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DIOXIN REGISTRY REPORT

**REPORT PREPARED BY REVIEW DOCUMENTS FROM
DIAMOND SHAMROCK CORPORATION
DIAMOND ALKALI COMPANY
Newark, New Jersey**

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Abstract

The National Institute for Occupational Safety and Health (NIOSH) Dioxin Registry is a compilation of demographic and work history information for all U.S. production workers who have synthesized products known to be contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxins (2,3,7,8-TCDD) and/or hexachlorodibenzo-p-dioxins (HxCDD). Currently, there are fourteen production sites and approximately 7000 workers included in the Registry. The first use of this information is a retrospective cohort mortality study for which the comparison group is the U.S. male population. This study will evaluate the cause of death among the workers exposed to products contaminated with 2,3,7,8-TCDD and/or HxCDD.

The Diamond Alkali Company, in Newark, New Jersey, is a site included in the Registry. This site was owned and operated by the Diamond Shamrock Corporation. Sodium 2,4,5-trichlorophenate (Na 2,4,5-TCP) and 2,4,5-trichlorophenoxyacetic (2,4,5-T) acid, esters, and amines, all contaminated with 2,3,7,8-TCDD, were produced at this site from 1951 to 1969. Presented in this report is a description and history of the facility, workforce, processes, past exposures and personnel record systems taken from company documents, interview notes and published articles related to the site.

Introduction

The National Institute for Occupational Safety and Health (NIOSH), Division of Surveillance, Hazard Evaluations, and Field Studies (DSHEFS), Industrywide Studies Branch (IWSB), is conducting an investigation of the health effects resulting from occupational exposure to polychlorinated dibenzo-p-dioxins, and in particular 2,3,7,8-tetrachlorodibenzo-p-dioxins (2,3,7,8-TCDD) and hexachlorodibenzo-p-dioxin (HxCDD) isomers. This study, referred to as the Dioxin Registry, is a compilation of demographic and work history information for all U.S. production workers who have synthesized products known to be contaminated 2,3,7,8-TCDD and HxCDD. The Registry, initiated in 1979, was prompted by animal studies showing 2,3,7,8-TCDD to be acutely toxic and a chloracneagen, as well as a carcinogen and teratogen.¹⁻⁷ 2,3,7,8-TCDD is a contaminant found in 2,4,5-trichlorophenol (2,4,5-TCP) and/or its sodium salt (Na 2,4,5-TCP), which are raw materials used to produce chemical compounds such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T acid). Currently, there are fourteen production sites and approximately 7000 workers included in the Registry. The first use of this information will be a retrospective cohort mortality study for which the comparison group is the U.S. male population. This study will evaluate the causes of death among workers exposed to products contaminated with 2,3,7,8-TCDD and/or HxCDD.

The Diamond Alkali Company's 2,4,5-T production facilities were located at 80 Lister Avenue in Newark, New Jersey. This site is one of the fourteen sites included in the Dioxin Registry and produced Na 2,4,5-TCP and 2,4,5-T acid, esters and amines from August 1951 to August 1969. The Diamond Alkali Company was a predecessor of the Diamond Shamrock Corporation. Presented is a compilation of information and data obtained from documents provided to NIOSH by Diamond Shamrock, notes from interviews with former employees, published articles and other sources (i.e. Agent Orange studies and Public Health Service reports). This report updates an earlier draft report dated April 1, 1983.

Description and History of the Facility

The Diamond Alkali Company, a division of the Diamond Shamrock Chemical Company, Diamond Shamrock Corporation was a facility located at 80 Lister Avenue, Newark, New Jersey. The facility was located on a site of approximately 3.12 acres currently bound on the south by Sherwin Williams Company and Duralac Chemical Corporation, on the west by a large industrial building owned by the Sherwin Williams Company, on the west by Sergeant, EM Pulp and Chemical Company, and on the north by the Passaic River (see Figure 1).

The Kolker Chemical Works, Incorporated originally operated the facility from February 1946 to August 1951 when Diamond Shamrock acquired the site by an exchange of stock. Most of the workers employed by Kolker stayed on to work for Diamond. Diamond owned and operated the facility until March 1971 when the site was sold to Chemicaland Corporation. Production at the

facility ceased on August 1, 1969. Currently the facility is not operating, is unoccupied and is covered with plastic tarpaulins (see Figure 2). The chemical products produced, throughout the years of operation, at this facility during the years Diamond operated it are listed in Table 1 along with the years of production and their acronyms. The products which are relevant to the NIOSH Dioxin Registry, are Na 2,4,5-TCP, and 2,4,5-T acid, esters and amines.

Figure 3 depicts the plant layout for the time period of 1951 through 1960, showing the general locations of the production processes. Figure 4 is a more detailed layout of the main manufacturing building shown in Figure 3 as location 1. As shown in Figure 4, the Na 2,4,5-TCP production was located in the north-eastern section of the build, indicated by location 2, adjacent to the hexachlorobenzene (HCB) production process (location 6), but physically separated by walls. An explosion and fire occurred in the Na 2,4,5-TCP autoclave reactor at noon on Saturday, February 20, 1960. The pressure and temperature rose rapidly in the reactor first causing a rupture disc on the reactor to blow and venting the reactor material to the Passaic River. Within a few minutes after the rupture disc blew, a manhole cover on the reactor blew off, allowing methanol vapors to escape from the reactor into the building. The methanol vapors ignited, blowing up the reactor and burning down the building. A chemist walking by the Na 2,4,5-TCP production area was killed, dying of lung edema, and twelve others including the plant manager were injured. As a result of this accident, the buildings, designated as locations 1 and 5 in Figure 3, were demolished and tanks in location 4 were moved to facilitate the construction of three new buildings shown in Figure 5 as locations 6, 7, 8, 9, 10, and 11. The production processes for 2,4,5-T and 2,4-dichlorophenoxyacetic (2,4-D) acids, esters and amines (shown as location 2, Figure 3) were unaffected by the accident and commenced production within two weeks. Na 2,4,5-TCP stocks along with Na 2,4,5-TCP purchased from the Monsanto Company was used to produce 2,4,5-T acid. In January 1961, the production of Na 2,4,5-TCP was restarted in location 8 shown in Figure 5, alongside the monochloroacetic acid (MCA) and 2,4-dichlorophenol (2,4-DCP) production process, locations 7 and 6 respectively. Also shown in Figure 5 is the layout of the 2,4-D Building (the building unaffected by the explosion and fire) as shown by locations 1 through 5. While there was no information made available as to the layout of the 2,4-D/2,4,5-T Building prior to the explosion and fire of 1960 it is reasonable to assume that the layout was the same (from 1951 through 1960). In 1967, some building expansion was done, as shown in Figure 6, due to an increased demand for more 2,4,5-T and 2,4-D (i.e. government contract to produce Agent Orange) increasing production capacities 67% and 54% respectively. Also in September 1967, Na 2,4,5-TCP activated charcoal purification column was added to the Na 2,4,5-TCP production process (location 3 in Figure 6). The purification column was added to the process to remove the unwanted 2,3,7,8-TCDD contaminant from the Na 2,4,5-TCP. All production ceased on August 1, 1969, and the site including the equipment was sold to Chemical and Corporation in March 1971.

Description of the Records

Representatives from the corporate office sent copies of existing personnel, worker compensation and medical records from the closed Newark facility to NIOSH along with a list of all persons employed at the facility. There is variation in the amount of detailed information available for each person. For many individuals, there are complete personnel files, and for a few persons, there exists only a single index card with demographic information, dates of hire and termination, and (usually) one or more job titles. The medical records for many individuals contain detailed listings of all jobs held at Diamond, some with commentaries describing the job responsibilities.

For most individuals, it is possible to construct detailed work histories from careful review of all of the records for each person. Tables 2 and 3 list the job titles and job descriptions which were obtained from our review of the records. For a few salaried individuals, there are no personnel or medical records because they were sent with the individual when the person was transferred to another Diamond plant. Our review of the records indicated that Diamond hired some workers from Manpower, an agency which supplies temporary workers. There are no records to identify any of these individuals.

Description of the Workforce

Table 3 lists those job titles along with their descriptions that were associated with processes relevant to the scope of the Registry. One to two men per shift were assigned to the Na 2,4,5-TCP process, 2 men per shift were assigned to the 2,4,5-T acid process, and 32 men over 4 shifts were responsible for 2,4-D and 2,4,5-T esters, amines production and formulations. There were approximately twenty mechanics/maintenance men assigned plant wide at any given time. In addition there were 3 technicians, 12 persons in the office and 3 or 4 men in the yard. The 2,4-D and 2,4,5-T acid, ester and amine workers all worked in the same building (2,4-D/2,4,5-T Building, see Figure 3) but the formulations workers were in an area adjacent to the 2,4-D/2,4,5-T Building.

In a report written in 1963 by Birmingham and Key,⁸ the following comments were made relative to the workforce:

"The population at risk is about 60, all males. Currently, the plant operates three shifts per day, seven days a week."

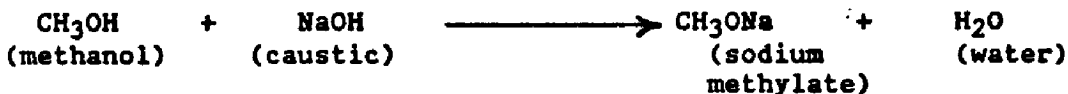
Description of the Production Processes

The following sections are process descriptions for processes in the scope of the Registry as they were most recently operated. Through the years of operation many major process changes were made. Table 4 list these changes and the time periods in which they took place.

A. Na 2,4,5-TCP

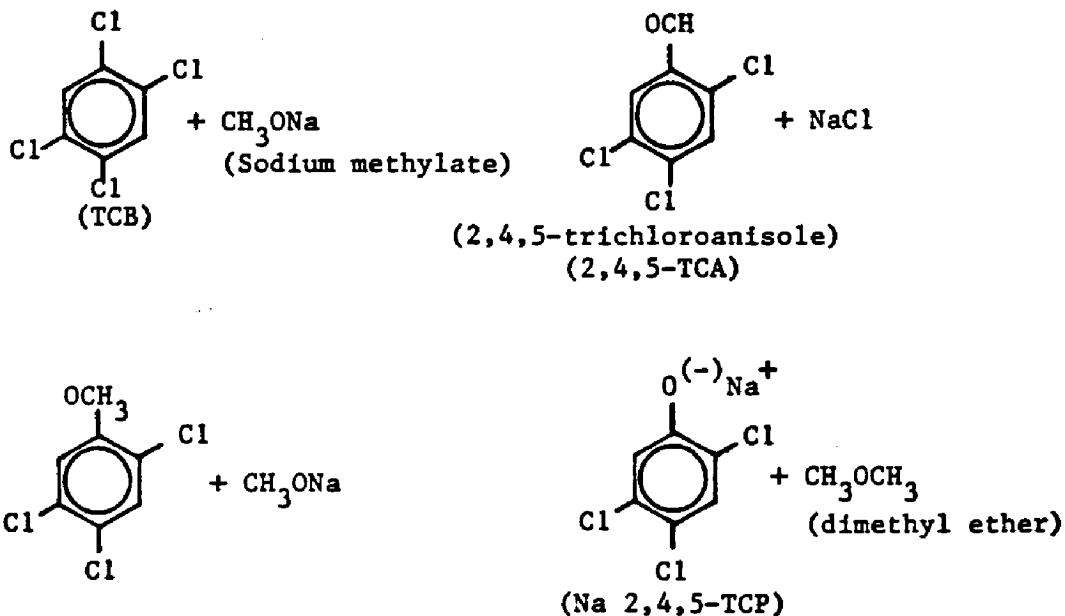
Diamond Alkali produced an aqueous solution of Na 2,4,5-TCP in a batch operation using the following raw materials: 1,2,4,5-tetrachlorobenzene (TCB), flaked caustic (NaOH), and methanol (MeOH). Methanol and water were also used as solvents. A block flow diagram of the process is shown in Figure 7.

In the first step of the process, methanol was pumped into the methanol-caustic mix tank. Methanol, recovered from previous batch runs and supplemented with fresh methanol, was pumped into the methanol-caustic mix tank. Flaked caustic was dumped from drums into the methanol and sodium methylate was formed by the following reaction mechanism:



Methanol was added in excess of 1:1 mole ratio and acted as a solvent for the sodium methylate formed. The sodium methylate solution was pumped from the methanol-caustic mix tank to a drop tank where it was heated to 60°C.

TCB was stored in steel tanks and heated to 165°C to keep it in a molten state. The TCB was pumped to an autoclave reactor, a closed agitated, jacketed reactor. Once the TCB was added to the autoclave, the sodium methylate solution was gradually fed to the TCB over a period of 1/2 to 2 hours depending on the batch size. The critical mole ratio in the system was that between caustic and TCB, with the process normally operated with a caustic to TCB ratio of 2.6 moles/mole. The reaction mass was maintained at a temperature range of 165-175°C under a pressure of 350 to 375 pounds per square inch gauge (psig). The following reaction took place.



The formulation of dimethyl ether was kept to a minimum due to the presence of water. The reaction time was approximately 3 to 5 hours after which the reactor was cooled down to a temperature range of 50 to 60°C and the pressure reduced to less than 25 psig. During this cooled down period, the reactor was vented to remove vaporized methanol and any dimethyl ether which might have been formed. After the reactor was cooled, steam was applied to the reactor jacket to distill off the remaining methanol. The temperature of the reaction mass was raised to approximately 120°C during this operation.

The methanol vapors that came off during this simple distillation were condensed in the crude methanol condenser and collected in the crude methanol storage tank. From the crude methanol storage tank, the crude methanol was purified in the crude methanol still. The methanol was distilled off as an overhead and was condensed in a series of condensers and collected in the redistilled methanol receiver. The crude methanol still bottoms was basically water with traces of organics. These still bottoms were discharged to the sewer. In 1962 the crude Na 2,4,5-TCP holding tank was converted for use as a methanol still. Methanol coming from the Na 2,4,5-TCP holding tank was recycled for reuse without further distillation.

Once the majority of the methanol was removed from crude Na 2,4,5-TCP, the crude Na 2,4,5-TCP was pumped from the autoclave reactor to the crude Na 2,4,5-TCP holding tank. Six batches of Na 2,4,5-TCP were made in this manner and stored in the crude Na 2,4,5-TCP holding tank. After six batches had been made, the contents in the crude Na 2,4,5-TCP holding tank were pumped to the anisole still. In the anisole, the crude Na 2,4,5-TCP was steam stripped to remove TCB, TCA and unrecovered methanol.

The distillate, consisting of TCB, TCA and MeOH was collected in the anisole receiver, where at a later time, when sufficient material had been collected, a batch of Na 2,4,5-TCP was produced from this material. A batch of this type occurred, on the average, once a month. The process to make Na 2,4,5-TCP from recovered unreacted materials was the same as the process just described with the exception that less caustic was added to the reactor.

The steam stripped Na 2,4,5-TCP was pumped from the anisole still through a Monel screen filter, which removed crystals of sodium chloride (Na Cl) suspended in the Na 2,4,5-TCP. After the batch of Na 2,4,5-TCP had been pumped through the filter, residual liquid remaining on the filter was blown out. The wet salt cake which collected on the filter was back flushed with water and discharged to the sewer. The use of the Monel filter to remove Na Cl from the Na 2,4,5-TCP solution was suspended soon after TCP Production resumed in 1961. The Na Cl was left

in the Na 2,4,5-TCP and remained in the reaction mass until removed during filtration of Na 2,4,5-T slurry. The operation continued this way until the plant was shut down.

From the Monel screen filter, the Na 2,4,5-TCP was pumped to Na 2,4,5-TCP holding tank. The Na 2,4,5-TCP product in the holding tank was approximately 36% by weight solution of NaTCP. Water was added to the Na 2,4,5-TCP to make a 30% by weight solution ready to be use as a raw material in the production of 2,4,5-T acid.

The recovery and purification of crude Na 2,4,5-TCP from the reaction mass was originally conducted by a method called "Dilution-Filtration Method." This procedure of recovery and purification took place from February 1951 through September 1954. The method consisted of diluting the crude Na 2,4,5-TCP reaction mass in the autoclave reactor with water to a concentration of 5 to 10%, adding filter aid and filtering it through a precoated plate and frame filter. This removed any non-water soluble materials including unreacted TCB and TCA. The Na 2,4,5-TCP was then concentrated back to approximately 30% by acidification to form 2,4,5-TCP, decantation to remove the aqueous layer and the neutralization of the 2,4,5-TCP with caustic back to Na 2,4,5-TCP. After September 1954 the "Dilution-Filtration Method" was replaced by steam stripping in the anisole still.

As noted early in this report, there was an explosion and fire in the Na 2,4,5-TCP process resulting in having to replace the unit. As a result of this replacement some changes were made. Initially, from 1951 to 1960, all raw materials were charged directly to the autoclave reactor and then heated to reaction conditions. In 1961, with the new Na 2,4,5-TCP process, the methanol and caustic were mixed together then gradually added to molten TCB as described previously. Also there were two 1000 gallon autoclave reactors installed in the new Na 2,4,5-TCP unit, instead of one reactor, as was the case prior to 1961.

In September 1967, a purification column was added to the process to remove 2,3,7,8-TCDD from the Na 2,4,5-TCP. The column was filled with activated charcoal, and in activated charcoal, and was fed material from a holding tank where the Na 3,4,5, TCP was transferred following anisole distillation. The product was diluted prior to carbon treatment to a concentration of approximately 10% Na 2,4,5-TCP. Reconcentration was achieved by acidifying a portion of the stream coming from the purification column to 2,4,5-TCP, followed by decantation to remove the aqueous layer. After decantation the 2,4,5-TCP was neutralized with caustic soda back to Na 2,4,5-TCP, then combined with the remaining 10% Na 2,4,5-TCP to form the desired 30% Na 2,4,5-TCP solution. The activated charcoal in the column was replaced once during the two years

A molten mixture of 2,4,5-T acid and water overflowed from the secondary acidification tank into the decanter where the mixture was allowed to settle and form two layers, an aqueous layer and an organic layer. The aqueous layer containing water, Na_2SO_4 and small amounts of unreacted Na 2,4,5-T was pumped from the decanter to the settling tank (the Na_2SO_4 filter feed tank). The organic layer containing molten 2,4,5-T acid was pumped from the bottom of the decanter to the wash column.

The setting tank was used to recover Na 2,4,5-T from the decanter and the wash column. In the setting tank, the aqueous solutions were cooled to temperatures ranging from 40 to 50°C. Water was sometimes added to settling tanks contents to aid in the cooling process. Cooling the aqueous solution resulted in a solid precipitate forming out of the solution. The solid precipitate was then collected by pumping the contents of the settling tank through a pressure filter to the sodium sulfate makeup tank. The solid precipitate would collect on the pressure filter and was recovered by flushing the filter with water and pumping the precipitate to the slurry hold tank where it was held for future 2,4,5-T acid batches. Only limited quantities of 2,4,5-T acid were recovered for recycle.

The molten 2,4,5-T was pumped from the decanter to the top of the wash column where it washed with a counter current flow of hot water at 120°C. The washed molten 2,4,5-T would come from the bottom of the wash column and was collected in the washed acid receiver while the wash water which came from the top of wash column was pumped to the settling tank.

From the washed acid receiver, the wet molten 2,4,5-T was pumped either to amine tanks to make up water soluble amine salts of 2,4,5-T or to a Luwa thin film evaporator dryer. The wet molten 2,4,5-T was fed to the top of the dryer and flowed down over the heated surface as a mechanically created thin film. The dry molten 2,4,5-T was then collected in a heated tank, the dry acid receiver. The water vapor coming from the dryer was pumped to a condenser collected in the Na_2SO_4 filter feed tank.

The dry molten 2,4,5-T in the dry acid receiver was then either pumped to the ester process for esterification or fed to the flaker. The flaker was a 24-inch diameter cylinder, 36 inches long that was rotated. This cylinder was water cooled. Molten acid was picked up on the external face of the cylinder as the drum rotated in a shallow pool of molten 2,4,5-T acid. The solidified 2,4,5-T was removed continuously as the drum rotated. The 2,4,5-T flakes so formed were then packaged using a bag packer. From the monthly operating reports it appears the 2,4,5-T acid was only flaked once (80,000 lb) in May 1968.

Prior to the 1966-67 time period, the recovery of 2,4,5-T acid was different than the "Melt-Wash Method" just described. The 2,4,5-T acid was recovered by a "Dustless Acid" method where the acid was collect as a wet cake containing 10 to 12% water. The wet cake was collected by the use of a centrifuge which separated the 2,4,5-T acid from the mother liquor.

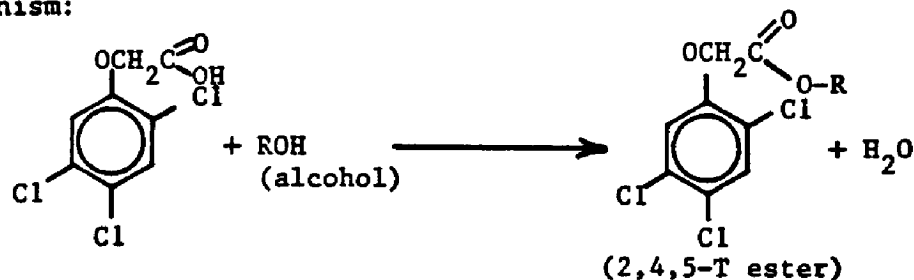
The 2,4,5-T acid process was contained in the Acid Building where both 2,4-D acid and 2,4,5-T acid were made. The original 2,4,5-T acid unit was dismantled to make space available for the installation of an expansion of the 2,4-D unit in 1966-67. The old 2,4-D unit was refurbished and used for the production of 2,4,5-T acid using the melt-wash method.

During 1960 when the Na 2,4,5-TCP process was under reconstruction, Na 2,4,5-TCP was purchased from the Monsanto Company and perhaps other manufactures on a small scale.

C. 2,4,5-T Esters

Diamond Alkali produced esters of 2,4,5-T using the following raw materials: 2,4,5-T acid, alcohols (mainly n-butanol, 2-ethylhexanol or isopropanol), and H₂SO₄ as a catalyst. A block flow diagram of the process is shown in Figure 9.

The first step in the process was to charge an alcohol to the esterifier, a closed jacketed agitated reactor, along with one gallon of sulfuric acid which was added as a catalyst. Next 2,4,5-T acid was added to the esterifier and the contents in the reactor was heated to approximately 140°C. The reaction took place via the following mechanism:



where R represents n-butyl, 2-ethylhexyl (2-EH), or isopropyl groups. Alcohol and the water of reaction were removed by azeotropic distillation during the reaction period. Alcohol was injected into the reactor continuously during the esterification to provide an excess of alcohol. Recycled alcohol was used during the early phase of the reaction and fresh "dry" alcohol was used during the later phase of the reaction to ensure completion of the reaction. The progress of the reaction was monitored by taking samples from the reactor and testing the sample for residual 2,4,5-T acid. When the esterification was complete, alcohol injection was stopped and the excess alcohol removed by simple distillation. Additional quantities of sulfuric acid were added as required to maintain a certain rate of reaction.

Further processing of the 2,4,5-T ester after alcohol removal was optional and depended upon the end use of the product. The additional processing steps included water washing to remove residual sulfuric acid, sodium sulfate, and sodium chloride that might have been present

from previous process steps, decoloring to improve the product color; and air stripping to remove alcohol below the level attainable by simple distillation.

Washing a batch of 2,4,5-T esters was accomplished by pumping the ester from the esterification reactor to an agitated vessel. Then 1000 gallons of water was added to the ester, mixed, and then allowed to settle. The water was then decanted and the wet ester was returned to the esterification reactor and dried by application of heat (140°C) under a vacuum.

The reaction conditions of the esterification process varied with the molecular weight of the alcohol being used. The higher the molecular weight the higher the reaction temperature.

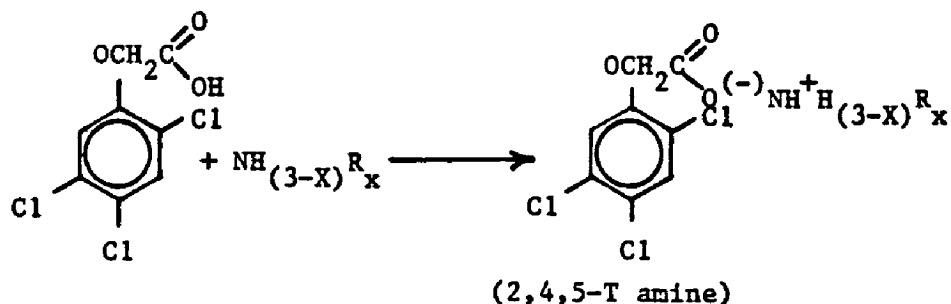
The only significant change to the ester process was made in 1966-67. Prior to this time only wet 2,4,5-T was available for the process. The presence of water in the 2,4,5-T resulted in longer esterification reaction time. After this time, dry molten 2,4,5-T was available. This resulted in a reduced reaction time.

The esterification system consisted of five 1000 gallon reactors. The capacity of 2,4,5-T esters was the equivalent of 3 million pounds per year of 2,4,5-T acid and for 2,4-D esters was equivalent to 12 million pounds per year of 2,4-D acid. Thus the approximate time the esterifiers were used for the 2,4,5-T esters was usually 20 percent.

D. 2,4,5-T Amines

Two types of 2,4,5-T amine processes were operated, one for the production of water soluble 2,4,5-T amines and the other for the production of oil soluble 2,4,5-T amines. The formation of the 2,4,5-T amine salts was a simple acid base titration which generated a significant heat of reaction.

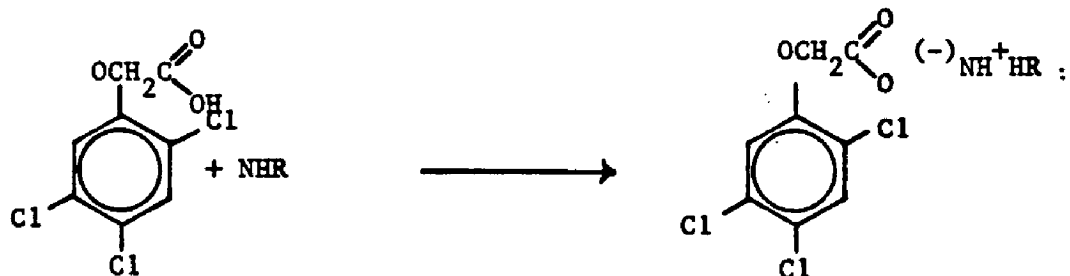
Aqueous 2,4,5-T amines were prepared by charging a small amount of water into a jacketed agitated reactor followed by the charging of wet, molten 2,4,5-T acid. The agitator was turned on and the aqueous amine was fed to the reactor while cooling water was applied to reactor's jacket. The reaction mechanism to form the 2,4,5-T amines was as follows:



R = (CH₃)₂ - or (CH₃CH₂)₃-

The amine was added until a specific pH was reached.

Oil soluble 2,4,5-T amines were prepared in a similar manner as the aqueous 2,4,5-T amines except a heavy aromatic naphtha was used as the solvent instead of water. The heated naphtha solvent charged into a jacketed reactor followed by the charging of dry, molten 2,4,5-T acid. The agitator was turned on and the anhydrous amine was fed to the reactor while cooling water was applied to the reactor's jacket. The reaction mechanism to form the 2,4,5-T amine was as follows:



This type of amine was referred to as Dacamine. ●

The finished 2,4,5-T amines were diluted to the correct specific gravity using the appropriate solvent and sent to formulation for packaging. Samples to measure specific gravity were collected from the reactors using dip tubes.

The amine salts of 2,4-D acid were also prepared in the systems. The systems were dedicated, one for aqueous amines and one for oil soluble amines. Generally the 2,4,5-T amines required approximately 20% of the production time with balance required to produce 2,4-D amines. The T-oil soluble amines were particularly low volume items and production might only be a few thousand gallons per year.

E. Additional Process Information

In addition to the descriptions of how the processes of interest to the Dioxin Registry operated, Diamond Shamrock also provided 2,4,5-T acid production quantities for Diamond Alkali Company for the time periods of 1960 to 1968. These data are listed in Table 5, originally from The Pesticide Review, 1968, USDA. The annual production quantity of 2,4,5-T acid ranged from 600,000 to 2.9 million pounds. The year the Na 2,4,5-TCP process was not in operation, 1960, had the lowest production quantity at 600,000 pounds, and 1968, the year the new 2,4,5-T acid process was in operation, had the highest production quantity at 2.9 million pounds.

Also provided to NIOSH were Diamond monthly reports which contained Summary of Vacancies, Operating Data, and Operating Comments from Production, Maintenance and Utilities, and Plant Technical groups. The monthly reports provided cover the months from January 1966 to December 1968, and provide a detailed account of monthly costs and production quantities, as well as a commentary on equipment changes and repairs, production problems, process data and personnel activities.

Table 6, Production Quantities for Products of interest to the Dioxin Registry, was constructed from data extracted from the monthly reports and lists the production quantities for Na 2,4,5-TCP, 2,4,5-T acid, amines (both 2,4-D and 2,4,5-T water soluble amines), Dacamines[®] (both 2,4-D and 2,4,5-T oil soluble amines), and formulations (both 2,4-D and 2,4,5-T esters and amines formulations).

Several observations can be made by reviewing Table 6, such as the relative activity of these processes from month to month and from year to year, and the percent of 2,4,5-T ester produced as compared to total esters produced (both 2,4,5-T and 2,4-D ester). Virtually all Na 2,4,5-TCP produced was further processed to produce 2,4,5-T acid. Table 7, constructed by Diamond technical personnel in April 1966 for the purpose of process expansion, provides a breakdown of the product mix. Examination of Table 7 provides some insight as to the percentage of amines and dacamines which were 2,4,5-T products. For example, approximately 2.5% of the oil soluble amines produced were 2,4,5-T amines and approximately 7.0% of the water soluble amines were 2,4,5-T amines. Because of the requirement to use most of the 2,4,5-T produced to manufacture Agent Orange, the project product break-down was never achieved, therefore, the actual quantities of T-amines were something less than the percentages listed.

Beginning in January 1967, process operating data were also included in the monthly reports. Table 8 is a summary of these data for the Na 2,4,5-TCP, 2,4,5-T acid and 2,4,5-T esters processes. For Na 2,4,5-TCP, Table 8 provides the mean number of batches produced per month, the mean batch size per month, the mean reaction/digestion time per month, the mean/maximum autoclave reactor temperature and the mean/maximum anisole still temperature. For the 2,4,5-T acid process, Table 8 provides a summary of the mean Na 2,4,5-TCP conversion percentage, the mean 2,4,5-T acid production cycle time per month, the mean 2,4,5-T acid reaction time per month and the mean condensation reactor temperature per month. For 2,4,5-T esters, Table 8 provides the mean number of batches of butyl T and 2-EH-T produced per month, the mean batch size for butyl and 2-EH 2,4,5-T esters per month, the mean production cycle time for butyl and 2-EH 2,4,5-T esters per month and the mean reaction temperature for butyl and 2-EH 2,4,5-T ester per month.

Description of Past Exposure

No industrial hygiene measurements for 2,3,7,8-TCDD were made available, by the company. However, the review of the monthly reports from September to December 1968 showed references were made to an investigation of possible sources of 2,3,7,8-TCDD contamination. This investigation, initiated because of continuing incidence of chloracne, was directed toward determining whether there was 2,3,7,8-TCDD surface contamination on tanks, pipes, floors, etc. throughout the facility. The results of this investigation indicated that no 2,3,7,8-TCDD was detected in any of the areas tested. There is a possibility that these negative results could have been a result of interferences between 2,4,5-T esters and 2,3,7,8-TCDD on the chromatograms (from October 1968 monthly report).

According to John Burton, plant manager at the time, dermatitis problems in two persons first occurred during the period January 1951 and January 1952 when the company was producing TCB by chlorination of monochlorobenzene. According to Burton the problem cleared up when the company began to purchase TCB from Hooker Chemical Company in January 1952.

In September 1954 the dilution-filtration system, which removed insoluble organics from Na 2,4,5-TCP reaction mixture, was replaced by the anisole steam stripping system. According to Burton, about six months later TCP operators developed chloracne (7 in total). As a result of the chloracne cases more ventilation was installed in the Na 2,4,5-TCP production area and more attention to housekeeping and personnel hygiene was recommended by Burton.

On March 28, 1963 a dermatoses investigation⁸ was conducted by Donald J. Birmingham, M.D. and Marcus M. Key, M.D. of the Occupational Health Research and Training Facility, Division of Occupational Health, Public Health Service in Cincinnati, Ohio. The investigation was requested by the New Jersey State Department of Health in Trenton, New Jersey. In the report, the nature of the problem was stated, "In the 12 years of operation of the Newark plant, about 46 of 48 cases of chloracne have occurred in the production of 2,4,5-T. Forty of the affected workers are currently employed at the plant. The population at risk is about 60, all males." Small outbreaks of chloracne occurred in 1961 shortly after the new Na 2,4,5-TCP process started and in the summer of 1962. An observation made during the visit was, "although most of the production operations are enclosed, there are breaks in the process, evidenced by contamination of equipment, ceilings, floors, stairs and hand railings, particularly in the old building." The "old building" referenced was the 2,4-D/2,4,5-T Building where 2,4-D and 2,4,5-T acids, esters, and amines were produced. Reference to personal hygiene practices were also made, "Clean uniforms are furnished by the company. Separate locker rooms for street and work cloths are provided. Clean modern shower stalls and Bradley basins are provided, along with towels and soap. Daily showers at the end of the shift are encouraged, but are not mandatory." During the visit, Drs. Birmingham and Keys examined 17 cases of chloracne, several of which had findings suggestive of porphyria

(red urine, hyperpigmentation of exposed areas, and hirsutism, but no bullae or atrophic scars). The chloracne was manifested by comedones and cysts on exposed areas (especially the face) and at sites of friction. In one case, the chloracne was generalized.

Recommendations made in the report were as follows:

1. "The old production building should be renovated as soon as possible. Enclosure of the process and good housekeeping are most effective ways of preventing contamination of the workmen.
2. All workmen with severe chloracne, hyperpigmentation, hirsutism, accompanied or unaccompanied by red urine, should be hospitalized to investigate the possibility of liver damage in general or porphyria in particular.
3. In the future, when the company purchases new work clothing, it should be the one piece coverall type. This will help prevent chloracne at the belt line.
4. Showers after work should be made mandatory."

While there is no indication whether recommendations 2, 3 or 4 were followed, recommendation 1 was never accomplished. A report⁹ dated October 2, 1968, from F.G. Steward to G.L. Pratt entitled "Ester Plant Replacement" states that the equipment requires replacement because it was installed in the late 40's and early 50's, was poorly arranged and required much maintenance. The report noted that the unit includes five 1000-gallon esterifiers used for batch processing, and that "the Dacamine[®] reactor is in the middle of the 'T' ester area." A recommendation was also made to renovate the Formulation Building and equipment which "is old and has close proximity and a close working relationship with the Ester unit."

Two published reports of medical evaluations of Diamond workers also described past 2,3,7,8-TCDD exposure. In a publication by Bleiberg et al, entitled "Industrially Acquired Porphyria,"¹⁰ a medical evaluation was presented for 26 workers. This study involved 18 individuals having chloracne and 8 without the condition, and concluded that hyperpigmentation and hirsutism were proportional to the severity of chloracne in these individuals. Eight of the 26 workers and three additional hospitalized individuals with chloracne had evidence of porphyria cutanea tarda, but this was not proportional to the severity of chloracne. The authors stated that neither chloracne nor porphyria corresponded to the degree of chemical contact (mild, moderate, or severe) estimated for the 26 workers. However, they note that it was difficult to truly judge the extent of exposure. The authors concluded that some intermediate or products were responsible for both chloracne and porphyria cutanea tarda. This was the first published report relating porphyria cutanea tarda to chloracne or to industrial exposure.

Poland, et. al.,¹¹ studied all male volunteers employed at Diamond in February 1969. The emphasis of this study was placed on observation of chloracne, porphyria cutanea tarda, hepatotoxicity, and neuropsychiatric symptoms. Seventy-three men were divided in four groups: 1) (n=20) administrators, technical and clerical help, lab technicians and engineers housed in the building in location 11 in Figure 3; 2) (n=11) supervisors and foremen spending most of their time in the production areas; 3) (n=28) on-line production area workers; and 4) (n=14) maintenance workers, some confined to the shop and some frequently in production areas. The total group included 55 white and 18 black employees, with an average duration of employment of 8 years.

Poland, et. al., found 18% of the workers had moderate to severe chloracne; maintenance men (group 4) had the most acne and the administrative group; (group 1) had the least acne. Severity of chloracne correlated significantly with the presence of hyperpigmentation, hirsutism, eye irritation and high score on the manic scale of the Minnesota Multiphasic Personality Inventory (MMPI). Chloracne was not correlated significantly with duration of employment or coproporphyrin excretion, a characteristic of porphyria cutanea tarda. In fact, no clinical porphyria cutanea tarda was found, and only one worker had persistent uroporphyrinuria. The workers were divided into groups by their current work locations: Na 2,4,5-TCP production, 2,4-DCP production, phenoxyacetic acid production, ester production, formulation and storage tanks, maintenance, supervisory laboratory help, and administration. There were no statistical differences found, and the authors suggest this might be due to the small size of each group and the mobility of the workers.

A recent report by Jones and Chelsky of the Diamond Shamrock Corporation¹³ reviewed the papers by Bleiberg and Poland as well as production and medical records at the company. The authors suggest that the porphyria cutanea tarda may have been caused by hexachlorobenzene which was produced in the plant in small amounts until 1960.

An office correspondence¹² dated March 25, 1965 from E.L. Chandler to John Cort, Jr., described the events of a meeting with representatives from Dow, Hooker Chemical, Hercules and Diamond. The meeting was held by Dow in order to inform others of the hazards of chloracne which they had determined was caused by 2,3,7,8-TCDD. Using surface wipe testing methods, Dow industrial hygienist had determined the presence of 2,3,7,8-TCDD on tool handles, benches, instruments, etc. using a gas-liquid chromatography analytical method which they provided to other companies.

As a result of this meeting with Dow, Diamond began analyzing its products and process streams for 2,3,7,8-TCDD. Figure 10 shows the analytical procedure used for 2,3,7,8-TCDD analyses in Na 2,4,5-TCP and chromatograms for such analyses. Table 9 lists analytical results for 2,3,7,8-TCDD from various samples which were made available to NIOSH by Diamond. The analytical results for 2,3,7,8-TCDD date from May 1965 to January 1969.

Table 10 summarizes the analytical results listed in Table 9. Note that the Na 2,4,5-TCP dioxin content dropped from a mean of 16 ug/g in 1965 (with all samples having detectable levels) to a mean of 1.1 ug/g in 1967 (with 19 out of 22 samples being non-detectable). The decrease was a result of the addition of the activated charcoal purification column.

Table 11 is a compilation of monthly Na 2,4,5-TCP assays obtained from monthly reports starting with April 1967 through January 1969. Assays for percent 2,4,5-TCP, 2,4,6-TCP, DCP, and TCA as well as 2,3,7,8-TCDD concentration (ug/g) are listed in Table 11.

Table 12 lists analyses for 2,3,7,8-TCDD in Diamond products collected from sources other than Diamond Shamrock (i.e. Agent Orange studies and Dow Chemical Company). From Table 12 it can be noted that dioxin analyses of Agent Orange range from <0.05 to 17 ug/g. Close examination of these values seems to indicate that the Agent Orange supplied to the Air Force could be divided into two groups, one prior to the installation in September 1967 of the activated charcoal purification column (8.0-17 ug/g 2,3,7,8-TCDD) and one after the installation of the column (<0.05-0.07 ug/g 2,3,7,8-TCDD). This observation is supported by data on 2,4,5-T acid generated by Dow, also listed in Table 12. In 1965 Dow measured dioxin content in 2,4,5-T acid at 5 and 16 ug/g, but in 1969 the products contained less than 1 ug/g.

Conclusions

This report describes production processes, personnel information and the history of Diamond Shamrock Newark plant relevant to production of Na 2,4,5-TCP, 2,4,5-T acid, ester and amines. Except where noted, information used to write this report was sent to NIOSH by Diamond Shamrock. For most individuals, it is possible to construct detailed work histories. The operation and activities of the processes of interest is comprehensive, particularly for the years 1966 through 1968 when monthly reports were made available. Based on the knowledge of the processes, the available dioxin analytical data, and job title description potential dioxin exposure assessment can be made.

Based on process and job descriptions and available dioxin analytical data, we concluded that operators involved in the production of Na 2,4,5-TCP had potential exposure to 2,3,7,8-TCDD while performing the tasks of 1) operating the autoclave reactor, 2) collecting samples from the autoclave reactor, 3) operating the dilution-filtration product recovery system (from 1951-1954), and 4) operating the anisole still and product recovery system. The 2,3,7,8-TCDD concentrations associated with the autoclave reactor, dilution filtration, and anisole still were approximately 20, 10, and 70 ug/g respectively.

There were two operators associated with the 2,4,5-T acid production process, the 2,4,5-T Reactor Operator and the 2,4,5-T Centrifuge Operator (1951-1967) or the 2,4,5-T Melt Operator (1967-1969). The tasks for the 2,4,5-T Reactor Operator, which posed potential exposure to 2,3,7,8-TCDD

were 1) the loading and operation of the condensation reactor and 2) the collection of samples from the condensation reactor. 2,3,7,8-TCDD concentration levels associated with these tasks were approximately 20 ug/g prior to 1967 (the addition of TCP activated charcoal purification tower occurred on September 1967) and 1 ug/g from 1967 to 1969. For the 2,4,5-T Centrifuge operator, the tasks of 1) operating the reslurry tank, 2) operating the acidification tank, and 3) operating the "Mother Liquor" recovery separation systems represented the tasks with potential 2,3,7,8-TCDD exposure. The reslurry tank and acidification tank operations had approximately 20 ug/g 2,3,7,8-TCDD concentrations in the process stream while the "Mother Liquor" had approximately 10 ug/g concentration.

The 2,4,5-T Melt Operator performed the tasks of 1) operating the primary and secondary acidification tanks, 2) operating the decanter, 3) operating the wash column, and 4) operating the dryer all of which had potential 2,3,7,8-TCDD exposure to substances with concentrations of approximately 1 ug/g. The tasks of 1) loading and operating the esterifier, 2) collecting samples from the esterifier, and 3) cleaning the esterifiers represented tasks during which the Ester Operator had potential 2,3,7,8-TCDD exposure. Prior to 1967, the 2,3,7,8-TCDD concentrations in substances at these points in the process were approximately 20 ug/g for loading and operating the esterifier and 10 ug/g for collecting samples and cleaning the esterifier. After 1967 to 1969 the concentrations in substances at these points in the process dropped to approximately 1 and 0.5 ug/g, respectively.

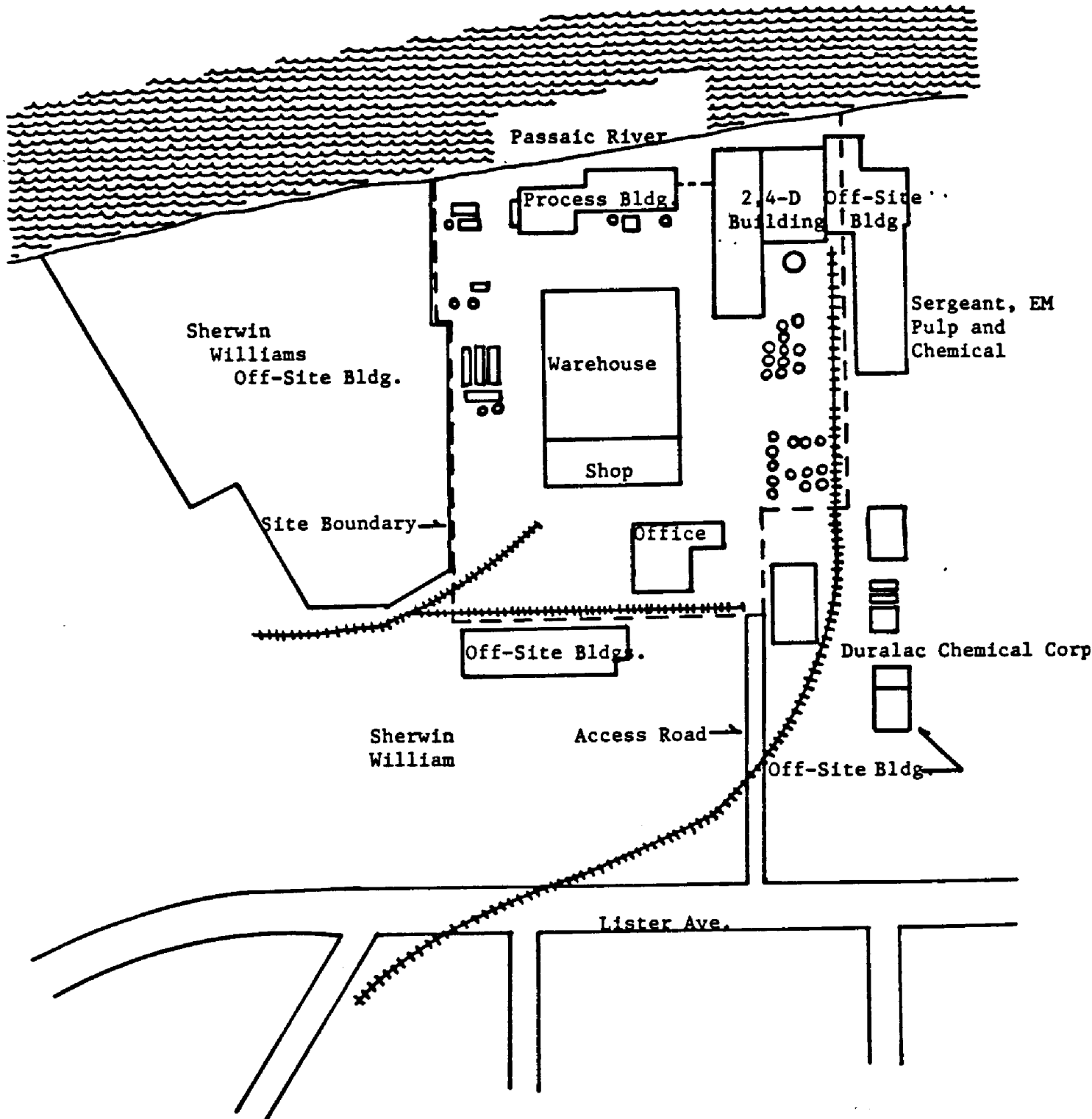
The production and operator helpers performed formulations and aminizations. Potential 2,3,7,8-TCDD exposures were associated with the tasks of 1) loading and operating reactor and/or mixing vessels, 2) collecting samples, and 3) cleaning reactors and/or mixing vessels. As with the ester operations prior to 1967 the 2,3,7,8-TCDD concentration in the process stream was approximately 20 ug/g for loading and operating operations and approximately 10 ug/g for sample collection and reactor and/or mixing vessel cleaning. After 1967 the concentrations in the process stream dropped to approximately 1 and 0.5 ug/g, respectively.

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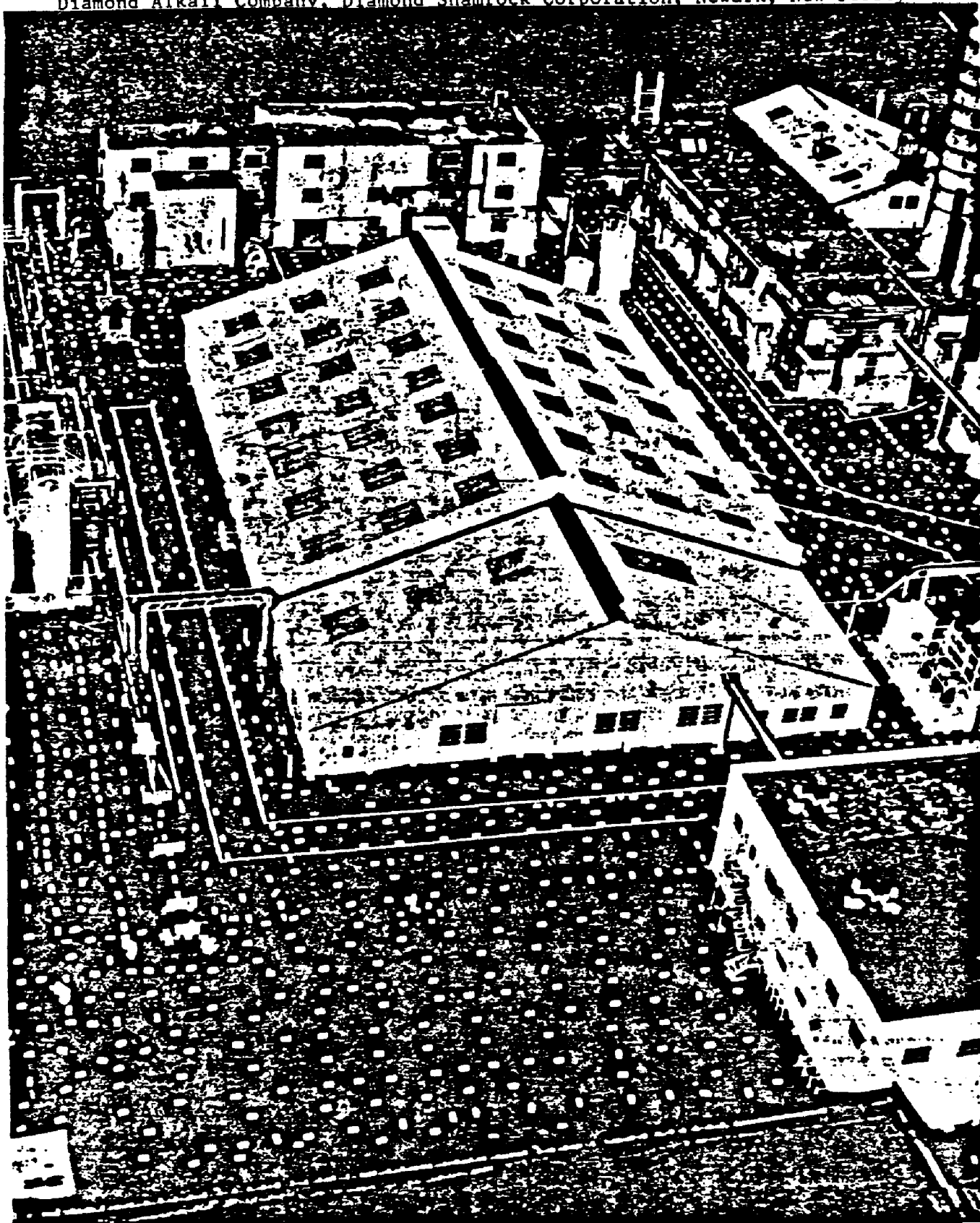
Figure 1
Diamond Alkali Company and Surrounding
1983

Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey



Aerial View of Diamond Alkali Company
1985

Diamond Alkali Company, Diamond Shamrock Corporation, Newark, New Jersey



Plastic tarpaulins cover much of the open area of the Diamond Alkali Company plant in Newark, New Jersey, because the soil was found to contain levels as high as 50 parts per million 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Federal and state officials had the tarpaulins put down to prevent TCDD contamination to the surrounding areas.

Figure 3
 Plant Layout 1951-1960
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

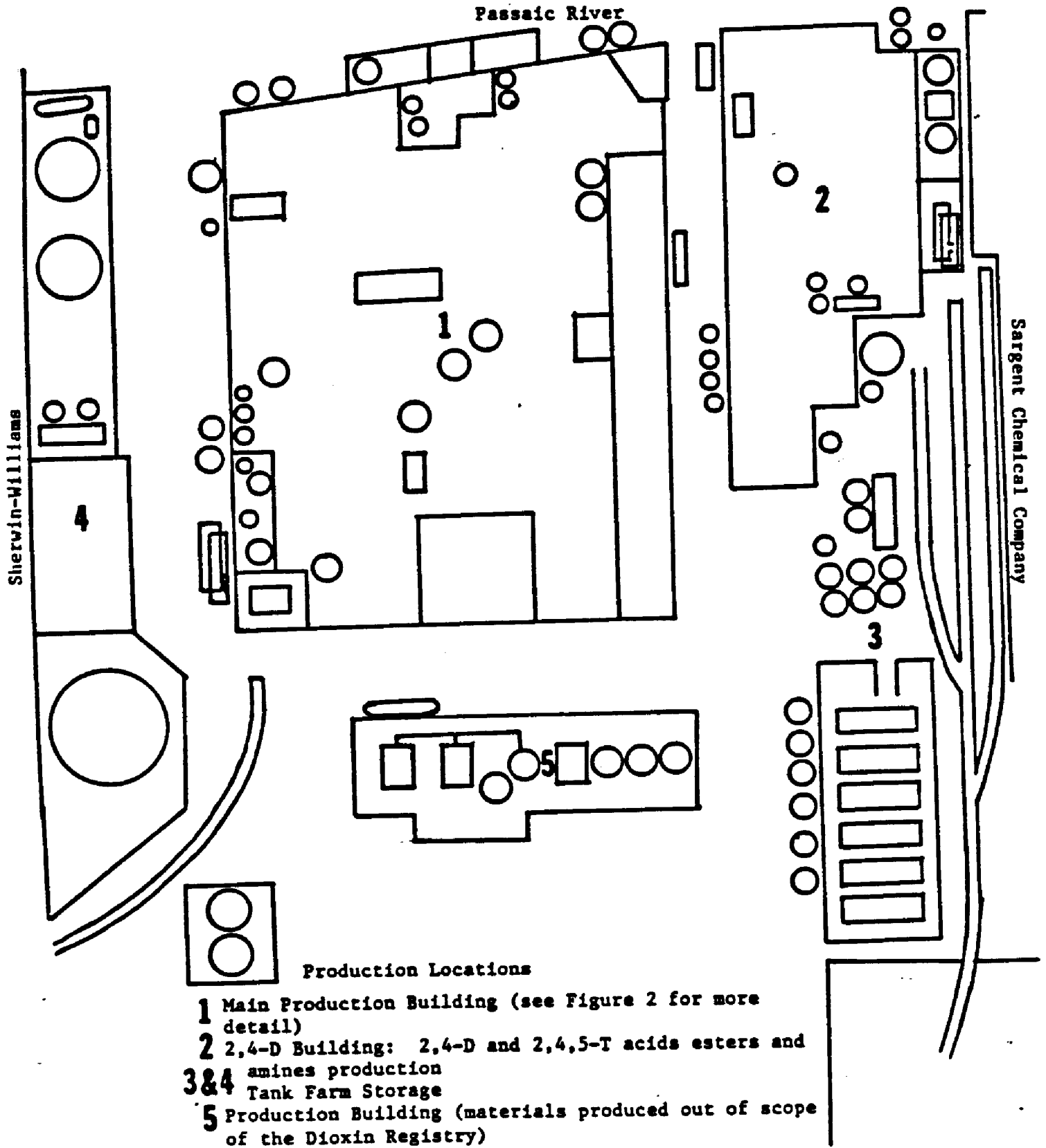
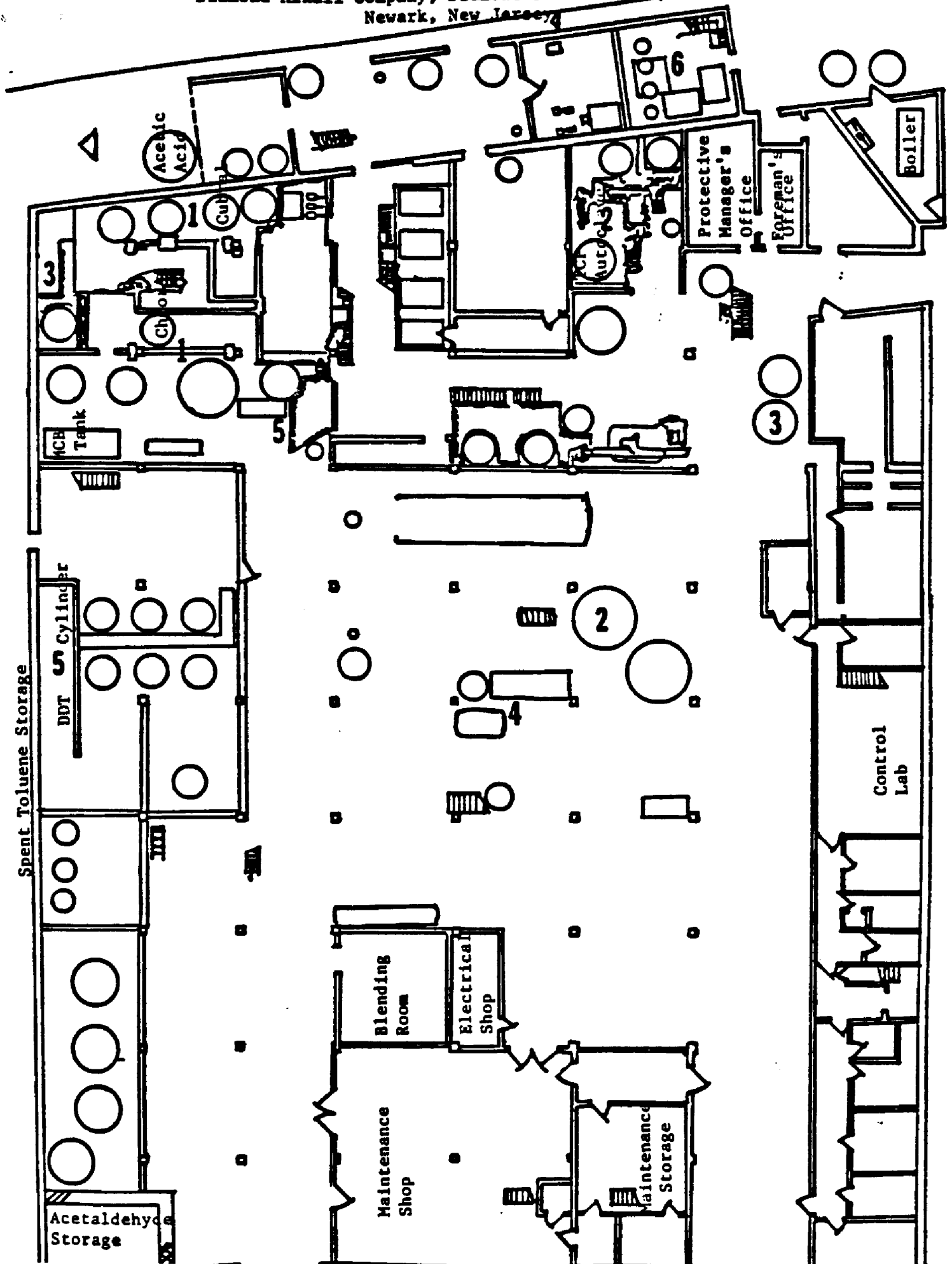


Figure 4
Main Manufacturing Building Floor Layout
1st Floor

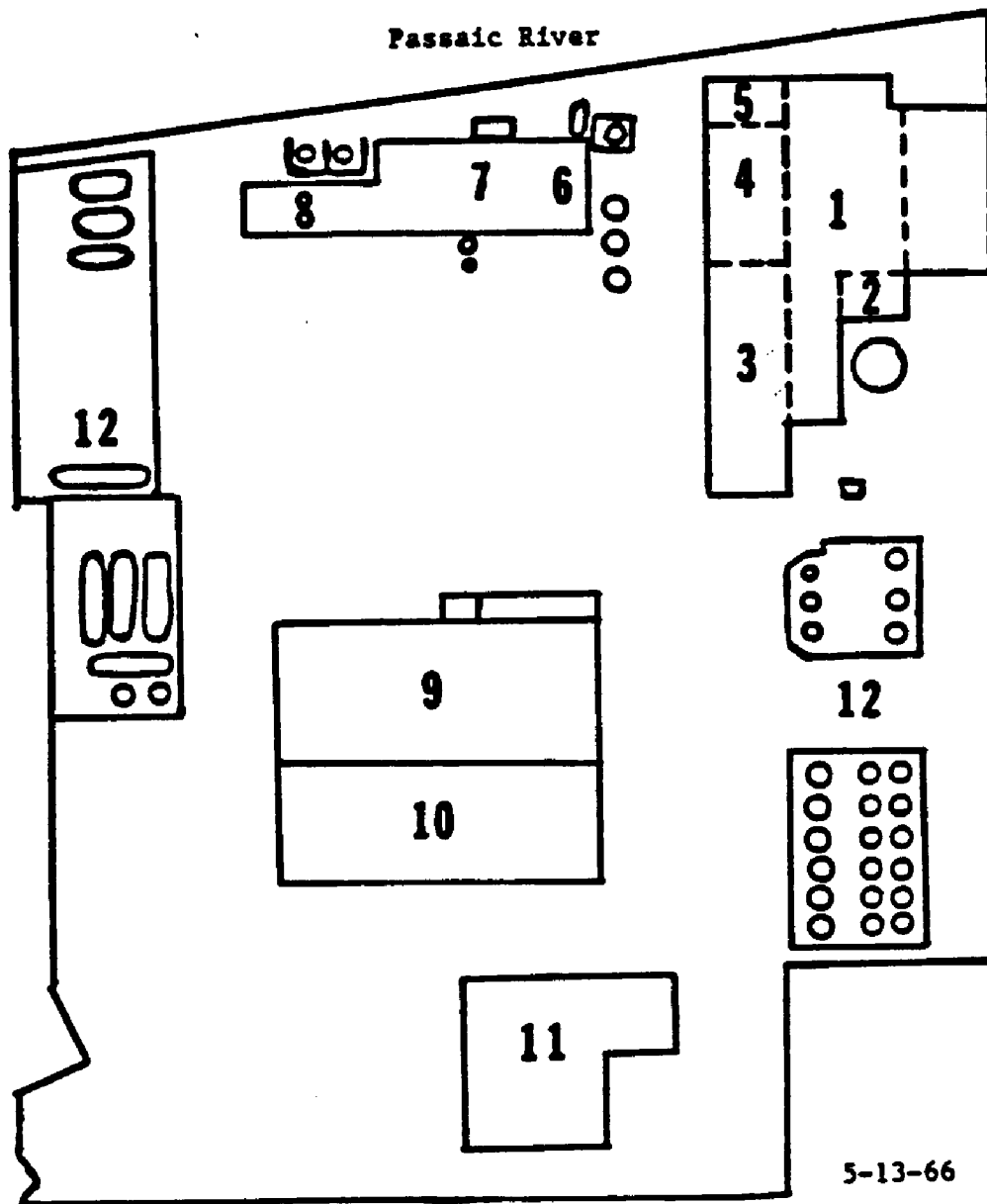
Production Locations

Chloral	1
NaTCP	2
MAC	3
Miticide	4
DDT	5
HCB	6

Figure 4
 Main Manufacturing Building Floor Layout, 1946-1959
 Diamond Alkali Company, Diamond Shamrock Corporation
 Newark, New Jersey



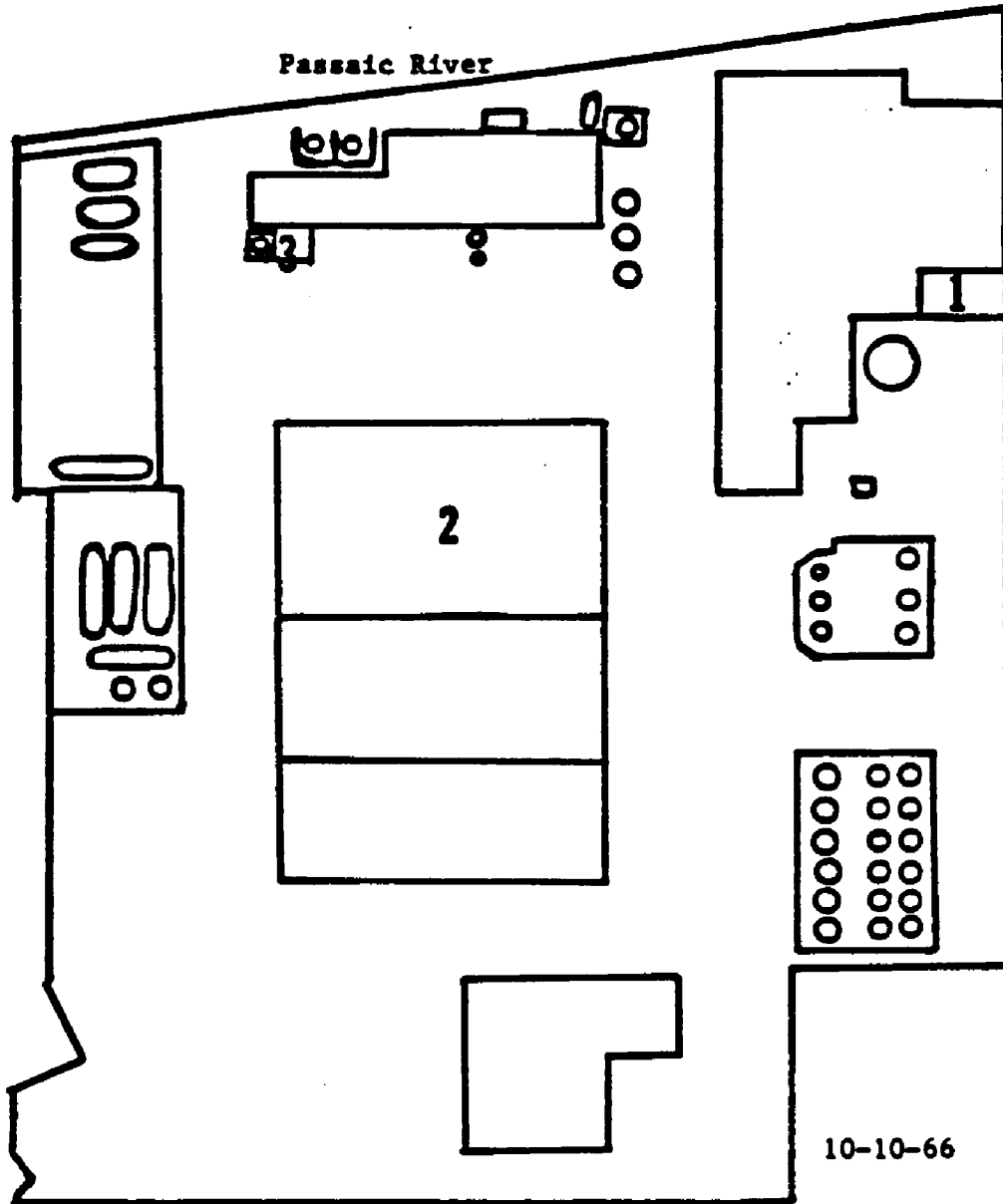
Plant Layout 1961-1966
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey



Production Locations

- 1 2,4-D and 2,4,5-T Acid area 1A 2,4-D and 2,4,5-T Acid Flaking Building.
- 2 Amine salts area (water soluble)
- 3 Formulations area
- 4 Esters area
- 5 Amine salts area (oil soluble)
- 6 2,4-DCP area
- 7 MCA area
- 8 Na 2,4,5-TCP area
- 9 Warehouse area
- 10 Shipping and Maintenance area
- 11 Laboratory, Plant Office and Change House area
- 12 Formulations and Storage Tank area

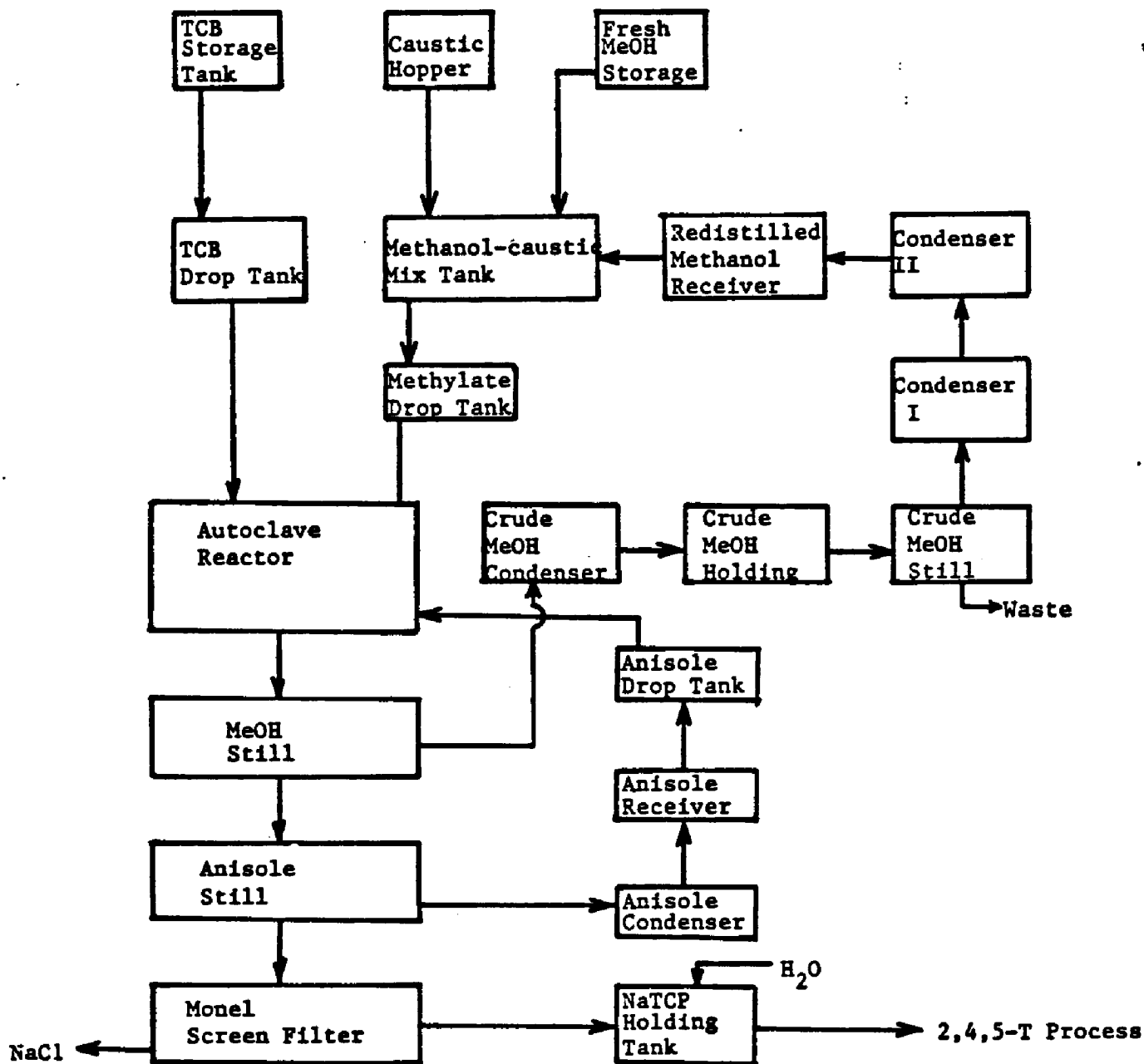
Plant Layout 1967-1969
New Structure Additions 1967
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey



Building Expansion Locations

- 1 Flaker Building Extension
- 2 Warehouse Extention
- 3 Process Building Extension

Figure 7
 Na 2,4,5-TCP Process Block Flow Diagram
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey



Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey

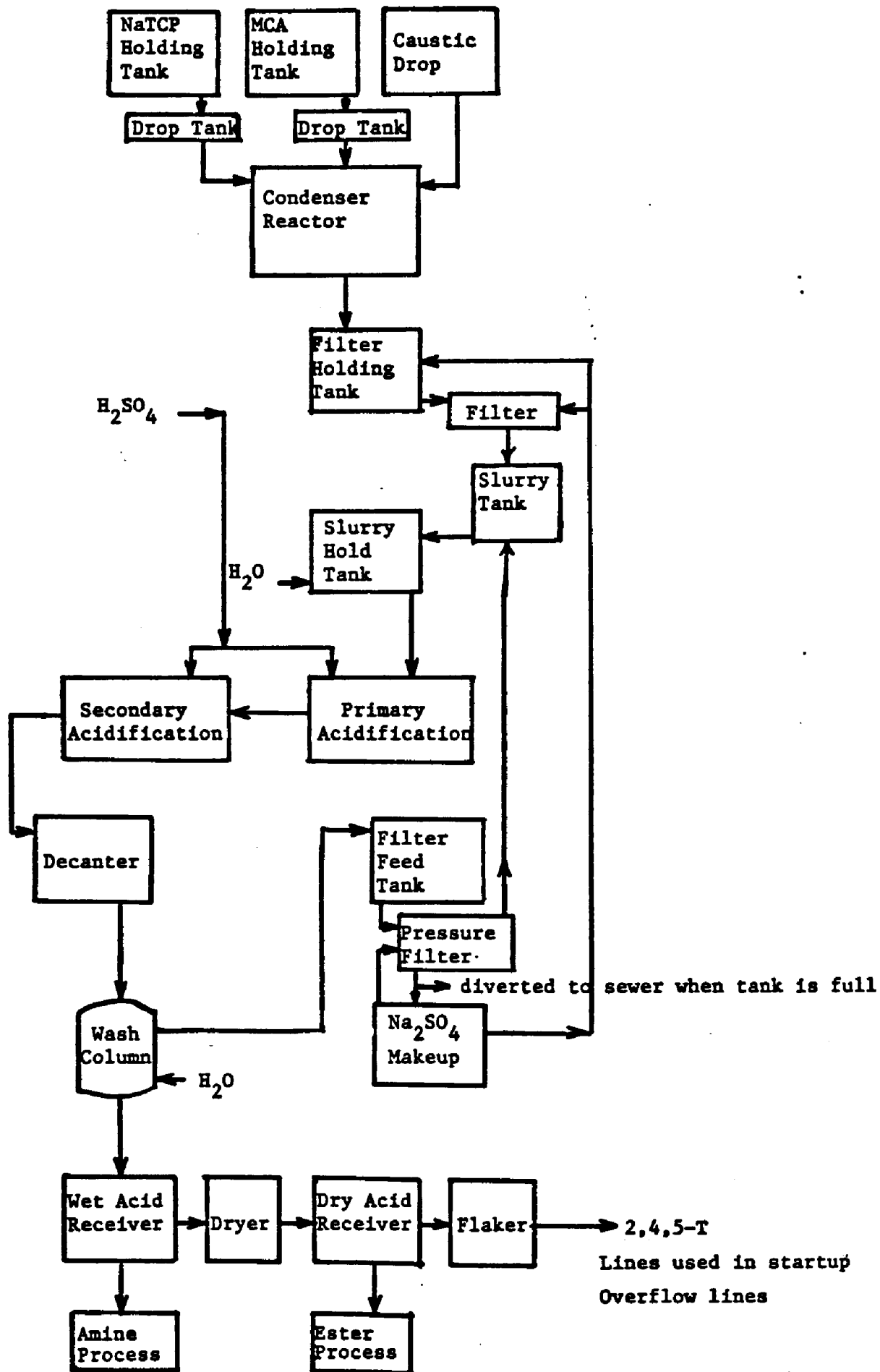


Figure 9
 2,4,5-T Ester Block Flow Diagram
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

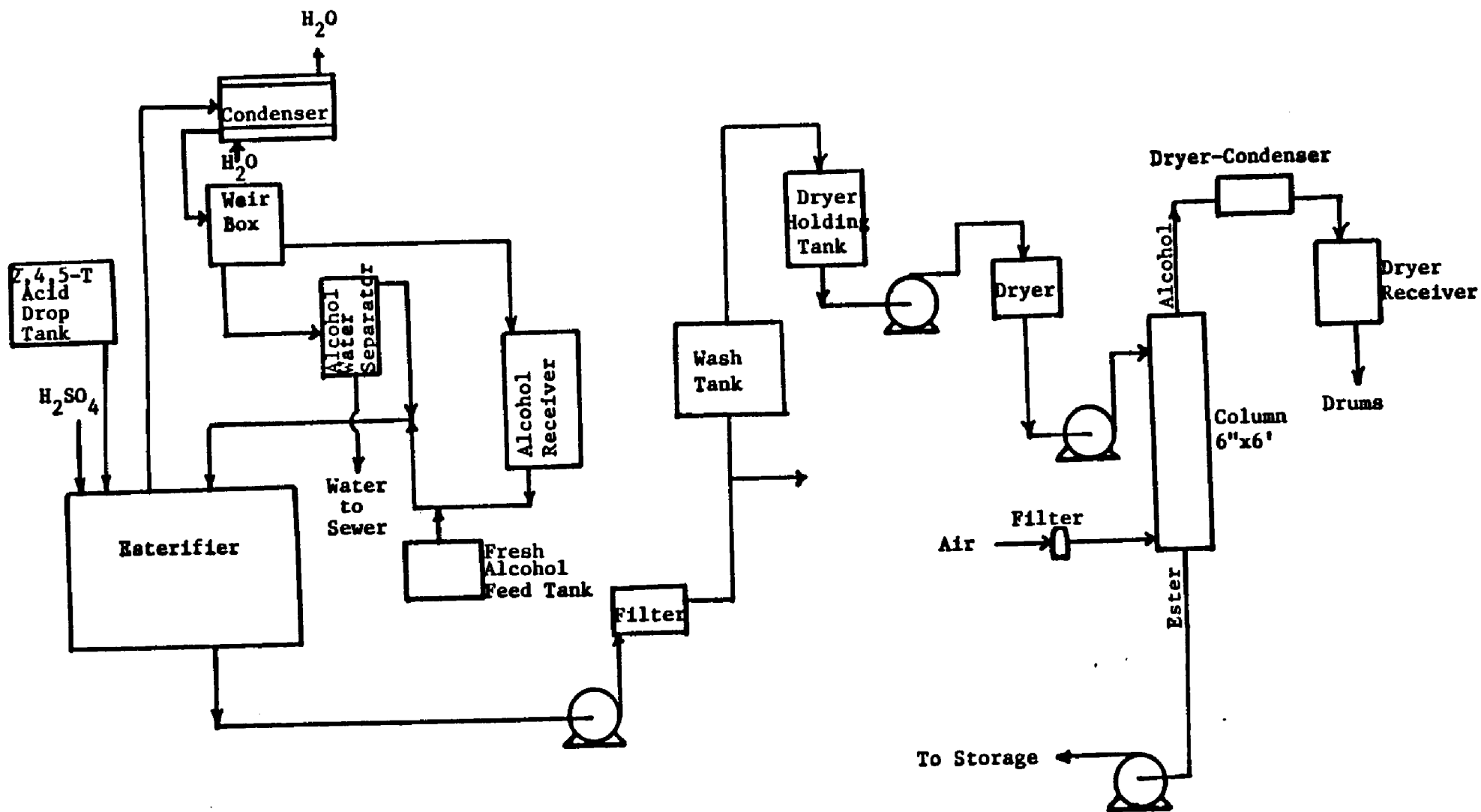


Figure 10
 Analysis of TCP for p-Dioxin
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

ANALYSIS OF TCP FOR p-DIOXIN

PROCEDURE:

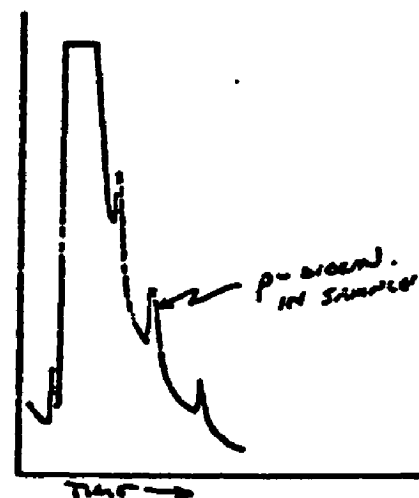
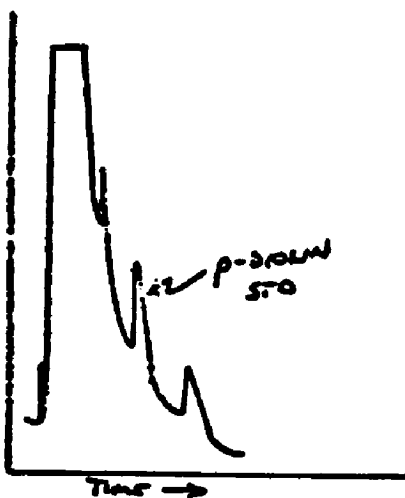
An equivalent of 50 grams of 100% TCP (example: 250 grams of 20% TCP = equivalent of 50 grams of 100% TCP) is weighed into an iodine flask (500 ml) and 50cc of benzene are added. This mixture is agitated for 2 hours and the mixture transferred to a separatory funnel. The bottom (TCP) layer is discarded and the benzene layer filtered through glass wool into a 100cc beaker, evaporated to 5cc and transferred to a 10cc volumetric flask which is brought to mark with benzene. This sample is injected vs. a 100 ppm p-dioxin standard.

Temperature °C - 215
 Attenuation - 8
 Range - 10
 Sample Size - 1 μ l
 Column - 5' 5% SE 30 on Chromasorb W 60/80

CALCULATIONS: ppm p-Dioxin = $\frac{\text{ppm of standard} \times (\text{peak height of sample})}{\text{peak height of standard} \times 5}$

CONDITIONS:

F & M 1609
 C = 5' 5% SE 30
 A = 10/8
 S = 1 μ l
 T = 215°C



CONDITIONS:

NaTCP (After purification column)
 No p-Dioxin present
 Condition:
 C = 5' 5% SE 30
 A = 10/8
 S = 1.0 μ l
 T = 245° on proportional controller
 Gas Rates:
 Air = 11.5 on rotometer
 Helium = 9.5 on rotometer
 Hydrogen = 8.0

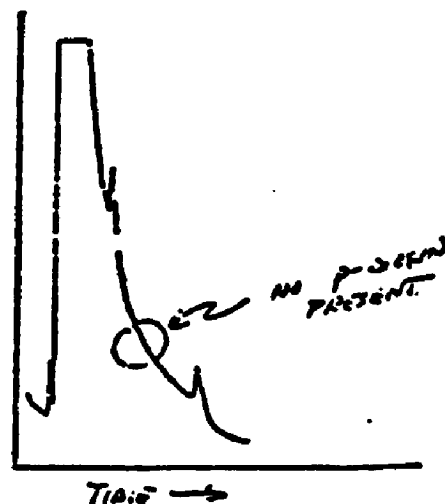


Table 1
 Products and Production Periods
 Diamond Shamrock Corporation
 Diamond Alkali
 Newark, New Jersey

Product	Production Period	Yearly Production Capacity (MM lbs)
Sodium 2,4,5-trichlorophenate (Na 2,4,5-TCP)	1/51-8/69	25
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T acid)	1/51-8/69	
2,4,5-T esters		
ethyhexyl (2-EH)	?/52-8/69	
butyl	?/53-8/69	
isopropyl	?/52-8/69	
2,4,5-T amines (water soluble)		
dimethylamine (DMA)	?/52-8/69	
triethylamine (TEA)		
2,4-Dichlorophenol (2,4-DCP)	2/46-8/69	
2,4,6-Trichlorophenol (2,4,6-TCP)	2/46-8/69	
2,4-Dichlorophenoxyacetic acid (2,4-D acid)	2/46-8/69	25
2,4-D esters		
ethyl hexyl (2-EH)	?/52-8/69	
butyl	?/53-8/69	
isopropyl	?/52-8/69	
2,4-D amines (water soluble)		
dimethyl amine (DMA)	?/52-8/69	
triethylamine (TEA)		
Monochlorobenzene (MCA)	2/46-2/60	
Hexachlorobenzene (HCB)	2/46-2/60	10
Dichlorodiphenyl trichloroethane (DDT)	2/46-8/58	100
p-Chlorophenyl-p-chlorobenzene sulfonate (Ovex, Miticide K-101)	5/52-1/58	10
2,5-Dichlorophenyl-p-chlorobenzene sulfonate (Compound 923)	2/46-?/57	
1,1,1-Trichloroacetaldehyde (Chloral)	2/46-8/61	
Benzene sulfonyl chloride (BSC)	2/46-?/59	
p-Chlorobenzene sulfonyl chloride (PCBSC)	2/46-?/59	
p-Chlorobenzene sulfonamide (PCBSA)	2/46-?/59	
4,4-dichlorodiphenylsulfone (44-DDS)	2/46-?/59	
p-Acetylamino benzene sulfonyl chloride (PAABSC)	2/46-?/59	
p-Methoxy benesulfonyl chloride (PMBSC)	2/46-?/59	
1,2,4,5-Tetrachlorobenzene (TCB)	1/51-1/52	
N-Oleyl-1-3-propylene diamine (Dacamine) (oil soluble)	?/62-8/69	
Salts of 2,4-D and 2,4,5-T		

Table 2
Job Titles
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey

I. OPERATOR

- A. General (no specific process given)
 - 1. Operator helper
 - 2. Chemical operator trainee
 - 3. Chemical operator 4th class
 - 4. Chemical operator 3rd class
 - 5. Chemical operator 2nd class
 - 6. Chemical operator 1st class
 - 7. Chemical operator (no "class" given)
 - 8. Head operator
 - 9. Foreman
 - 10. Flaker trainee
 - 11. Flaker operator
 - 12. Ester helper
 - 13. Ester & Ester Unit operator
 - 14. Centrifuge operator
 - 15. Reactor operator
 - 16. Platform operator
 - 17. Still operator (1, 2, or 3 class)
 - 18. Production operator (1, 2, or 3 class)
 - 19. Production helper
- B. TCP/2,4,5-T
 - 1. TCP operator trainee
 - 2. TCP operator 3rd class
 - 3. TCP operator 2nd class
 - 4. TCP operator 1st class
 - 5. TCP operator (no "class" given)
 - 6. TCP or 2,4,5-T (no Area or Unit given)
 - 7. 2,4,5-T Centrifuge trainee
 - 8. 2,4,5-T Centrifuge operator (1, 2, or 3 class)
 - 9. 2,4,5-T Melt operator
 - 10. 2,4,5-T Reactor operator
 - 11. 2,4,5-T other
- C. DCD/2,4-D/DDT
 - 1. 2,4-D trainee
 - 2. 2,4-D operator
 - 3. 2,4-D operator helper
 - 4. 2,4-D Centrifuge operator
 - 5. 2,4-D Centrifuge and Flaker operator

Table 2 (continued)
Job Titles
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey

I. OPERATOR

- C. DCP/2,4-D/DDT (continued)
 - 6. 2,4-D ass't Still operator
 - 7. 2,4-D Still operator
 - 8. 2,4-D Platform operator
 - 9. 2,4-D Melt Unit operator
 - 10. 2,4-D Ester Unit operator
 - 11. DDT helper
 - 12. DDT Grinder labor or helper
 - 13. DDT Grinder
 - 14. DDT Flaker operator
 - 15. DDT Bagger
- D. Other
 - 1. MCA operator
 - 2. MCP operator
 - 3. Miticide
 - a. Production helper
 - b. Flaker operator
 - c. Grinder
 - 4. HCB Unit operator
 - 5. "TC" operator

II. MAINTENANCE

- A. General
 - 1. helper
 - 2. trainee
 - 3. 3rd class
 - 4. 2nd class
 - 5. 1st class
 - 6. labor
 - 7. operator
 - 8. "maintenance" (no specifics)
 - 9. foreman
 - 10. leader (AKA "lead mechanic")
- B. Mechanic
 - 1. 3rd class
 - 2. 2nd class
 - 3. 1st class
 - 4. "905 mechanic"
- C. Other (specified) Maintenance
 - 1. welder/mechanic
 - 2. welder
 - 3. electrician
 - 4. pipefitter
 - 5. insulator (vessels)

Table 2 (continued)
Job Titles
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey

II. MAINTENANCE

C. Other (specified) Maintenance (continued)

6. lubricated man
7. utilities
8. carpenter
9. mason helper
10. bricklayer
11. Painter 3rd class
12. Painter
13. Stores and Inventory

III. OTHER HOURLY

A. General

1. helper
2. labor
3. general worker
4. foreman

B. Job Specified

1. Fork lift (AKA "lift truck" and "Hi-Lo")
2. Material helper
3. Material handler
4. Janitor (AKA "porter")
5. Janitor: Personnel offices
6. Warehouseman
7. Warehouse Solution Man
8. Solvent man
9. Stock Room helper
10. Stock Room worker
11. Plant Storeroom attendant (AKA "storekeeper")
12. Lab assistant
13. Lab worker
14. Lab technician
15. Safety/First Aid man

IV. CLERICAL

- A. Stock clerk
- B. Production clerk
- C. Operations clerk
- D. Inventory Control clerk
- E. clerk/typist
- F. secretary/typist
- G. Administrative secretary
- H. Switchboard operator
- I. accountant

Table 2 (continued)
Job Titles
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey

IV. CLERICAL (continued)

- J. Office manager
- K. Purchasing Agent
- L. other

V. MANAGEMENT

A. Manager

- 1. Plant
- 2. Ass't Plant
- 3. Acting Plant
- 4. Production
- 5. Personnel and Safety
- 6. Technical Staff

B. Superintendent

- 1. Plant
- 2. Operations
- 3. Technical
- 4. Production and Maintenance
- 5. Warehouse and Formulations

C. Supervisor

- 1. Field
- 2. Shift
- 3. Relief Shift
- 4. Esters
- 5. Maintenance Shift
- 6. Assistant Maintenance
- 7. Assistant Maintenance & Construction
- 8. Maintenance & Construction
- 9. Maintenance & Utilities
- 10. Production
- 11. Formulation
- 12. Laboratory
- 13. Control Laboratory
- 14. Purchasing & Stores
- 15. Shipping & Formulation
- 16. Personnel
- 17. Personnel & Safety
- 18. Safety Director

Table 3
Job Titles and Descriptions Associated
with Processes in the Scope of the Dioxin Registry
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey

Job Title	Associated Production Process	Job Description
TCP Operator (1st and 2nd classes)	Na 2,4,5-TCP	Primarily responsible for operating the Na 2,4,5-TCP production process which involved; 1) loading autoclave reactor, 2) operating autoclave reactor, 3) collecting samples from autoclave reactor, 4) operating methanol recovery system, 5) operating dilution-filtration product recovery system (1951-1954), 6) operating anisole still and product recovery system (1954-1969), 7) operating Monel screen filter (1961-1969), 8) operating activated charcoal purification column (1967-1969)
TCP Operator (3rd and trainee classes)	Na 2,4,5-TCP	Assisted the TCP operator (1st and 2nd class) in operating the Na 2,4,5-TCP production process
2,4,5-T Reactor Operator	2,4,5-T Acid	Responsible for the operations which produced the crude 2,4,5-T Acid which involved 1) loading and operating the condensation reactor, 2) collecting samples from the condensation reactor, 3) operating filtration to remove NaCl and unreacted organics
2,4,5-T Centrifuge Operator (1st and 2nd classes)	2,4,5-T Acid	Responsible for recovery and purification of 2,4,5-T acid which involved 1) operating reslurry tank (1951-1967), 2) operating acidification tank (1951-1967), 4) operating "Mother Liquor" recovery and separation systems
2,4,5-T Centrifuge Operator (3rd and trainee classes)	2,4,5-T Acid	Assisted the 2,4,5-T centrifuge operator in the recovery and purification of 2,4,5-T acid operations

Table 3 (continued)
 Job Titles and Descriptions Associated
 with Processes in the Scope of the Dioxin Registry
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

Job Title	Associated Production Process	Job Description
2,4,5-T Melt Operator	2,4,5-T Acid	Responsible for recovery and purification of 2,4,5-T acid which involved: 1) operating primary and secondary acidification tanks (1967-1969), 2) operating decanter (1967-1969), 3) operating wash column (1967-1969), 4) operating dryer (1967-1969)
Ester Operator	2,4,5-T and 2,4-D Esters	Responsible for the operations to produce 2,4,5-T and 2,4-D esters which involved: 1) loading and operating the esterifier, 2) collecting samples from esterifier, 3) operating filtration and dryer systems, 4) operating alcohol condenser and recovery systems, 5) cleaning esterifiers when switching from 2,4,5-T to 2,4-D products or visa versa
Production or Operator Helper	2,4,5-T and 2,4-D amines and formulations	Responsible for production and packaging of 2,4,5-T and 2,4-D amine, 2,4,5-T and 2,4-D ester formulations, and 2,4,5-T and 2,4-D amine formulations which involve 1) loading and operating reactors and/or mixing vessels, 2) collecting samples, 3) cleaning reactor and/or mixing vessels

Table 4
Major Process Changes
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey

<u>Date</u>	<u>Major Changes</u>
February 1951	Initiated production of Na 2,4,5-TCP and TCB in a 500 gallon reactor. Used a dilution process with filtration to remove water insoluble organics from reaction mixture.
January 1952	Eliminated TCB production and began purchasing TCB.
February/March 1953	New Na 2,4,5-TCP reactor installed increasing production capacity from 40,000 lb/mon to 120,000 lb/mon (from 500 gallon reactor to 1000 gallon reactor).
September 1954	Anisole steam stripping substituted for dilution process for the removal of insoluble organics from Na 2,4,5-TCP reaction mixture.
December 1954	Began carrying NaCl produced during Na 2,4,5-TCP production to 2,4,5-T acid process instead of removing it by filtration in the Na 2,4,5-TCP process.
January 1955 to November 1956	No major process changes were made during this time period.
December 1956	Initiated the recovery and recycling of the steam stripped anisole in the Na 2,4,5-TCP process.
January 1956 to February 1960	No major process changes were made during this time period.
February 20, 1960	An explosion in the Na 2,4,5-TCP autoclave reactor occurred. The process building was destroyed. Production of Na 2,4,5-TCP ceased.

Table 4 (continued)
Major Process Changes
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey

<u>Date</u>	<u>Major Changes</u>
January 1961	The rebuilt Na 2,4,5-TCP process was started. Two 1000 gallon autoclave reactor were installed and NaCl formed during the reaction step was removed from the Na 2,4,5-TCP product following anisole steam stripping and before it was used in the 2,4,5-T acid process.
July 4, 1967	The 2,4,5-T acid process was shut down and dismantled to make room for an expansion of the 2,4-D acid process.
September 18, 1967	The 2,4,5-T acid process was restarted in the refurbish 2,4-D acid process. Production capacity was increased from 1.5 million lb/year to 3.0 million lb/year. With restart of the 2,4,5-T acid process the 2,4,5-T acid product was now in a dry molten state, before the 2,4,5-T acid product was in a wet (10-12% H ₂ O) crystalline state.
September 27, 1967	An activated charcoal purification column was installed in the Na 2,4,5-TCP process for the removal of 2,3,7,8-TCDD.
October 30, 1967	A new 2,4-D acid process was completed, increasing the production capacity from 8 million lb/year to 12 million lb/year.
August 1, 1969	All production was terminated.

Table 5
2,4,5-T Acid Production Quantities Summary
1960-1968
Diamond Alkali Company
Diamond Shamrock Corporation
Newark, New Jersey

<u>Year</u>	<u>2,4,5-T Acid (millions of pounds)</u>
1960	0.6
1961	1.2
1962	1.3
1963	1.5
1964	1.3
1965	0.7
1966	0.7
1967	1.5
1968	2.9

Table 6
 Production Quantities for Products in the Scope
 of the Dioxin Registry
 January 1966-December 1968
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

Date	Na 2,4,5-TCP (lb/mon)	2,4,5-T Acid (lb/mon)	Esters		Amines (gal/mon)	Dacamines (gal/mon)	Formulations (gal/mon)
			Total (lb/mon)	T (%)			
1/66	38655	62366	392489	1.6	18349	871	UK
2/66	92367	77011	431589	UK	4204	14528	180
3/66	103067	92262	447244	UK	19822	14462	10304
4/66	52299	0	640269	UK	42687	26657	1943
5/66	66551	110329	585815	UK	8689	10542	29377
6/66	38373	65444	682300	UK	11224	4441	20486
7/66	68846	24719	599165	UK	31028	0	8879
8/66	28411	35740	157212	UK	13562	1001	2838
9/66	40719	0	463055	UK	30718	4000	1129
10/66	56612	76224	491421	UK	3860	11157	23458
11/66	47951	36433	551954	0.0	3429	28686	8759
12/66	54690	98146	330305	32.5	17259	13653	8759
Total	688541	678675	5772818	UK	204831	129998	27651
1/67	38937	170640	776765	2.6	7556	38170	6665
2/67	89420	103331	634704	21.4	6218	8602	12092
3/67	132725	123193	807945	26.0	15912	27378	38321
4/67	155272	198154	880029	36.6	4574	30662	41253
5/67	173978	210659	1081079	38.7	33553	25790	45353
6/67	175364	196891	865144	26.5	9361	19741	37203
7/67	51223	17718	670677	12.7	0	10721	16604
8/67	0	0	405930	0.0	0	0	1650
9/67	57775	26522	628573	0.0	0	9000	5498
10/67	99373	129092	870183	18.6	16644	4784	28731
11/67	150073	200227	832603	33.4	31475	18384	37511
12/67	264371	245339	1153298	27.8	6697	6382	44696
Total	1388511	1621766	9606930	20.6	131990	199614	315577
1/68	194230	224286	932286	21.1	9709	0	50444
2/68	265367	229554	1274863	27.9	660	7450	52961
3/68	250330	277789	1297649	30.4	31254	12378	82841
4/68	235440	252825	1544550	18.6	53550	45246	32988
5/68	244721	254887	1639486	12.8	67615	32787	18271
		80000+					

Start of 2,4,5-T Acid in molten liquid form
 Flaked 2,4,5-T Acid

Table 6 (continued)
 Production Quantities for Products in the Scope
 of the Dioxin Registry
 January 1966-December 1968
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

Date	Na 2,4,5-TCP (lb/mon)	Esters		T (%)	Amines (gal/mon)	Dacamines (gal/mon)	Formulations (gal/mon)
		2,4,5-T Acid (lb/mon)	Total (lb/mon)				
6/68	226270	281639	1460270	26.0	23611	26126	35101
7/68	261921	300404	1179621	33.6	2707	0	82989
8/68	152763	236417	442516	45.8	0	0	25093
9/68	196300	228073	996434	34.4	20466	20917	49752
10/68	230096	249970	1178771	30.3	23890	14078	40973
11/68	175692	205131	1211866	21.9	38807	8812	14005
12/68	169756	163388	816659	5.9	1490	6000	3617
Total	2602886	2984363	13974971	25.7	273759	174694	414475

Start of 2,4,5-T Acid in molten liquid form
 Flaked 2,4,5-T Acid

Table 7
 Projected Product Mix After Expansion to 12,000 lb/yr
 2,4-D Acid and 3,000,000 lb/yr of 2,4,5-T Acid
 April 1966
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

Form	Annual Production Quantity	gal/mon	Annual lbs. Acid Equivalent	% of Total Acid Equivalen
Flaked 2,4,5-T Acid	810,000 lb.	—	810,000	27.0
Butyl 2,4,5-T Ester	400,000 lb.	3,000	315,000	10.5
2-EH 2,4,5-T Ester	2,020,000 lb.	16,500	1,378,000	46.0
Isopropyl 2,4,5-T Ester	162,000 lb.	1,200	133,000	4.5
2,4,5-T Amine (water soluble)	775,000 gal.	6,700	320,000	10.8
Dacamine 4T (oil soluble)	4,500 gal.	400	18,000	0.7
Dacamine 2D/2T (oil soluble)	13,000 gal.	1,100	26,000	0.9
Flaked 2,4-D Acid	3,600,000 lb.	—	3,600,000	30.0
Butyl 2,4-D Ester	3,740,000 lb.	30,100	3,030,000	25.2
2-EH 2,4-D Ester	1,650,000 lb.	14,200	1,257,000	10.5
Isopropyl 2,4-D Ester	254,000 lb.	2,000	217,000	1.8
#4 DMA (water soluble)	68,000 gal.	5,700	272,000	2.3
#6 DMA (water soluble)	117,000 gal.	9,800	705,000	5.9
#6 Crude (water soluble)	146,000 gal.	12,200	920,000	7.7
Dacamine	373,000 gal.	31,100	746,000	6.2
Dacamine 4D	309,000 gal.	25,600	1,235,000	10.3
Dacamine 2D/2T	13,000 gal.	1,100	26,000	0.2

Basis: 30% of 2,4-D Acid and 27% of 2,4,5-T Acid to flake, Dacamines at 700,000 gal. total with same mix as budgeted in 1966, remainder of both 2,4-D and 2,4,5-T Acids divided between esters and amines in same ratio as budgeted in 1966.

Table 8
 Process Operating Data Summary
 (January 1967 to January 1969)
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

Basis: One Month

Na 2,4,5-TCP

Mean # of Batches	75 (32)	n*=24
Mean Batch Size	2263 (130) lb.	n=24
Mean Reaction/Digestion Time	2.2 (0.4)/5.0 (0.1) hr.	n=24
Mean Avg/Mx Autoclave Temp	168 (.24)/173 (2.4)°C	n=24
Mean Max. Anisole Still Temp	105 (0.9)°C	n=24

2,4,5-T Acid

Mean TCP Conversion	76.2 (2.6)%	n=21
Mean Cycle Time	8.3 (2.3) hr.	n=20
Mean Cooking Time	3.5 (1.5) hr.	n=21
Mean Cooking Temp.	100 (2.2)°C	n=21

Esters

	<u>Butyl-T</u>	<u>2-EH-T</u>
Mean # of Batches	29 (16) n=22 (26(15)%)	15 (9) n=9 (12(8)%)
Mean Batch Size	5655 (992) lb. n=22	7153 (449) lb. n=9
Mean Cycle Time	24.8 (3.8) hr. n=21	18.3 (3.2) hr n=9
Mean Reaction Temp	144 (4.4)°C n=21	154 (3.0)°C n=9

*n=sample size

()=number in parenthesis is the arithmetic standard deviation

All means are arithmetic means.

The percentages listed for the esters represent the percent of the total esters (both 2,4-D and 2,4,5-T Esters) produced.

Table 9
 2,3,7,8-TCDD Analyses Conducted by Diamond
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

<u>Date</u>	<u>Sample Description</u>	<u>2,3,7,8-TCDD Conc.</u> <u>(ug/g)</u>
May 1965	Na 2,4,5-TCP solution (40%)	16
May 1965	Na 2,4,5-TCP solution (40%)	10
May 1965	Recovered TCA	73
May 1965	Recovered Methanol	10
May 1965	2,4,5-T Acid	10
May 1965	2,4,5-T Acid	10
May 1965	2,4,5-T Acid	10
May 1965	2,4,5-T Acid	10
May 1965	2,4,5-T Acid	28
May 1965	2,4,5-T Acid	40
May 1965	2,4,5-T Acid	25
May 1965	2,4,5-T Acid	40
June 1965	Na 2,4,5-TCP solution (31%)	28
June 1965	2,4,5-T Acid	10
June 1965	Na 2,4,5-TCP solution (44%)	38
June 1965	Na 2,4,5-TCP solution (44%)	35
June 1965	Na 2,4,5-TCP solution (36%)	19
June 1965	Na 2,4,5-TCP solution (40%)	25
September 20, 1965	2,4,5-T Acid	13
September 20, 1965	2,4,5-T Acid	7.0
September 20, 1965	2,4,5-T Acid	7.0
March 23, 1966	Na 2,4,5-TCP solution (36%)	7
December 1965	Crude Na 2,4,5-TCP solution (39%) in crude Na 2,4,5-TCP holding tank	22
December 1965	Na 2,4,5-TCP solution (34%)	10
December 1965	Na 2,4,5-TCP solution (35%)	12
February 1966	Crude Na 2,4,5-TCP solution (40%) in Crude Na 2,4,5-TCP holding tank	16
February 1966	Crude Na 2,4,5-TCP solution (46%) in crude Na 2,4,5-TCP holding tank	10
February 1966	Crude Na 2,4,5-TCP solution (30%) prior to methanol distillation	7
March 1966	Recovered 2,4,5-TCP (93%) from 2,4,5-T acid mother liquor	10
May 1966	Na 2,4,5-TCP solution (40%)*	17
July 1966	Na 2,4,5-TCP solution (40%)*	19
August 1966	Na 2,4,5-TCP solution (40%)*	11
November 1966	Na 2,4,5-TCP solution (40%)*	13
November 1966	Na 2,4,5-TCP solution (40%)*	20
December 1966	Na 2,4,5-TCP Solution (40%)*	21
January 1967	Na 2,4,5-TCP solution (40%)*	38

* 40% Na 2,4,5-TCP solution assumed

Table 9 (continued)
 2,3,7,8-TCDD Analyses Conducted by Diamond
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

Date	Sample Description	2,3,7,8-TCDD Conc. (ug/g)
September 8, 1967	Purified Na 2,4,5-TCP (15%)	1.4
November 18, 1967	Purified Na 2,4,5-TCP	1
November 20, 1967	Purified Na 2,4,5-TCP	1
November 17, 1967	2,4,5-T Acid	1
October 23, 1967	Purified Na 2,4,5-TCP	1
October 25, 1967	Purified Na 2,4,5-TCP	1
October 12, 1967	Purified Na 2,4,5-TCP	0.9
October 13, 1967	Purified Na 2,4,5-TCP	1.1
October 16, 1967	Purified Na 2,4,5-TCP	1
October 17, 1967	Purified Na 2,4,5-TCP	1
October 18, 1967	Purified Na 2,4,5-TCP	1
October 1, 1967	Purified Na 2,4,5-TCP	0.5
October 2, 1967	Purified Na 2,4,5-TCP	0.5
October 3, 1967	Purified Na 2,4,5-TCP	0.5
October 4, 1967	Purified Na 2,4,5-TCP solution	0.5
September 25, 1967	Purified Na 2,4,5-TCP solution	1.0
September 25, 1967	Purified Na 2,4,5-TCP solution	1.0
January 15, 1969	Purified Na 2,4,5-TCP solution	1.0
November 22, 1967	Purified Na 2,4,5-TCP solution	1.0
November 20, 1967	Purified Na 2,4,5-TCP solution	1.0
November 24, 1967	Purified Na 2,4,5-TCP solution	1.0
November 26, 1967	Purified Na 2,4,5-TCP solution	1.0
November 25, 1967	Purified Na 2,4,5-TCP solution	1.0
September 26, 1967	2,4,5-T Acid	1.5

Table 10
 2,3,7,8-TCDD Analyses Summary
 Diamond Alkali Company
 Diamond Shamrock Company
 Newark, New Jersey

<u>Year</u>	<u>Sample Description</u>	<u>Number of Samples</u>	<u>Number of Non-Detectable</u>	<u>Limit of Detection (ug/g)</u>	<u>Detectable Sample Range (ug/g)</u>	<u>Detectable Sample Mean (ug/g)</u>	<u>Detectable Sample Standard Deviation (ug/g)</u>
1965	Na 2,4,5-TCP Solution	10	0	1.0	10-38	22	10
1965	2,4,5-T Acid	12	4	1.0	7-40	23	13
1965	Recovered TCA	1	0	1.0	73	--	--
1965	Recovered Methanol	1	1	10	--	--	--
1966	Na 2,4,5-TCP Solution	11	0	1.0	7-38	16	9
1966	Recovered Na 2,4,5-TCP from 2,4,5-T Acid Mother Liquar	1	0	1.0	10	--	--
1967	Purified Na 2,4,5-TCP	22	19	0.5-1.0	0.9-1.1	1.1	0.3
1967	2,4,5-T Acid	1	0	1.0	1.5	--	--
1969	Purified Na 2,4,5-TCP	1	1	1.0	--	--	--

Table 11
 Na 2,4,5-TCP Assay
 April 1967 to January 1969
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

<u>Date</u>	<u>% 2,4,5-TCP</u>	<u>% 2,4,6-TCP</u>	<u>% DCP</u>	<u>% TCA</u>	<u>% Unknown</u>	<u>2,3,7,8-TCDD (ug/g)</u>
4/67	91.6	NA	3.7	0.7	NA	115
5/67	87.0	NA	1.4	0.5	NA	71
6/67	92.3	NA	1.6	0.8	NA	NA
7/67	NA	NA	NA	NA	NA	NA
8/67	NP	NA	NP	NP	NA	NA
9/67	NA	NA	NA	NA	NA	NA
10/67	NA	NA	NA	NA	NA	NA
11/67	NA	NA	NA	NA	NA	1.7
12/67	NA	NA	NA	NA	NA	2.8
1/68	91.3	0.5	1.2	0.0	7.0	3.0
2/68	91.5	0.7	0.6	0.0	7.1	7.0
3/68	88.8	0.7	0.5	0.2	9.8	1.5
4/68	93.4	0.7	0.5	0.1	5.1	1.8
5/68	94.0	0.7	0.5	0.3	4.5	1.0
6/68	93.3	0.3	0.1	0.0	6.7	NA
7/68	91.0	0.5	0.3	0.0	8.1	1.0
8/68	95.0	NA	NA	NA	NA	1.0
9/68	94.9	NA	NA	NA	NA	1.0
10/68	88.1	NA	NA	NA	NA	8.4
11/68	92.9	NA	NA	NA	NA	9.3
12/68	94.8	0.3	1.1	NA	3.7	9.6
1/69	93.8	0.9	1.1	0.1	3.9	5.2

NA = not analyzed

Table 12
 2,3,7,8-TCDD Analytical Results
 for Diamond Products from Other Sources
 Diamond Alkali Company
 Diamond Shamrock Corporation
 Newark, New Jersey

Date	Sample Description	2,3,7,8-TCDD Conc.		Source
		(ug/g)		
12/26/72	Agent Orange	0.05	0.05 (re-check)	Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	9.7		Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	0.05	0.05 (re-check)	Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	8.0		Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	8.1		Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	8.7		Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	12		Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	17		Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	0.07, 0.07	(re-check)	Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	12		Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	15		Gulfport, Missouri Agent Orange Stocks (1)
12/26/72	Agent Orange	15		Gulfport, Missouri Agent Orange Stocks (1)
1965	2,4,5-T Acid	5		Dow Chemical Company
1965	2,4,5-T Acid	16		Dow Chemical Company
1965	2,4,5-T Acid	Mod-Severe(2)		Dow Chemical Company
1969	2,4,5-T Acid	1		Dow Chemical Company
1969	2,4,5-T Acid	Moderate(2)		Dow Chemical Company

(1) Analyses of the Airforce Gulfport Agent Orange stocks were conducted by Dow Chemical Company in Midland, Michigan

(2) Rabbit Ear Bioassay follicular response