is manually dumped from drums through a manhole into the vessel; simultaneously, an aqueous solution of triethylamine is pumped into the vessel. Next, a sample of the resulting solution is collected and analyzed for pH and percent 2,4,5-T acid content. More triethylamine is added if the pH is below 8.5 - 9.0; more 2,4,5-T or water is added as necessary to achieve the desired strength. The triethylamine and 2,4,5-T react to form the triethylamine salt of 2,4,5-T, via the following mildly exothermic reaction:



(2,4,5-T) (triethanolamine) (triethanolamine salt of 2,4,5-T)

The reaction occurs at atmospheric pressure and a temperature of 50-60°C. The salt product is written above in the ionic form, as it exists in solution. The next step in the process is the addition of relatively small quantities of the sequestering agent described previously in this section. After that addition, similar quantities of the antifoam agent are added. The final step is the pumping of the product solution from T-19, through a 50-u-pore-size bag filter, to the packaging operation. The changing of the filter bags was a manual operation. For a description of the packaging operation, see the description provided in the previous section for the packaging of the esters; the amine packaging uses the same equipment and procedures. The packaged product is ready for shipment.

Supplemental Information About the Production of 2,4,5-T and Related Products

For the 2,4,5-T (as well as 2,4-D) and esters, formulation included blending the completed acids and/or esters, and mixing solutions to the proper strengths. For the amines, the synthesis from the appropriate acid, dilution, addition of additives, and filtering were all considered part of the formulation operation, as noted in the previous section.

The esters of 2,4,5-T and 2,4-D were synthesized in the same equipment on a time-sharing basis. Conversely, 2,4,5-T acid and 2,4-D acid were not synthesized with analogous routes, and different equipment was used for these two syntheses. However, they did share between them the final acidification and vacuum filtration steps, and the acidification vessel (Q2) and the Bird-Young vacuum filter were time-shared by them (see Figures 2 and 3).

There have never been any "pressure releases" or "blowouts," which can result in occupational overexposures, in the processes producing 2,4,5-T or related products. This is because the processes were operated at near-atmospheric pressures, or under vacuum, and over-pressure conditions did not develop.

The aqueous sodium 2,4,5-trichlorophenate solution which was purchased by Chipman Chemical for use as a raw material in 2,4,5-T production was used exclusively for this purpose; none was resold. Conversely, 2,4,5-T acid and 2,4-D acid were both used as raw materials for ester and amine production, as well as formulated and sold in the acid form.

No industrial hygiene data characterizing worker exposure to materials found in the 2,4,5-T and related-product processes are available. No analyses of Na 2,4,5-TCP or any Chipman, Rhodia, or Rhone-Poulenc product for dioxin contamination are available. The Company believes that either 2,4,5-T ester, Silvex ester, or both were analyzed for dioxin content, but no record of the results can be found.

Conclusions

Although the personnel records do not identify which jobs were held by each individual (see Personnel Records section), workers assigned to Cost Center 602 had potential exposure to 2,4,5-T or other TCP-derived products during the periods when they were being synthesized. Therefore, the cohort of workers employed in Cost Center 602 by Chipman Chemical during the following periods should be included in the Dioxin Registry:

February 1961 through May 1961
October 1961 through May 1962
October 1962 through December 1962.

The concurrent exposure to 2,4-D and MCPA should be recognized.

The personnel records are well organized and complete, and permit identification of employees assigned to the cost center 602 between February 1961 and December 1962. The other workers at the plant, who formulated insecticides, can be separated out by their cost center assignment of 600 and removed from any further consideration. Hourly workers, salaried employees and maintenance personnel can be identified.

Workers employed at this site after December 1962, when syntheses of TCP-derived products were discontinued, should not be included in the Registry. The reason for this conclusion is that there is a relatively good chance that any individual employed after 1962 may never have been exposed to 2,4,5-T or other TCP-derived products, as noted in the Department Operations and Personnel section of this report; additionally, there is no way to identify which workers were exposed to these products, as noted in the Personnel Records section.

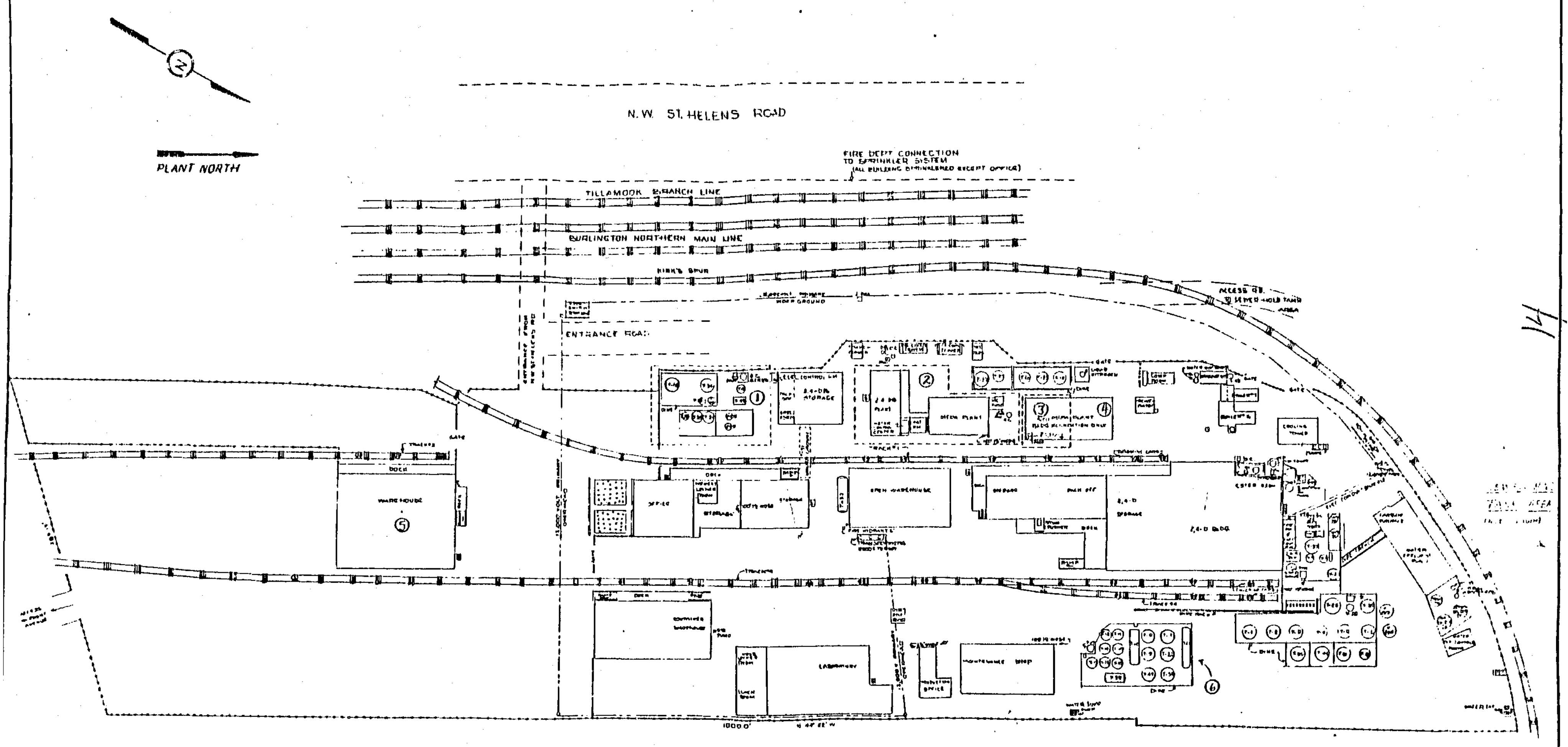
Formulators at Chipman, Rhodia, or Rhone-Poulenc sites other than Portland should not be included in the Dioxin Registry because of their mixed exposures to a wide variety of products and the likelihood that any particular individual may not have been exposed to 2,4,5-T products or derivatives.

Claims for Workers' Compensation benefits are in the personnel files. The company believes that chloracne was not a frequent problem at this plant.

Acknowledgements

Mr. Robert Briggs, Plant Manager, and Mr. Thomas Henshaw, Plant Engineer, spent many hours researching information. We appreciate their pleasant and helpful cooperation.

Figure 1. Plant Layout Diagram, Rhone-Poulenc, Incorporated, Portalnd, Oregon



① Dashed line surrounds Specialty Ester Area.
② Dashed line surrounds 2,4-DB Plant and current MCPA Plant which were nonexistent during 1960-62 period.
③ Dashed line indicates location of MCPA Plant during 1960-62 period.
④ New MCPA Plant Bldg. (Foundation Only) was nonexistent during 1960-62 period.
⑤ Insecticide Formulation Area during 1960-62 period.
⑥ Former 2,4,5-T products Formulation Area.

LEGEND
S SPRINKLER SYSTEM CONTROL STATION

Figure 2. Flow Diagram for 2,4,5-T Production Process, Rhone-Poulenc, Incorporated, Portland, Oregon

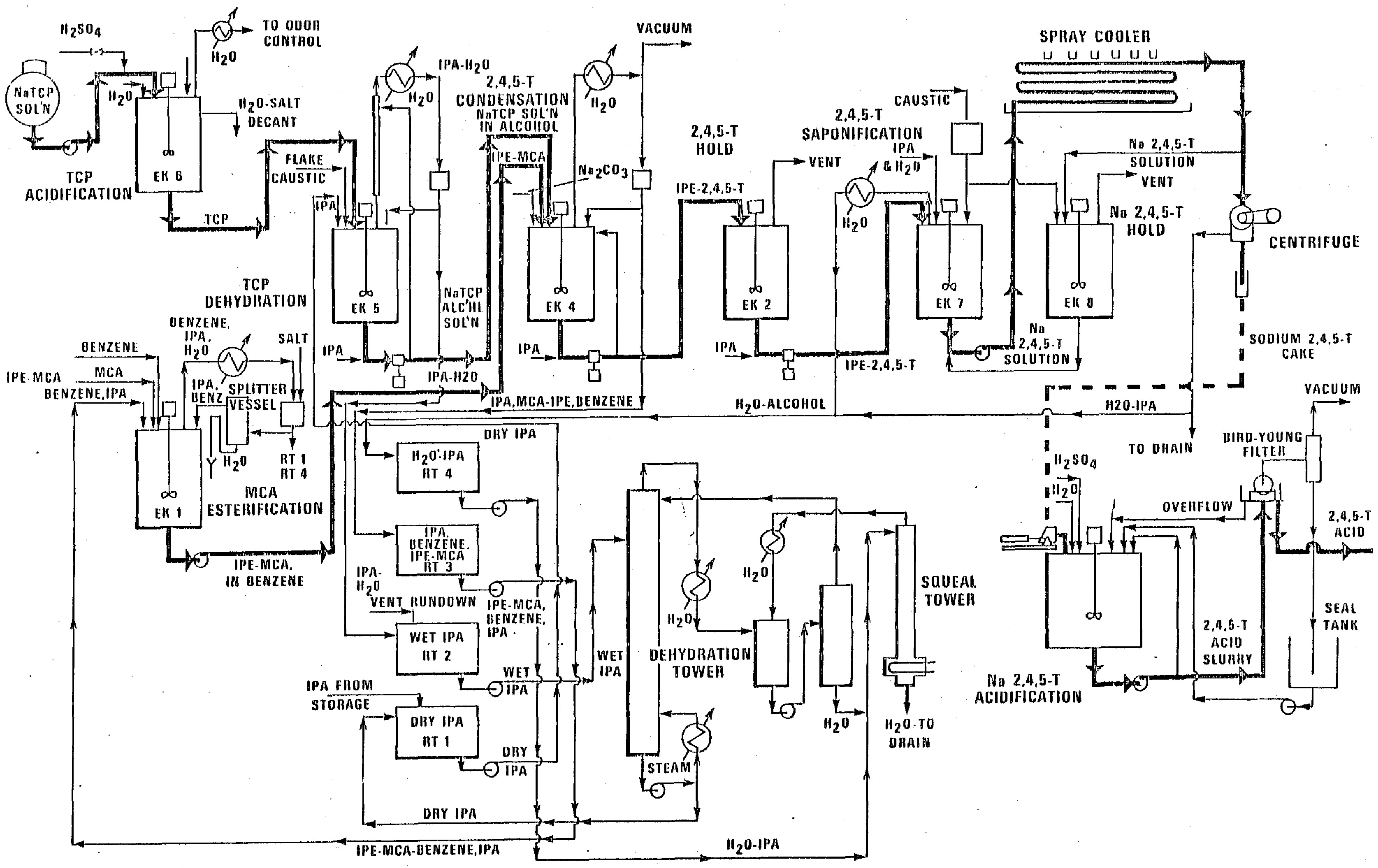


Figure 3. Equipment Location Diagram, Rhone-Poulenc, Incorporated, Portland, Oregon

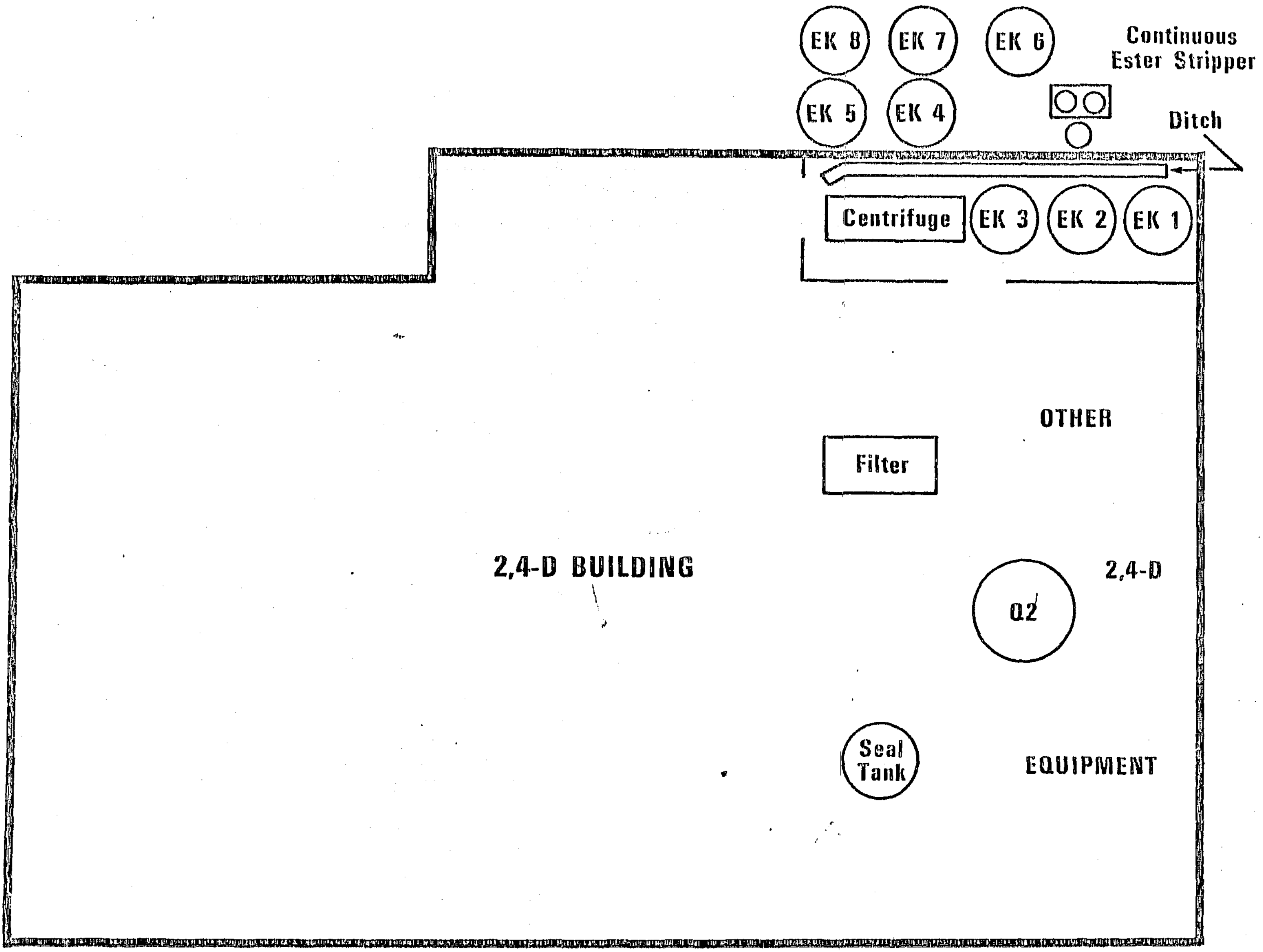


Figure 4. Flow Diagram for 2,4,5-T Ester Production Process, Rhone-Poulenc, Incorporated, Portland, Oregon