DIOXIN REGISTRY REPORT
FOR
Hercules, Inc.
and
Vertac Chemical Corporation
Jacksonville, Arkansas

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PURPOSE:

This site, which was last operated by Vertac Chemical Corporation produced 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and its esters and amines from 1957 through 1979. Presented is a compilation of demographic and work history information, process information, and analytical data pertaining to 2,4,5-T production. This information was collected over several site visits and visits to corporate headquarters by several investigators.

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STANDARD INDUSTRIAL CLASSIFICATION: 2869 - Industrial Organic Chemicals

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-dioxin (TCDD) and/or hexachlorodibenzo-p-dioxins (HxCDD). Currently, there are fourteen production facilities 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 causes of death among workers exposed to products contaminated with TCDD and/or HxCDD.

A facility, located in Jacksonville, Arkansas, produced sodium 2,4,5-trichlorophenate (NaTCP), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2,4,5-T esters and amines from 1957 to 1979. NaTCP and 2,4,5-T have been shown to be contaminated with TCDD. This facility was operated by Reasor-Hill, Incorporated from 1946 to 1961, by Hercules, Incorporated from 1962 to 1971, and by Transvaal, Inc./Vertac Chemical Company from 1971 to 1988. Presented in this report is a description of the facility, the workforce, the production processes, past exposures, and record systems. This information and data will be used as a part of the NIOSH Dioxin Registry study.

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 health effects resulting from occupational exposure to polychlorinated dibenzo-p-dioxins (dioxins), and in particular the isomers 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and/or hexachlorodibenzo-p-dioxins (HxCDD). 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 with TCDD and/or HxCDD. The Registry, initiated in 1979, was prompted by animal studies showing TCDD to be acutely toxic and a chloracnegen, as well as a carcinogen and teratogen.[1,2,3,4,5,6,7] TCDD is a contaminant found in 2,4,5-trichlorophenol (2,4,5-TCP) and/or its sodium salt (NaTCP), which are raw materials used to produce chemical compounds such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T acid) and 2,2'-methylenebis(3,4,6-trichlorophenol) (hexachlorophene). Currently, there are fourteen production facilities and approximately 7000 workers included in the Registry. The first use of the Registry will be a mortality study for which the comparison group will be 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 Registry will also be used in a morbidity study of workers from two sites in the Registry. Presented is a compilation of information and data pertaining to NaTCP and 2,4,5-T production processes at a facility in Jacksonville, Arkansas. This facility, which was last operated by Vertac Chemical Company, produced NaTCP and 2,4,5-T products from 1957 to 1979. Descriptions of the facility, the workforce, the processes, past exposures and the record systems for the NaTCP and 2,4,5-T production operations are included in this report.

Description and History of the Facility

The 80 acre site located on Marshall Road in Jacksonville, Arkansas was originally a part of the Jacksonville Ordinance plant which was built and used as a munitions plant by the U.S. Army in the late 1930's and early 1940's. In November, 1946, Reasor-Hill, Incorporated purchased the facility from the Army and began producing cotton insecticide dusts (methyl parathion and malathion). A year or so later, they began producing the insecticides: DDT, dieldrin and aldrin. In 1955, production of 2,4-dichlorophenoxyacetic acid (2,4-D), esters and amines was started. After approximately a year of laboratory work on the production method, the production of 2,4,5-T began in October, 1957. Reasor-Hill went out of business and company records are no longer available, therefore the study group to be included in the Dioxin Registry will not included persons who only worked for Reasor-Hill.

The Hercules Powder Company (now Hercules, Inc.) purchased the facility from Reasor-Hill on December, 1961. Hercules continued to produce 2,4,5-T and 2,4-D products, but discontinued the production of the insecticides. The production of 2,4,5-T and 2,4-D products continued under Hercules until the spring of 1970. In 1965, there was a two month shutdown in 2,4,5-T production due to changes and expansion of the NaTCP process. During the late 1960's, Hercules produced "Agent Orange" (50% 2,4,5-T butyl ester and 50% 2,4-D butyl ester) for the U.S. Government.[8] Hercules at that time was required by the government to supply the U.S. military with 100% of its 2,4,5-T production. The company supplied the government with 2,406,041 gallons of "Agent Orange". When the government demand for "Agent Orange" dropped, the 2,4,5-T production process was shut down from February, 1969 until March, 1970. 2,4,5-T was produced for the final time under Hercules in May, 1970. The facility was shutdown in June, 1970 and all employees were released except for three who remained as caretakers.

In October, 1971, the facility was leased to Transvaal, Inc., a subsidiary of Vertac, Inc. Transvaal resumed the production of 2,4,5-T and 2,4-D products at this time and also began producing 2(2,4,5-trichlorophenoxy)propionic acid (silvex). Silvex production usually took only one month per year. Transvaal purchased the facility from Hercules in August, 1976. Later in 1978, Transvaal was dissolved, Vertac, Inc. was sold and the new company became Vertac Chemical Corporation, which operated the facility until 1988.

In addition to the products named above, Transvaal also produced 2,2-dichloropropionic acid (Dalapon) from June 1975 to June, 1976 and monochloropropionic acid once in 1974. The company estimates that until 1974, 2,4-D products constituted about 80% of production and 2,4,5-T only about 20%. Thereafter, 2,4-D products made up only about 60% of production, and 2,4,5-T products increased to about 35-40%. 2,4,5-T, 2,4-D and Silvex were synthesized by the same workers using much of the same equipment.

The NaTCP produced at the Jacksonville facility was used mainly for the production of 2,4,5-T and silvex although some was used to produce 2,4,5-TCP. No NaTCP was sold, but some of the 2,4,5-TCP was sold. The 2,4,5-T produced at this facility was mainly used to produce 2,4,5-T esters and amines, but some of the crystalline solid was sold. Most of these sales occurred after 1975 although some bagged 2,4,5-T was sold to Dow Chemical Company in 1973. The majority of the 2,4,5-T ester produced was formulated on site although some was sold to other companies for formulation. Most of the Silvex ester produced was also formulated on site although some may have been sold as the pure substance.

The production facility is located on approximately 10 of the 80 acres. Figure 1 provides a layout of the facility indicating the locations of the various production processes. The reactors and equipment for the production of NaTCP and toluene recovery were located in the open air. The equipment used for the production of 2,4,5-T was located in the Acid Building. The esterification holding and mixing tanks were located outside, and the formulation and packaging operations were located in the Formulation Building.

Description of the Workforce

The workforce size at the Jacksonville facility when Hercules produced 2,4,5-T (1962-1965) is not known. After the expansion and modifications of the NaTCP and 2,4,5-T processes the number of salaried and wage personnel peaked to 90 in late 60's when "Agent Orange" was being produced. Among the 90 were between 15 to 20 salaried professional staff employees. The size of the maintenance crew varied and peaked at 15 workers. The normal operating shift consisted of 8 to 9 workers per shift. The day shift included 8 to 9 workers per shift in production, 3 to 4 workers per shift in formulation and packaging, one worker per shift in the boiler house, and 6 to 8 in the laboratory.[9]

Job descriptions in the usual sense were not used by Hercules at the Jacksonville facility. Production, formulation and package workers were considered chemical operators of which there were several grades and pay rates. The operators were trained in the job that they normally performed; however, as the operator gained experience in the initial job assignment, training in other jobs were required.

The size of the workforce for Transvaal/Vertac was very similar to the workforce size for Hercules. Clayton Environmental Consultants, Inc.[11],conducted a survey of the Jacksonville facility in February, 1979 during which time they observed the following breakdown in the Vertac personnel:

Operator	35
Maintenance	16
Laboratory	6
Laborers	3
Change House Operator	1
Guard	1
Professional Staff	16

Similarly, in a Arkansas Department of Health epidemiological investigation in May, 1979 a total of 79 Vertac employees were reported.[10] Job titles along with duties were obtained from this report and are listed in Table 1.

Description of the Processes

The following subsections describe the processes of interest to the Dioxin Registry study. The descriptions of these processes cover the time period from 1965 to 1979, when Hercules and Transvaal/Vertac operated them. During this time relatively no changes were made to these processes except were noted in the text.

A. NaTCP Production Process

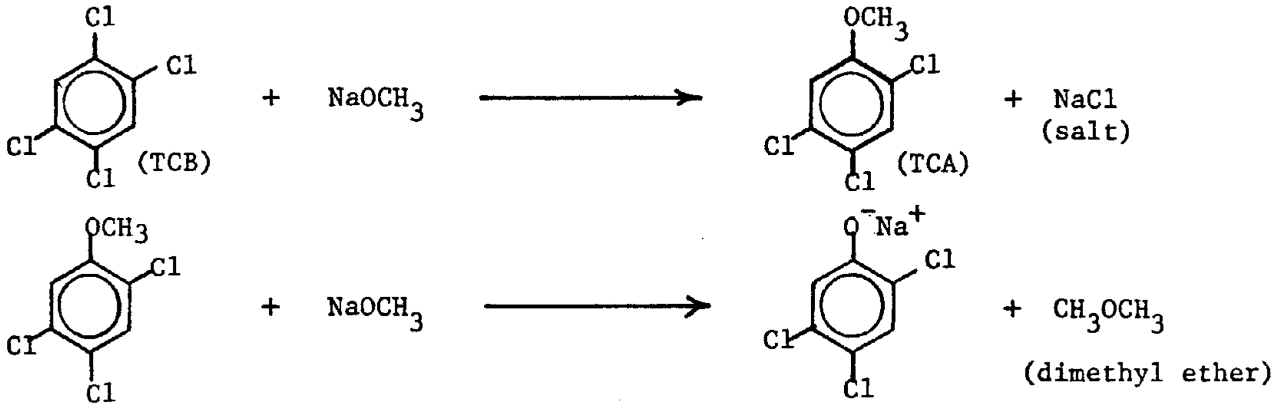
NaTCP was produced at the Jacksonville facility using the following raw materials: methanol (MeOH), sodium hydroxide (caustic soda or NaOH), and 1,2,4,5-tetrachlorobenzene (TCB). Water and toluene were used as solvents in the process. The process to be described was first installed and operated by Hercules in October, 1965. No significant changes were made to the process as it is described, during the years it was operated by Hercules and Transvaal/Vertac, with the exception of the following: For a 2- or 3-year period beginning in 1973, mixed isomers of TCB were purchased, and an additional step was added to the beginning of the process to separate the 1,2,4,5-TCB isomer from the mixture. The step initially utilized carbon tetrachloride, which was soon replaced by toluene. A flow diagram of this process is shown in Figure 2.

The first step in this process, the dechlorination of TCB, was conducted in one of three 500-gallon, nickel-clad, jacketed reactors and includes a multi-step chemical reaction sequence. This was a batch process and the vessel was agitated. The first reaction occurred upon the addition of MeOH, a liquid which was metered into a drop tank from drums, and NaOH, a granular solid which was dumped from drums through a manhole in the drop tank. The MeOH was added in amounts in excess of the 1:1 stoichiometric ratio with NaOH and acted as a solvent, as well as a reagent. The reaction which occurred was:

$$CH_3OH + NaOH \longrightarrow NaOCH_3 + H_2O.$$

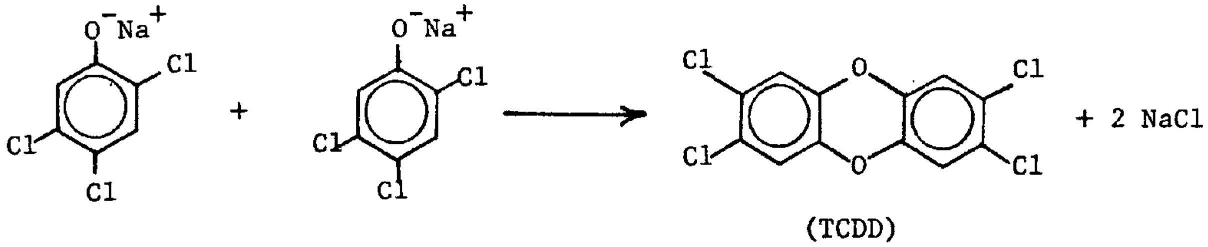
(MeOH) (sodium methoxide)

The sodium methoxide solution was fed to the reactor from the drop tank. At this point, TCB was dumped from drums through a manhole into the reactor. The methoxide reacted with the TCB to form 2,4,5-trichloroanisole (TCA), and the TCA intermediate also reacted with methoxide to form NaTCP product. These reactions can be written as follows:



(NaTCP)

The quantity of TCB added to fuel these reactions was less than that which would be required to provide the 2:1 stoichiometric ratio with methoxide. The dechlorination of TCB went essentially to completion. However, the reaction between TCA and methoxide did not go to completion, and small quantities of TCA remained after this step. An excess of methoxide also remained after this step. This reaction sequence was highly exothermic. The temperature was manually controlled to 160°C by routing cooling water through the reactor's jacket. The pressure inside the reactor was maintained at 250 pounds per square inch gauge (psig). If the pressure inside the reactor rose above 350 psig a pressure release valve would open releasing the reactor contents into a holding dike. The following unwanted reaction also occurred during this step at a much lower rate to form the contaminant being studied TCDD:



The resulting solution contained the excess MeOH and methoxide, water, the by-products sodium chloride (NaCl), dimethyl ether (DME), and TCA (in small quantities), the unwanted contaminant TCDD, and the product NaTCP. Water was added to the solution and it was pumped to the next step in the process.

The next step in the process, the methanol recovery operation, was conducted in a single distillation unit which consisted of four major pieces of equipment and related piping (see Figure 3). This distillation unit was operated at near-atmospheric pressure. The distillation pot was operated at a temperature of 100 to 120°C, while the operating temperature at the top of the methanol recovery column was 64°C. Essentially complete removal of the MeOH and DME was accomplished at this step. The DME was routed to a water scrubber unit, where it was absorbed by the water. The DME-water solution was drained to the industrial sewer. The recovered MeOH was recycled to the initial reactor for re-use. The product stream remaining in the distillation pot then contained an aqueous solution of NaOH, NaCl, NaTCP product, TCA, TCDD, and other trace contaminants. This solution was pumped to a storage tank where it was held until needed for the next step in the process.

The next step in the process was the toluene wash, which was conducted in an agitated tank. The toluene wash was used to remove organic contaminants from the product stream. The product stream and toluene were pumped into this tank and mixed. Some heat was applied, but the temperature was not greatly raised. After mixing, the contents of the tank were allowed to settle and form layers. The top layer was organic and consisted mainly of toluene, while the bottom layer was aqueous with dissolved ionic compounds. The TCA and TCDD were, for the most part, dissolved in the organic layer. This organic layer was decanted from the vessel and pumped to the toluene still. The aqueous layer remaining in the tank contained NaTCP product, NaCl, NaOH, and extremely small quantities of organic contaminants which would have included TCDD. This solution was drained from the tank and pumped to its next destination which was usually, but not always, the production of 2,4,5-T acid.

The organic layer was distilled to recover the toluene for re-use. The toluene still was a combined pot-and-column unit similar to the methanol recovery unit. This unit was operated at a pot temperature exceeding 110°C, but the company is unsure of the exact temperature. The overhead product of toluene was recycled to the toluene wash vessel. The "still bottoms" were periodically drained into storage drums. The "still bottoms" contents were predominantly TCA, relatively high levels of TCDD, and other dioxin isomers or other organic contaminants that may have been formed in the process.

In 1965, Hercules developed and installed the solvent-based NaTCP process just described. Prior to this time, starting in 1957 when Reasor-Hill was operating the facility, the toluene wash step that was in the process was not done. During the two month shut down in 1965, Hercules also tripled the production capacity for NaTCP by adding two additional reactors.

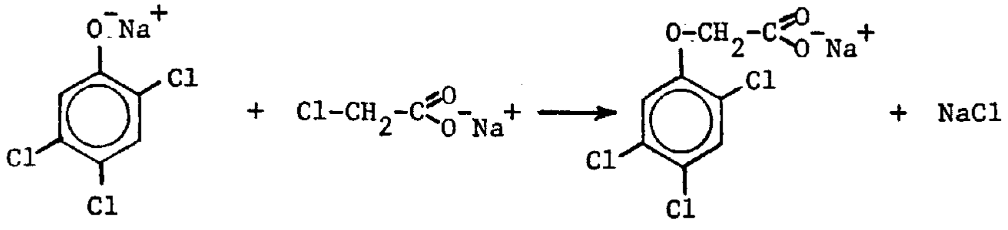
B. 2,4,5-T Acid Production Process

Hercules and Transvaal/Vertac produced 2,4,5-T acid using, almost exclusively, the product stream from the process described in the previous section, which was an aqueous solution of NaTCP, NaCl, smaller amounts of NaOH, and extremely small quantities of organic contaminants. However, according to company officials, purchased 2,4,5-TCP may have been used "a couple of times" in place of the internally produced material. Other raw materials included NaOH, monochloroacetic acid (MCA), and hydrochloric acid (HCl). Water and toluene were used as solvents in the process. The process to be described began operation in October, 1965 by Hercules. No significant changes were made to the process, as described below, during the years it was operated by Hercules and Transvaal/Vertac, except as previously noted. A flow diagram of this process is shown in Figure 4.3.

The first step of this process, the 2,4,5-T acid synthesis reaction, occurred in an agitated, brick-lined vessel and included a multi-step chemical reaction sequence. This step was a batch operation. After the NaTCP solution had been pumped into the reactor, the first reaction was initiated with the addition of toluene, NaOH (aqueous), and MCA. The NaOH solution was pumped into the vessel, while the MCA and toluene were gravity fed. The NaOH reacted with the MCA to form the sodium salt of MCA (NaMCA), and this intermediate reacted with NaTCP to form the sodium salt of 2,4,5-T acid (Na 2,4,5-T), as shown in the following sequence:

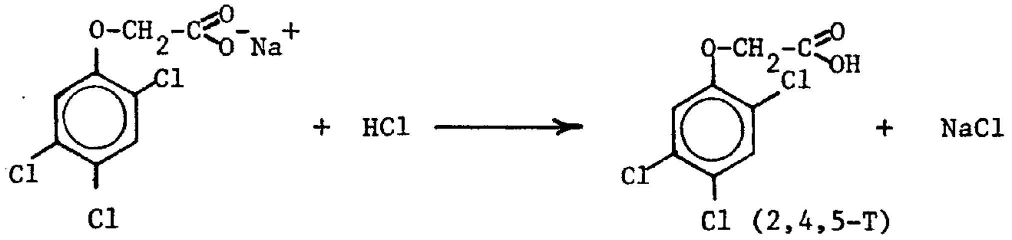
$$\mathrm{NaOH + Cl{-}CH_2{-}C(=O)OH \qquad Cl{-}CH_2{-}C(=O)O^-Na^+ + H_2O}$$

(MCA) (Na MCA)



(Na 2,4,5-T)

This exothermic reaction sequence occurred at 90°C and atmospheric pressure. NaTCP and NaOH were added to the MCA in excess of the required 1:1 stoichiometric ratio, and all of the MCA was consumed during the reaction. After these reactions were complete, HCl was pumped into the reactor. This addition cooled the mixture below 90°C, and the following reaction occurred:



The heat of reaction was insufficient to raise the temperature above 90°C. Additional reactions also occurred here between HCl and other minor constituents of the mixture, such as the excess NaTCP, which was acidified to produce 2,4,5-TCP. An excess quantity of HCl was used during the acidification. Additional water was added as a solvent, and the resulting solution, containing toluene, water, 2,4,5-T acid, NaCl, and small amounts of 2,4,5-TCP was pumped to a decantation vessel where it was allowed to settle and form an organic (toluene) layer and an aqueous layer. The organic layer, consisting of toluene, 2,4,5-T acid, small amounts of 2,4,5-TCP, MeOH, other residual organics, and residual NaCl and water, was decanted to the next step in the process. The aqueous layer, consisting mainly of NaCl water (brine) with residual organics such as TCP, MeOH, 2,4,5-T acid, and perhaps extremely small trace quantities of other organics, was drained to the toluene wash operation.

The toluene wash was a continuous operation which was conducted in a one-stage column-shaped vessel. Toluene was used to remove the residual organics from the brine solution. The brine was introduced at the top of the vessel, toluene was introduced at the bottom, and countercurrent flow occurred. A phase separation allowed the toluene phase to be decanted and the aqueous brine to be drained from the bottom of the vessel to the sewer. The levels of each phase were automatically controlled. The toluene phase, with the organic impurities noted above, was then pumped to the toluene still described in the preceding section of this report (see Figure 2).

The next step in the process was a two-part operation to remove the residual salt and water from the 2,4,5-T acid/toluene stream leaving the reactor. This purification step was added to the process in the mid-1970's; prior to that time, the residual water and salt remained in the stream, which went directly to the next step in the process. In the first part of this operation, the residual water was distilled off of the mixture by heating it to about 90 to 95°C in a unit called the evaporator. This water was condensed in a heat exchanger and pumped from there to a tank. Removing the water from the 2,4,5-T acid/toluene stream caused the residual salt to crystallize. The stream was pumped to a tray filter where the second part of this step, removal of the residual salt by filtration, occurred. The stream, which then contains toluene, 2,4,5-T acid, and impurities such as 2,4,5-TCP, MeOH, and other residual organics, was pumped to the next step in the process.

The next step in the process was a two-part operation to separate 2,4,5-T acid from the solvent (toluene) and the impurities. The product stream was pumped into a 2000-gallon glass-lined vessel, and chilled water was pumped through the reactor's jacket. As the solution cooled, the 2,4,5-T crystallized. The resulting slurry was pumped to a closed, automated centrifuge where the toluene and the organic materials dissolved in it were removed. Additional toluene was added and centrifuged off as a re-wash. The toluene recovered from this operation was re-used in the next batch by adding it to the 2,4,5-T acid synthesis reactor. The 2,4,5-T acid crystals, wet with toluene, automatically dropped into an enclosed conveyor which transferred the material to the final step in the process.

The final step in the process was the drying operation. Residual toluene was evaporated from the product crystals when the material was heated in the dryer. The toluene vapor was collected and routed by pipes to a heat exchanger where it was condensed and collected in a tank. The dry 2,4,5-T acid, a large granular product, was dropped from the bottom of the dryer through flexible hosing into tote bins. Each tote bin, a 7-foot-tall stainless-steel box with a 3- or 4-foot-square base, was completely enclosed except for a hole in the roof, which had a cover, and a 1-square foot hinged door at the base of one side. The tote bins were moved around the facility as needed to transport the product to packaging, esterification, or formulation areas. A relatively small percentage of the 2,4,5-T acid was not loaded into tote bins, but instead was directly packaged into 2000-lb boxes. An adapter was used to connect the dryer outlet to each box. The boxes of 2,4,5-T acid were then sold.

The two month shutdown of the NaTCP and 2,4,5-T acid processes in 1965 also saw changes and improvements to the 2,4,5-T acid process as well as the NaTCP process previously described. The 2,4,5-T acid process was also converted to a solvent-based process using toluene as the solvent. A centrifuge also was added to the purification steps.

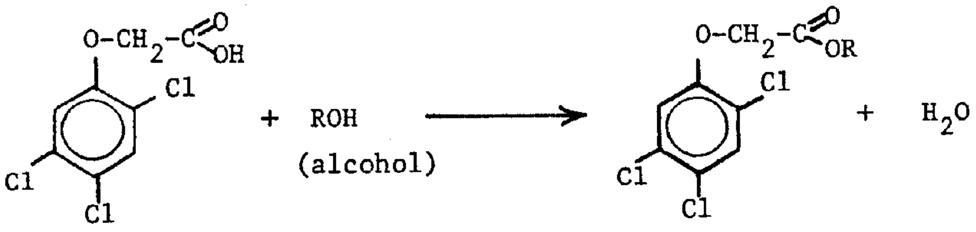
C. 2,4,5-T Esters Production Process

Reasor-Hill, Hercules and Transvaal/Vertac produced the butyl and 2-ethylhexyl esters of 2,4,5-T using butyl alcohol (butanol) (usually n-butanol, although isobutanol may have been used occasionally) and 2-ethylhexyl alcohol (2-ethylhexanol), respectively, and the 2,4,5-T acid product from the 2,4,5-T production process described in the previous section. No other materials were used in this process. The features of this process, which are described below, did not change during the years in which the process was operated by Reasor-Hill, Hercules and Transvaal/Vertac. A flow diagram of this process is in Figure 5.

The first step in this process consisted of the dumping of tote bins (for a description of a tote bin, see the previous section of this report) filled with 2,4,5-T acid crystals into the pickup bin of a screw conveyor, and the transporting of the crystals into the pre-esterification vessel. The tote bins were emptied by mechanical tote bin dumpers which tilted the bins to a 45° angle and shook them. The crystals were emptied through the doors at the bottom of the bins and entered an enclosed chute

At the pre-esterification vessel, the 2,4,5-T was mixed with one of the alcohols listed in the first paragraph in this section, and dissolved. (The alcohol was pumped in from a storage tank.) The reaction, shown below, began in this vessel but was inhibited by the buildup of water, a by-product. The entire mixture was pumped to the esterification vessel.

At the esterification vessel, the following reaction occurred between the alcohol (ROH) and 2,4,5-T to form the ester of 2,4,5-T:

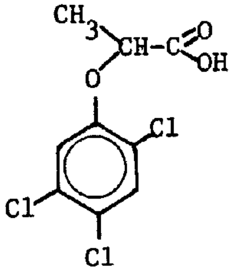


(2,4,5-T ester)

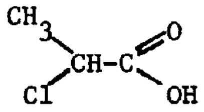
(where R is a butyl or 2-ethylhexyl group). The water formed by this reaction formed an aqueous layer which was continuously drawn off. After the reaction, the 2,4,5-T ester was pumped to a storage tank to await formulation or shipment.

D. Silvex and 2,4-D Acid and Ester Production Process

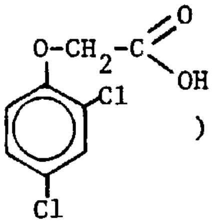
Silvex and 2,4-D acid were produced using the same process used for the production of 2,4,5-T acid described in a previous section of this report. Only the raw materials, intermediates, and products vary from those found in the description of the 2,4,5-T production process. For instance, silvex (chemical structure:



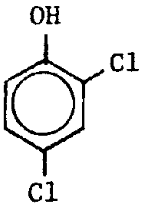
) production uses 2-chloropropionic acid (



in place of MCA. Similar propionic-substituted compounds were found throughout the process. The production of 2,4-D, which has continued to the present, (chemical structure:



) utilizes (2,4-dichlorophenol (DCP)



) in place of 2,4,5-TCP or NaTCP. Similar dechlorinated compounds are found throughout the process. The process for the production of 2,4-DCP was not similar to, and shared no steps or equipment with, the process used to produce NaTCP or 2,4,5-TCP.

The processes used to manufacture the esters of silvex and of 2,4-D were also identical to the one used to produce 2,4,5-T esters, except for the identity of the alcohols used to produce silvex esters. Specifically, only 2-ethylhexanol was used to esterify silvex, forming the 2-ethylhexyl ester of silvex. Both butyl and 2-ethylhexyl esters of 2,4-D are made.

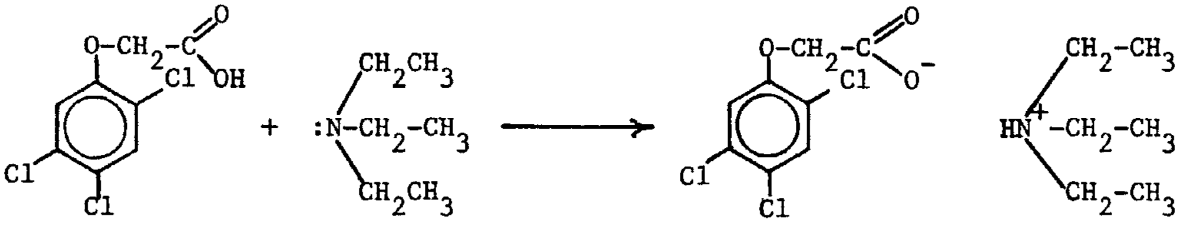
The 2,4,5-T, silvex, and 2,4-D acid and ester production processes shared the same operators and equipment on a rotational schedule. Production was alternated to meet market demands. The equipment was cleaned with emulsifiers when it was changed from the production of one product to the production of another. Normally, silvex was produced for only one month per year.

E. Formulation and Packaging of Phenoxyalkanoinc Products

Reasor-Hill, Hercules and Transvaal/Vertac formulated and packaged amine salts of 2,4,5-T and 2,4-D. Raw materials included the above-named phenoxyalkanoic acids, water, and either triethylamine (for 2,4,5-T formulations) or diethylamine (for 2,4-D formulations). The 2,4,5-T and 2,4-D used for these formulations were the products of the 2,4,5-T and 2,4-D production processes described previously in this report. The amine formulation operation was not changed during the years it was operated by Reasor-Hill, Hercules and Transvaal/Vertac.

The process for the formulation of 2,4,5-T amines began with the dumping of 2,4,5-T crystals from tote bins into a conveyor pickup bin, which transported the crystals to the amine formulation tank. For a complete description of a tote bin, see the section of this report describing the process for 2,4,5-T production. For a complete description of the tote bin dumping and conveying operation, see the section describing the 2,4,5-T ester production process.

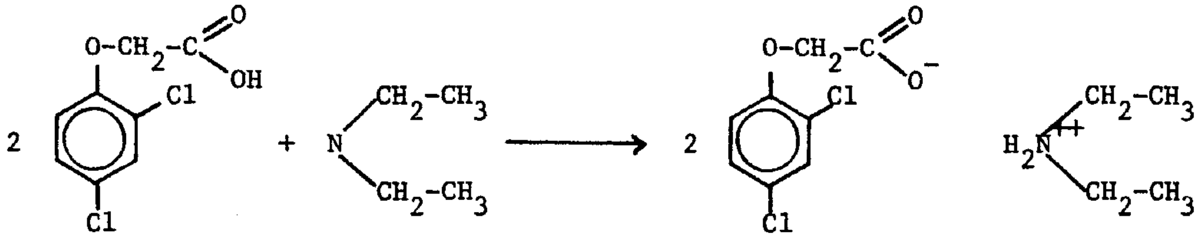
Water and triethylamine were also added to the amine formulation tank, and the contents were mixed. A reaction occurred to form the ionic triethylamine salt of 2,4,5-T, as shown:



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

The resulting solution was the finished formulation and was pumped to a storage tank for shipment in tank cars or packaging.

The process for producing the diethylamine formulation of 2,4-D is identical to that used for the 2,4,5-T triethylamine formulation, except for the chemicals used. The reaction is:



(2,4-D) (diethylamine) (diethylamine salt of 2,4-D)

Reasor-Hill, Hercules and Transvaal/Vertac produced formulations for each of the esters of phenoxyalkanoic acids which they synthesized. Each of these simple mixing operations consisted of pumping an ester, kerosene, and an emulsifier into an ester formulation tank, mixing the contents, and pumping the resulting formulation to a storage tank for shipment by tank car or packaging. These operations were not changed during the years they were operated by Reasor-Hill, Hercules and Transvaal/Vertac. The butyl (usually n-butyl and occasionally isobutyl) and 2-ethylhexyl esters of 2,4-D, 2,4,5-T and 2(2,4-dichlorophenoxy)propionic acid (2,4-DP), and the 2-ethylhexyl ester of Silvex were all formulated with this process. Some formulations were also produced which contained esters of both 2,4-D and 2,4,5-T. Only Transvaal/Vertac produced silvex esters (from 1971 to 1979).

Each of the liquid formulations discussed in the above paragraphs were also packaged by Reasor-Hill, Hercules and Transvaal/Vertac. Semi-automatic packaging lines were used for the packaging of these products in 1-gallon and 5-gallon containers. These lines moved the containers along and filled each one by inserting a spout into the container opening which started and stopped flow automatically. The products were also packaged in 30- and 55-gallon drums at the drumming station. A worker placed each drum onto the station's platform and manually controlled the flow.

Solid 2,4,5-T and 2,4-D acid granules were also packaged and sold. The packaging of this product into 2000-lb boxes was discussed previously in this report (see the 2,4,5-T acid production process description section). Some 2,4,5-T and 2,4-D acid was also bagged, using a pneumatic bagger, and sold. Tote bins of 2,4,5-T and 2,4-D acid were dumped into the feed bin of the bagger using a tote-bin dumper. The air-operated bagger filled the bags through tubes which were inserted into small openings at the tops of the bags.

Description of the Records Systems

A. Personnel Records

Hercules representatives stated that the only records for the Jacksonville workers in the possession of the company were computerized payroll records containing the employee's name, dates of birth, hire and termination, social security number, job status (hourly or salaried), and a Bureau of Labor statistic code indicating the job category. In addition to this information, NIOSH was able to obtained detailed job titles for many workers hired by Transvaal/Vertac because the information was entered on the Transvaal/Vertac application forms filled out by the employee. NIOSH also received Hercules seniority lists from a former Hercules employee.

Vertac maintains personnel files for all current and terminated, hourly and salaried workers. The files include application forms, records of pre-employment physicals, some job assignments and payroll change notices. The majority of files are contained in a manila folder entitled "Confidential Employee History" (CEH) which lists in chronological order the various positions held by the employee each time a payroll increase was received. A review of the personnel files indicated that the company began using these "Confidential Employee History" folders for workers hired after September, 1974. At some point (possibly February, 1975), the personnel office prepared CEH folders for employees hired before September, 1974, using payroll notices existing in the personnel file to list job positions and pay levels which dated back to time of employment with the company. This reconstruction of work histories seems fairly complete for most individuals. Therefore, the only files without "Confidential Employee History" folders are for persons who terminated before mid-1974. However, information on job assignments can be obtained from sheets in the personnel files of most employees who terminated before 1974. Clear job titles identify maintenance workers, laboratory personnel, grounds keepers, clerical personnel, storeroom workers, boiler operators, janitors, sales personnel, and engineers. A summary of job titles are presented in Table 1.

All formulations and packaging workers are identified only by the term "formulations." The term operator is used nonspecifically to include TCP operators, toluene recovery operators, acid operators, ester operators, chlorination and Dalapon operators. Only a few files specify the type of operator. Most operators worked in areas where 2,4,5-T, its precursors or products, were located. However, a small percentage of the total includes chlorination operators and Dalapon workers, who worked in areas where no 2,4,5-T operations were conducted. Most of these individuals cannot be identified.

B. Medical Records

No medical records were found for Hercules employees. The Transvaal/Vertac personnel files contain records of pre-employment physicals only, since annual physicals were not given until 1979, after the period of interest to this study.

C. Workers' Compensation Record

No workers' compensation records were obtained for the Hercules employees. Transvaal/Vertac records are maintained in an independent file in which records are ordered chronologically. A number of claims were made for chloracne problems. Some of these were associated with a 1974 incident in which a major pressure release occurred in the trichlorophenol reactor.

Description of Past Exposures

Hercules and Transvaal/Vertac have no available industrial hygiene records or data evaluating chemical exposures to the worker at the Jacksonville facility. The Occupational Safety and Health Administration (OSHA) Little Rock Area Office has made four general health inspections of the Jacksonville facility. OSHA investigators first visited the facility in February 11-12, 1975. This was a general health investigation and sampling for carbon monoxide using direct reading instruments was done. It was during this visit that OSHA investigators recognized exposures to 2,4,5-T and 2,4-D. A month later, from March 13 to April 17, 1975, OSHA investigators returned to the Jacksonville facility during which time they sampled for 2,4,5-T, 2,4-D and methylamine exposures in the packaging and drumming area. No violations were found during this survey. The case file containing the sampling results was found missing in October, 1977. The next visit to the Jacksonville facility by OSHA investigators occurred from October 12-21, 1977. During this visit, OSHA investigators sampled for 2,4-D. No NaTCP or 2,4,5-T had been produced at the facility since July, 1977. Air samples for 2,4-D were collected throughout the production areas with a total of 16 samples collected. All sample results for 2,4-D were nondetectable at a detection limit of 1.9 ug of 2,4-D per sample. The inspection was coded as being in compliance with OSHA regulations.

The fourth OSHA inspection took place from May 23 through November 14, 1979. Final production of NaTCP and 2,4,5-T was done in April, 1979. In this inspection sampling was done to assess worker exposures to 2,4-D, dichlorophenols (DCP), trichlorophenols (TCP), tetrachlorophenols (TetCP), dimethylamine (DMA) and diethylamine (DEA). The results of these samples are listed in Table 2. Personal air samples for 2,4-D were collected on glass fiber filters at an air flow rate of one liter per minute (Lpm). The filters were desorbed with methanol and analyzed for 2,4-D using liquid chromatography. Five personal air samples were collected and analyzed for 2,4-D with four of the five having non-detectable results and one (for the Ester Operator) having the result of 3.5 micrograms per cubic meter of air (ug/M3). Personal air sampling for chlorophenols was done using impingers containing isopropanol and an air sampling flow rate of 1 Lpm. The results of the personal air sampling for DCP ranged from 0.35 (for the Ester Operator) to 1.78 (for the Recovery Operator) milligrams per cubic meter of air (mg/M3). Personal air sample results for TCP ranged from 0.3 (for the Ester Operator) to 7.4 (for the Acid Operator) mg/M3. There were two nondetectable results for TetCP with the detectable personal air sample results for TetCP ranging from 0.24 (for the Ester Operator) to 0.29 (for the Acid Operator) mg/M3. A personal air sample was collected from a Formulator using 1 N sulfuric acid at an air flow rate of 1 Lpm and analyzed for DMA and DEA. The results for this sample were non-detectable for DMA and DEA at a detection limit of 5 parts per million (ppm).

Also collected during this inspection were personal air, area air and surface wipe samples for TCDD. The personal and area air samples were collected using impingers containing xylene at an air flow rare of 1 Lpm. Surface wipe samples were collected by wiping workplace surfaces with filter paper. These personal air, area air and surface wipe samples were extracted with hexane or isooctane and analyzed using gas chromatography/mass spectrometry (GC/MS). The results for these samples are listed in Table 3. Area air samples collected in the Acid plant and the Packaging plant yielded non-detectable results for TCDD, while an area air sample collected during a redrumming of toluene wash still bottoms operation yielded a result of 20.4 nanograms per cubic meter (ng/M3). Two personal air samples for TCDD exposure were collected from workers involved in the redrumming operation. One result for these personal samples was non-detectable for TCDD while the other sample result was 15.8 ng/M3. These workers wore personal protective equipment such as respirators, gloves, coveralls, etc. while redrumming. Surface wipe sample results ranged from 0.096 (for the lunchroom table) to 150 (for the floor in a truck in the redrumming area) nanograms per approximately 100 square centimeters of workplace surface area.

One incident which resulted in an acute exposure to NaTCP and its contaminants occurred at this facility in June or July 1974. NaTCP and its contaminants were released through a pressure relief valve in the reactor in which the 1,2,4,5-tetrachlorobenzene was being dechlorinated in the NaTCP production process. The reactor contents were released into a holding dike surrounding the reactor. This material in the holding dike caught fire and depositing a sooty oily film on workplace surfaces throughout the process. Five maintenance workers, who were involved in the cleanup, developed cases of chloracne. There have been other releases associated with this process, but only methanol was released in those instances. No other processes at this facility, involved with the production of 2,4,5-trichlorophenol derivatives, have had any incidents such as this.

The main duties for the various operators of the processes described in this report have been listed[11] and are shown in Table 1. Operations manuals for these processes may still exist. The following description given by company personnel, concentrates on the operations in which potential for exposures were greatest.

In the NaTCP production process, the "still bottoms" were drained by the recovery operator from the still into drums. This operator placed each drum next to the still, attached a hose to the still, placed the other end of the hose into the drum, and operated the valve on the still. This worker's main duties involved the operation of the toluene wash and toluene still, and assisting in the NaTCP (dechlorination) reaction area. After 1978, this worker was required to wear a respirator whenever he was draining "still bottoms".

The dechlorination operator most likely to incur exposure used a power unit which dumped drums of flaked caustic soda (NaOH) and molten 1,2,4,5-tetrachlorobenzene (TCB) into the dechlorination reactor through a manhole.

In the 2,4,5-T acid production process, the acid operators and the acid helpers were responsible for the cleaning of the centrifuge. This was done by scraping it out. The operators were always required to use respirators during this operation. During normal operation, the centrifuge was enclosed and, for the most part, automated. Other units either did not require cleaning, when switching products, or were cleaned by rinsing out and heating. For example, the salt filter was rinsed with hot water, which was pumped through it. The acid operators were also known as TCP loaders because they were responsible for loading the NaOH solution, the NaTCP, the hydrochloric acid (HCl), and the monochloroacetic acid (MCA) into the reactor vessel to produce 2,4,5-T. All of these substances were pumped or gravity fed from feed tanks, and were not necessarily a source of high exposures. The TCP loaders were also required to sample and analyze (by titration) the recycled toluene for residual TCP and 2,4,5-T content so that the proper amounts of reagents could be charged. These operators were also responsible for loading the dryer with 2,4,5-T acid granules and then discharging it from the dryer into tote bins. Each tote bin sat on a scale during loading, and the operator controlled the amount of acid loaded, 3000 lb. net.

The chlorination operator, who worked in the chlorination area, was potentially exposed to chlorine gas. Respirators were required in the area.

The esterification process was run by ester operators. Although the ester pre-reactor was mainly loaded with 2,4,5-T from tote bins, the operators adjusted the composition of the solution by manually dumping in bags of 2,4,5-T through manholes. This resulted in exposure to 2,4,5-T, Silvex, or 2,4-D dust.[11] The packaging of amine products resulted in splashing and spillage onto the floor.[11] Absorbent material was used to soak up the materials. At both the esterification and formulation areas, the covers on the vessels were sometimes left open for no apparent reason.[11]

In several areas of the plant, operators were required to draw samples of process streams. For sampling, the operators were always required to wear rubber gloves, face shields or goggles, and hard hats. Coveralls and shower facilities were always supplied for workers, but their use was not required. Beginning in 1979, all workers were required to change clothes and have work clothes laundered at the plant. Hard-hat and safety-glasses usage became mandatory at the plant at that time, also. The following observations were made about this facility[11]: the lunchroom was "adequate"; smoking and eating was prohibited in the work areas; and, housekeeping was good.

Environmental, Product, and By-Product Analyses

Measurements for TCDD content in products, process streams, and wasters produced at the Jacksonville facility have been collected from a number of sources. These data along with the source and date of analysis (from 1965 to 1978) are listed in Table 4. The earliest analyses of TCDD content in 2,4,5-T acid were conducted by the Dow Chemical Company in 1965 for 2,4,5-T acid samples produced by Hercules. Of the seven 2,4,5-T acid samples analyzed by Dow, 6 had less than 1 microgram TCDD per gram of sample (ug/g). One sample was found to contain 3 ug/g. Dow also applied Hercules 2,4,5-T acid to rabbit ears to determine if it caused folliculitis. All six samples applied to rabbit ears produced no folliculitis in the rabbit ears. With some assistance from Dow, Hercules began analyzing its own 2,4,5-T acid for TCDD concentrations. From April, 1965 to July, 1965, nine 2,4,5-T acid samples were analyzed for TCDD concentration with the results ranging from 0.2 to 3.3 ug/g. These 2,4,5-T acid samples were produced prior to the installation of the toluene wash system which was installed in October, 1965. Analyses by Hercules on its 2,4,5-T acid from 1967 to 1970 showed that it contained <0.2 ug/g.

In a January 26, 1971 letter to Dr. James G. Wilson, Chairman of the Environmental Protection Agency (EPA) Committee on Safety of 2,4,5-T, from Dr. John P. Frawley, Chief Toxicologist for Hercules, a table containing data results measuring TCDD concentrations in 2,4,5-T acid was enclosed. This table is shown in Table 5. Table 5 shows that the monthly analyses of 2,4,5-T acid for the years of 1966 through 1970 routinely had less than 0.1 ug/g. On one occasion, in September, 1966, the 2,4,5-T acid had a trace concentration of 0.1 ug/g. Also shown in Table 5 is the fact that very little 2,4,5-T acid was made in 1969 or 1970. Another table attached to the letter from Dr. Frawley was a summarization of a study characterizing the tetratogenic and other toxic effects observed in Charles River mice administered 2,4,5-T acid subcutaneously. These summary results are shown in Table 6. Hercules had contracted the Bionetics Research Laboratories to repeat a study performed by the National Institute Of Environmental Health Services. In that study, Charles River mice were administered subcutaneously 100 mg of 2,4,5-T acid per kilogram (kg) body weight dissolved in dimethyl sulfoxide (DMSO) from the 6th to the 15th day of gestation. Bionetics repeated this study using Hercules commercial 2,4,5-T acid and Dow purified 2,4,5-T acid dissolved in DMSO and in addition dissolved in propylene glycol. Hercules concluded from the results shown in Table 6 that this study failed to confirm that Hercules commercial and Dow purified 2,4,5-T acid are teratogenic.

Transvaal 2,4,5-T acid and its esters, as well as Silvex and its ester, were analyzed for their TCDD concentration by Dow in 1972, shortly after Transvaal had leased the facility from Hercules. In Table 4, the results of these analyses are shown. All results were less than 0.05 ug/g with the exception of Silvex which had a trace of TCDD at 0.05 ug/g. Transvaal and later Vertac routinely analyzed their 2,4,5-T products for TCDD concentration throughout the years the Na TCP and 2,4,5-T processes were operated by them (Oct., 1972 to May, 1979). Certificates of analysis were issued for their products and for 2,4,5-T products. The products routinely contained less than 0.1 ug/g of TCDD was normally reported. In one certificate of analysis from 1973, Transvaal reported detectable levels of 0.084 and 0.063 ppm TCDD for two different lots of 2,4,5-T butyl ester using a method described in an article by Elvidge[13]. Ten samples of Agent Orange produced by Hercules and sold to the U.S. Government was analyzed for its

TCDD concentration in 1975.[14] Eight of the 10 had non-detectable levels of TCDD at a detection limit of 0.05 ug/g. Two of the samples had detectable levels of 0.07 and 0.05 ug/g of TCDD. These sample results are shown in Table 4. The last data points in Table 4 are analyses of Vertac 2,4,5-T acid by Dow in 1978. The results of these analyses are 7 detectable results ranging from 0.009 to 0.21 ug/g.

The EPA visited the Jacksonville facility in 1978 and 1979 when Vertac was operating the Na TCP and 2,4,5-T processes and collected over 100 environmental, process stream and wastes samples from the facility site. Under contract with the EPA, the Wright State University Brehm Laboratory analyzed these samples for their TCDD concentrations. Selected from these results and listed in Table 7 are process stream samples analyzed for TCDD concentrations. The results of these process stream and waste analyses ranged from 609 parts per billion (ppb) of TCDD in the methanol still bottoms to 289 ppm of TCDD in toluene still pot residue. The EPA and Vertac also analyzed the general chemical composition of the toluene still bottom wastes drummed and stored at the facility at that time. The results of these analyses showed the waste to be composed of 1% methanol, 8% toluene, 3% di- and trichlorobenzene, 18% dichlorodimethoxybenzene, 56% TCA, 7% Na TCP, 7% Na 2,4,5-T and 15 to 20 ppm of TCDD.

Conclusions

The workers employed at Hercules and Transvaal/Vertac Chemical Corporation are suitable for inclusion in the Dioxin Registry. Hercules produced 2,4,5-T and 2,4-D products from December, 1961 through May, 1970. Transvaal/Vertac produced 2,4,5-T, 2,4-D and Silvex products regularly from December, 1971 to April, 1979. Almost all of the workers were employed in areas in which these products were made. Only a few workers worked in other areas; these were the chlorination workers who made monochloroacetic acid, and the Dalapon workers during the 1975 and 1976 production period. It is not possible to identify the chlorination and Dalapon production workers.

Maintenance workers and individuals employed in non-production positions in the plant can be identified. Formulations workers (who also packaged the products) can be identified and separated from all other production workers, but operators and helpers working in all other areas must be considered as one group because of the terminology used in the personnel files.

Based on the plant history, personnel records, process descriptions, and analytical data measuring TCDD concentrations in products, process streams, and waste, an exposure matrix assessing TCDD exposure can be constructed for the Hercules and Transvaal/Vertac workers. Because there are no personnel records for the workers who worked just for Reasor-Hill, TCDD exposures for these workers can not be assessed.

References

1. Esposito, M.P., Tiernan, T.O. and Dryden, F. (1980) Dioxins, Environmental Protection Agency Publication EPA-600/2-80-197.

2. Kimbrough, R., ed. (1980) Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products. Elsevier, New York.

3. Kociba, R., Keyes, D., Beyer, J., Carreon,E., Wade, C., et al. (1978) Results of a Two Year Chronic Toxicity and Oncogenicity Study of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Rats. Toxicol. Appl. Pharmcol. Vol.46, pp.279-303.

4. McConnell, E., Moore, J.A., Haseman, J. and Harris, M. (1978) The Comparative Toxicity of Chlorinated Dibenzo-p-dioxins in Mice and Guinea Pigs. Toxicol. Appl. Pharmacol. Vol.44, pp.335-336.

5. National Toxicology Program. Bioassay for 2,3,7,8-Tetrachlorodibenzo-p-dioxin. National Cancer Institute (1980) DHHS Publication No. NIH 80-1765.

6. Nicholson, W.J. and Morre, J.A., eds. (1979) Health Effects of Halogenated Aromatic Hydrocarbons. Ann. N.Y. Sci. Vol.320, p.1-730.

7. Poland, A. and Knutson, J. (1982) 2,3,7,8-Tetrachlorodibenzo-p-dioxin and Related Halogenated Hydrocarbons: Examination of the Mechanism of Toxicity. Am. Rev. Pharmacol. Toxicol. Vol.22, pp.517-554.

8. Craig, D.A. (1975) Use of Herbicides in Southeast Asia: Historical Report. San Antonio Air Logistics Center, Directorate of Energy Management, Kelly AFB, Texas, p. 58.

9. Treisback, A.L. Manufacture of 2,4,5-T - Notes from memory. February 20, 1981.

10. White, P.C., Gresham, E.A., Gaither, M., (1979) Epidemiological Investigation of a Dioxin Problem at the Vertac Chemical Plant, Jacksonville, Arkansas, Arkansas Department of Health, Bureau of Medical Care Services, Division of Communicable Diseases.

11. Unknown author, Jacksonville Plant (Industrial Hygiene Survey Report by Clayton Environmental Consultants, Inc. in February, 1979), Attachment to correspondence from Richard Karkkainen, Director of Environment & Safety, Vertac Chemical Corporation, to James H. Jones, Industrial Hygienist, NIOSH, March 28, 1980.

12. Woolson, E.A., Thomas, R.F. and Enson, P.D. (1972) Survey of Polychlorodibenzo-p-dioxin Content in Selected Pesticides. J. Agric. Food Chem. Vol.20(2), pp.351-354.

13. Elvidge, D.A. (1971) The Gas-chromatographic Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in 2,4,5-Trichlorophenoxyacetic Acid ("2,4,5-T"), 2,4,5-T Ethylhexyl Ester, Formulation of 2,4,5-T Esters and 2,4,5-Trichlorophenol. Analyst Vol. 96, pp. 721-727.

14. Fee, D.C., Huges, B.M., Tiernan, T.O. and Hill, C.H. (1975) Analytical Methodology of Herbicide Orange, Vol. II: Determination of Origin of USAF Stocks. Technical Report ARL-75-001100. Aerospace Research Laboratories, Wright Patterson AFB, Dayton, Ohio, p. 30.

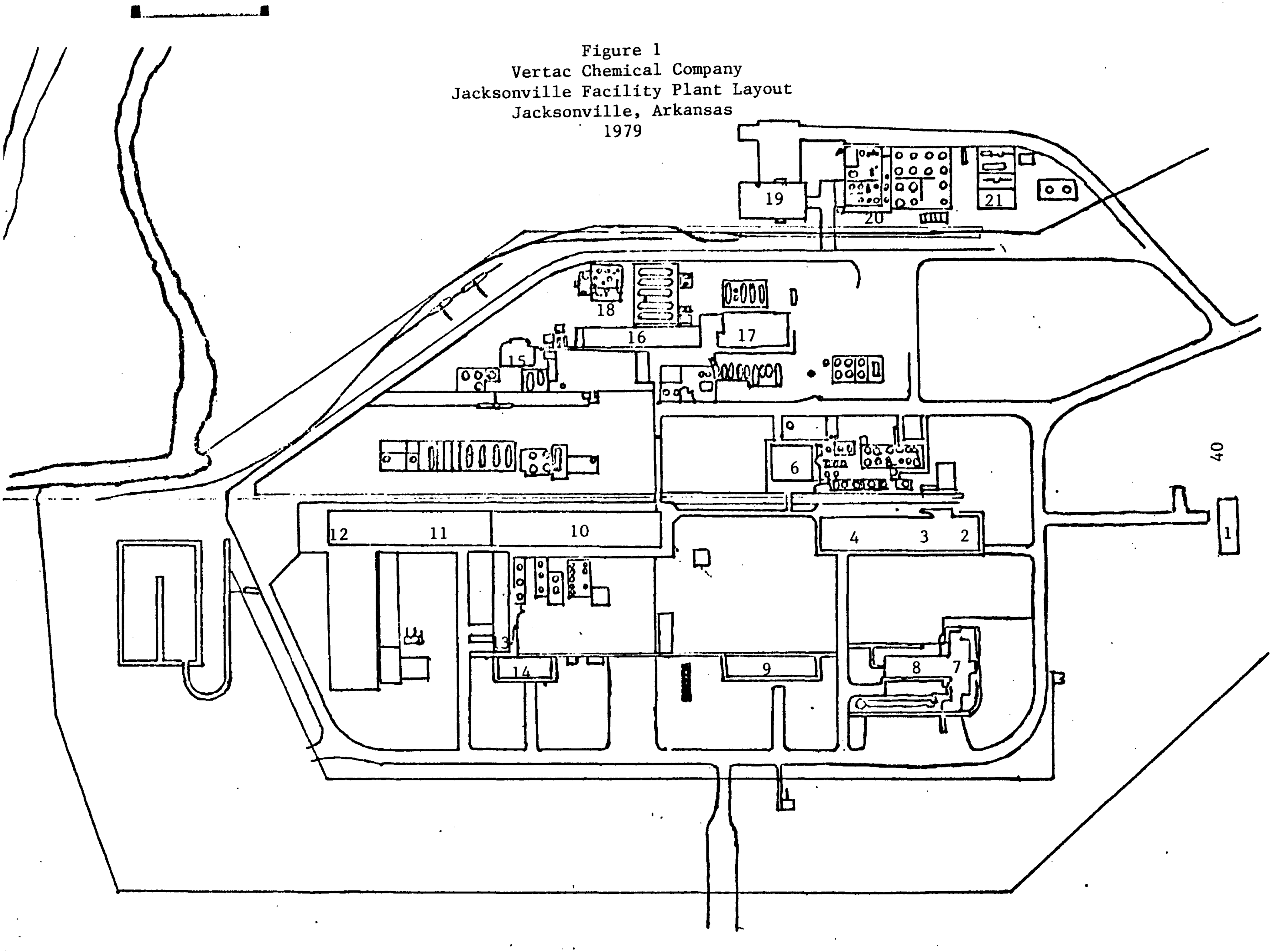


Figure 1
Vertac Chemical Company
Jacksonville Facility Plant Layout
Jacksonville, Arkansas
1979

Legend for Figure 1

Site Number	Site Description
1	Guardhouse
2	Change house
3	Na 2,4,5-TCP reactor area
4	Storage
5	Toluene wash, recovery, and distillation area
6	2,4,5-T and 2,4-D acid reactor area
7	Offices
8	Laboratory
9	Offices
10	Formulation and packaging area
11	Storage
12	Loading dock
13	Maintenance area
14	Storage
15	Monochloroacetic acid chlorination area
16	2,4,5-T and 2,4-D ester reactor area
17	Bagging area
18	1,2,4,5-Tetrachlorobenzene reactor area
19	Storage
20	Dalapon reactor area
21	Boiler house
22	Settling basin and neutralization area for wastewater

Figure 2.

Flow Diagram for Sodium 2,4,5-Trichlorophenate Production

1971-1979

Vertac Chemical Corporation

Jacksonville, Arkansas

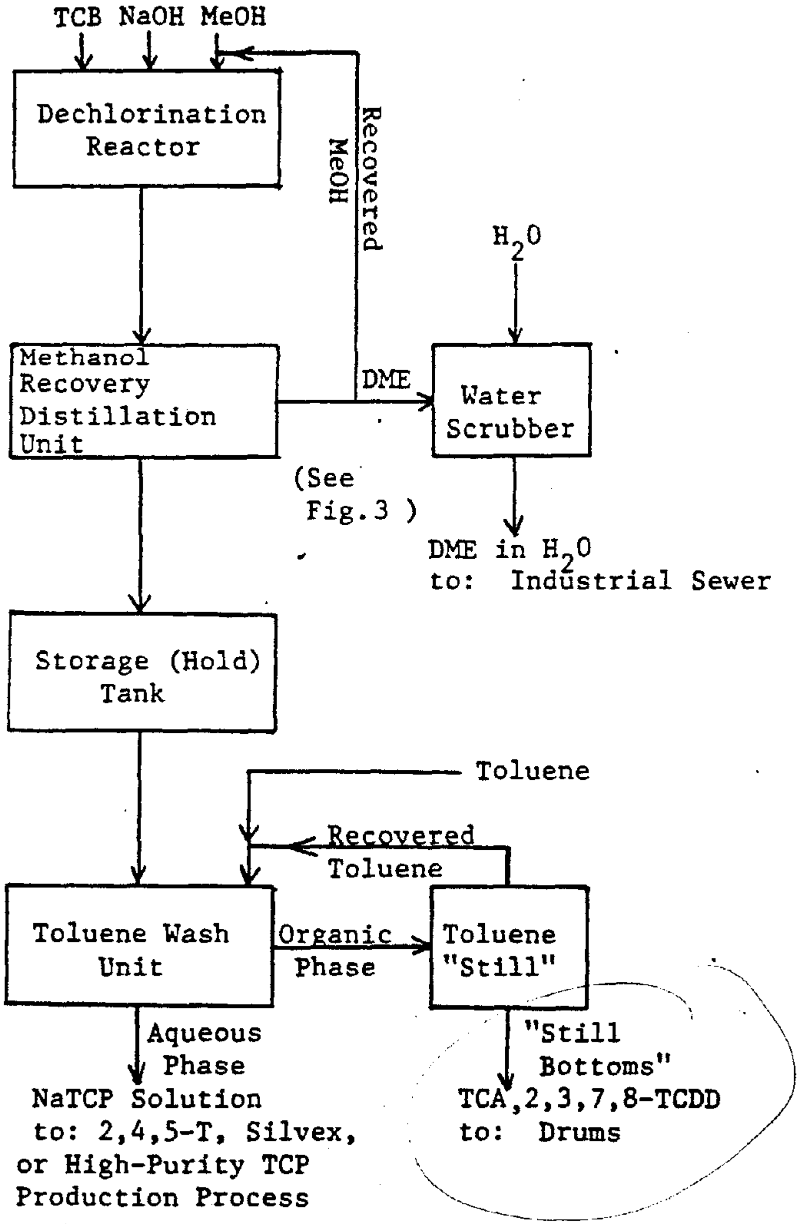


Figure 3.

Flow Diagram for Methanol Recovery Distillation Unit of Sodium 2,4,5-Trichlorophenate Production Process.

1971-1979

Vertac Chemical Corporation

Jacksonville, Arkansas

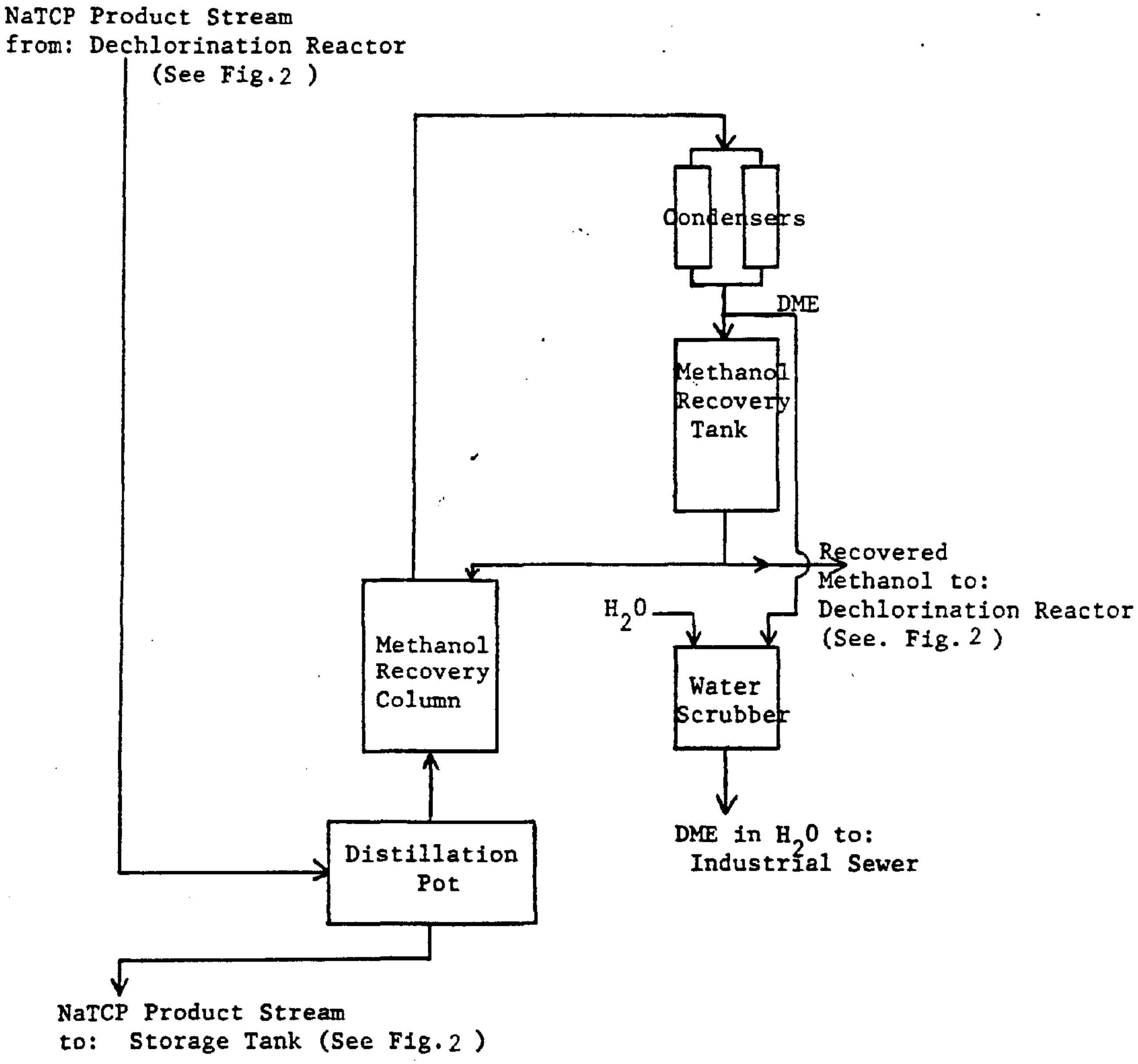


Figure 4.

Flow Diagram for 2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T) Production Process.

1971-1979

Vertac Chemical Corporation

Jacksonville, Arkansas

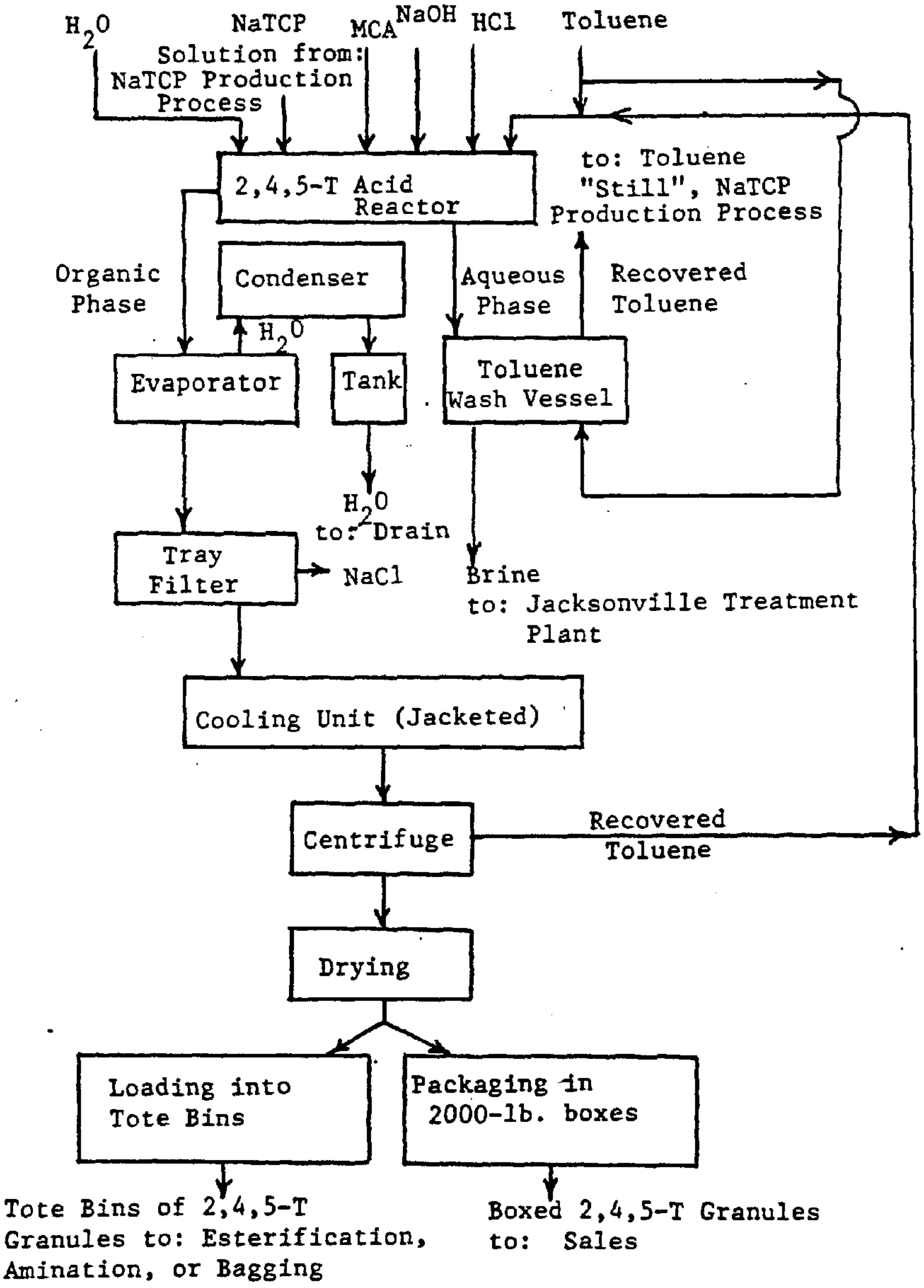


Figure 5.

Flow Diagram for Esters of 2,4,5-Trichlorophenoxyacetic Acid

(2,4,5-T) Production Process

1971-1979

Vertac Chemical Corporation

Jacksonville, Arkansas

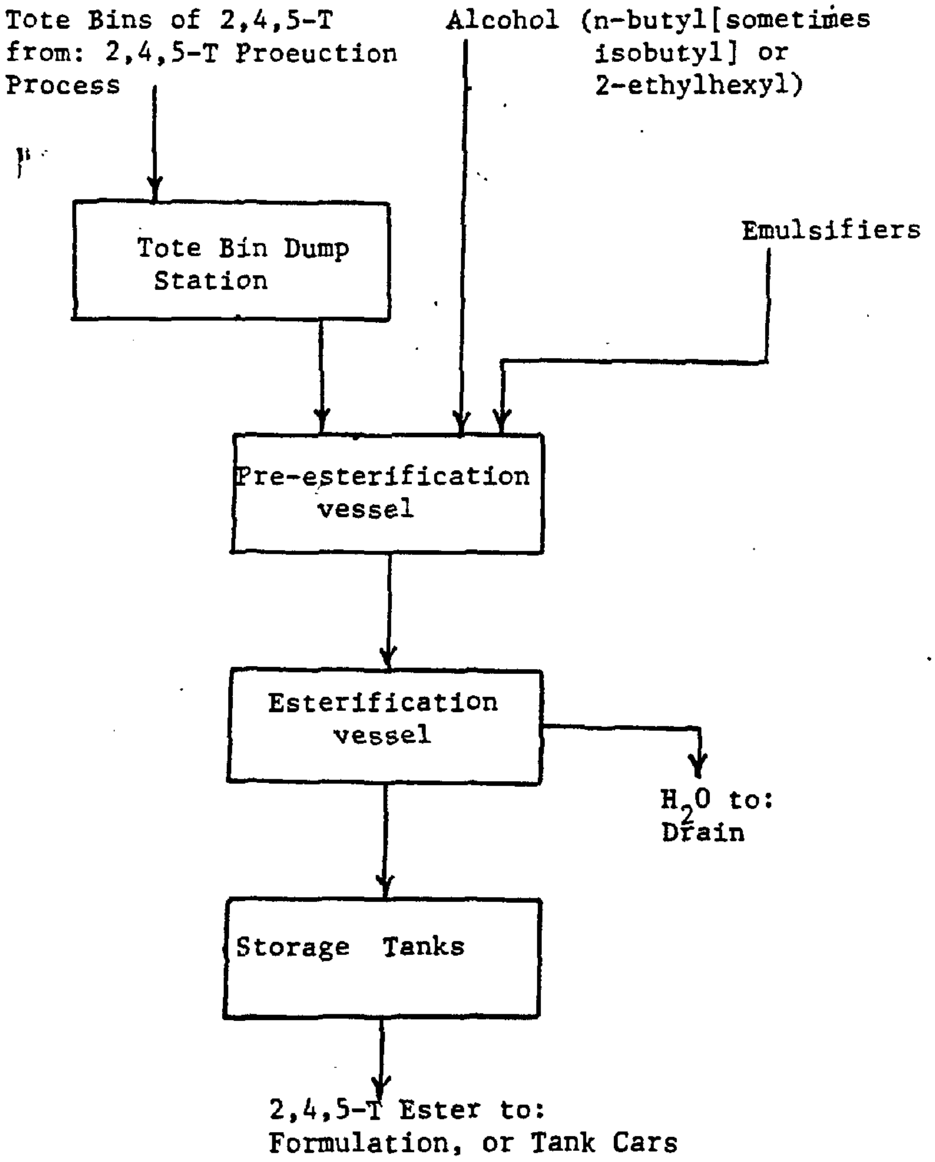


Table 1.

Operator Duties, Vertac Chemical Corporation, Jacksonville, Arkansas

1. Acid Operator	Work Place: Acid Area Duties: Calculated and measured raw materials and operated equipment to produce the herbicide acids. 1 per shift.
2. Acid Helper	Work Place: Acid Area Duties: Relieved and assisted the acid operator. 1 per shift.
3. Recovery Operator	Work Place: Recovery Area. Duties: Recovered spent solvents and extraction washed the trichlorophenol with solvent. Recovered the spent solvent from washing process. 1 per shift.
4. Dechlorination Operator	Work Place: Dechlorination (NaTCP) Duties: Charged batches and operated equipment in the production of sodium 2,4,5-trichlorophenate (NaTCP). Recovered solvent in process for reuse. 1 per shift.
5. Chlorination Operator	Work Place: Chlorination Area Duties: Charged batches and operated equipment in the production of monochloroacetic and 2,4-Dichlorophenol.
6. Ester Operator	Work Place: Ester Area Duties: Charge batches and operate equipment to produce esters of the herbicide acids. 1 per shift.

Table 1. cont.

Operator Duties, Vertac Chemical Corporation,
Jacksonville, Arkansas

7. <u>TCB Operator</u>	Work Place: TCB Area Duties: Charged batches and operated equipment to produce high purity 2,4,5-trichlorophenol.
8. <u>Boiler Operator</u>	Work Place: Boiler House Duties: Operated steam boiler to generate 150 psig steam.
9. <u>Formulator</u>	Work Place: Formulations Area Duties: Charged batches and operated equipment to formulate products for packaging. 4 per shift, shared with esterification.
10. <u>Packaging</u>	Work Place: Packaging Area Duties: Packaged formulated products for shipment.
11. <u>Helper</u>	Work Place: TCB Area and Recovery Area Duties: Relieved and assisted the TCB Operator and the recovery operator.
12. <u>Dalapon Operator</u>	Work Place: Dalapon Area Duties: Charged batches and operated equipment to produce Dalapon.
13. <u>Dalapon Helper</u>	Work Place: Dalapon Area Duties: Relieved and assisted the Dalapon operator.

Table 1. cont.

Operator Duties, Vertac Chemical Corporation,
Jacksonville, Arkansas

14. <u>Maintenance Personnel</u>	Work Place: Plant-wide Duties:Performed maintenance of equipment plant-wide, 10-20 persons.

Table 2
OSHA Personal Air Sample Results
June 1, 1979
Vertac Chemical Company
Jacksonville, Arkansas

Job Title	2,4-D (ug/M3)	DCP (mg/M3)	TCP (mg/M3)	TetCP (mg/M3)	DMA (ppm)	DEA (ppm)
			Analyte			
Acid Operator	<3.5	0.42	7.40	0.29	----	----
Recovery Operator	<4.0	1.78	4.32	<0.05	----	----
Ester Operator	3.5	0.33	0.30	0.24	----	----
Chlorination Oper.	----	0.47	0.47	<0.05	----	----
Formulator	<10.8	----	----	----	<0.5	<0.5
Packaging	<3.4	0.82	1.53	0.28	----	----

2,4-D = 2,4-dichlorophenoxyacetic acid
DCP = 2,4- and 2,6-dichlorophenols
TCP = 2,4,5- and 2,4,6-trichlorophenols
TetCP = 2,3,4,6-tetrachlorophenol
DMA = dimethylamine
DEA = diethylamine
ug/M3 = micrograms of analyte per cubic meter of air
mg/M3 = milligrams of analyte per cubic meter of air
ppm = parts analyte per million parts of air
OSHA = Occupational Safety and Health Administration

Table 3
OSHA TCDD Sample Results
Vertac Chemical Corp.
Jacksonville, Arkansas

Date	Sample Description	Sample Type	Sample Result	Units
6/01/79	Acid plant	A	<0.13	ng/M3
6/01/79	Packaging	A	<0.13	ng/M3
6/11/79	Redrumming	A	20.4	ng/M3
6/08/79	Lunchroom table	W	0.096	ng/wipe
6/08/79	Dechlorination table	W	0.22	ng/wipe
7/05/79	Changehouse bench	W	5.3	ng/wipe
7/05/79	Truck floor in redrumming area	W	150	ng/wipe
7/05/79	Redrummer	P	15.8	ng/M3
7/05/79	Redrummer	P	<20.4	ng/M3

A = area air sample
W = surface wipe sample
P = personal air sample
TCDD = 2,3,7,8-tetrachlorodibenzo-p-dioxin
ng/M3 = nanograms of TCDD per cubic meter of air
ng/wipe = nanograms of TCDD per approximately 100 square centimeters of workplace surface
OSHA = Occupational Safety and Health Administration
All samples were analyzed using GC/MS

Table 4
Summary of TCDD Concentrations in Products Produced at the Jacksonville Facility During During the Years of Operation

Hercules, Inc.
and
Vertac Chemical Corp.
Jacksonville, Arkansas
1965 - 1978

Date	Sample Description	TCDD conc. ug/g	Analysis Source	Analytical Method
3/65	2,4,5-T acid	<1	Dow	GLC
3/65	2,4,5-T acid	<1	Dow	GLC
3/65	2,4,5-T acid	<1	Dow	GLC
3/65	2,4,5-T acid	<1	Dow	GLC
3/65	2,4,5-T acid	<1	Dow	GLC
3/65	2,4,5-T acid	<1	Dow	GLC
3/65	2,4,5-T acid	3	Dow	GLC
3/65	2,4,5-T acid	neg	Dow	REFR
3/65	2,4,5-T acid	neg	Dow	REFR
3/65	2,4,5-T acid	neg	Dow	REFR
3/65	2,4,5-T acid	neg	Dow	REFR
3/65	2,4,5-T acid	neg	Dow	REFR
3/65	2,4,5-T acid	neg	Dow	REFR
4/15/65	2,4,5-T acid	3.2	Hercules	GLC
4/15/65	NaTCP	0.4	Hercules	GLC
4/19/65	NaTCP	0.8	Hercules	GLC
4/23/65	NaTCP	0.2	Hercules	GLC
6/01/65	2,4,5-T acid	3.0	Hercules	GLC
6/15/65	2,4,5-T acid	3.0	Hercules	GLC
7/01/65	2,4,5-T acid	3.3	Hercules	GLC
7/07/65	2,4,5-T acid	1.3	Hercules	GLC
4/30/67	2,4,5-T acid	<0.2	Hercules	GLC
5/08/68	2,4,5-T acid	<0.2	Hercules	GLC
10/12/68	2,4,5-T acid	<0.2	Hercules	GLC
11/14/68	2,4,5-T acid	<0.2	Hercules	GLC
12/07/68	2,4,5-T acid	<0.2	Hercules	GLC
1/19/69	2,4,5-T acid	<0.2	Hercules	GLC
2/23/70	2,4,5-T acid	<0.2	Hercules	GLC
2/27/70	2,4,5-T acid	<0.1	USDA/EPA	GC/ECD

Table 4 (continued)
Summary of TCDD Concentrations in Products Produced at the Jacksonville Facility During During the Years of Operation
Hercules, Inc.
and
Vertac Chemical Corp.
Jacksonville, Arkansas
1965 - 1978

Date	Sample Description	TCDD conc. ug/g	Analysis Source	Analytical Method
3/70	2,4,5-T acid (4/15/65)*	3.1	Hercules	GC/ECD
3/70	2,4,5-T acid (6/15/65)*	3.5	Hercules	GC/ECD
3/70	2,4,5-T acid (6/15/65)*	2.4	Hercules	GC/ECD
3/70	2,4,5-T acid (7/01/65)*	2.2	Hercules	GC/ECD
3/70	2,4,5-T acid (7/19/65)*	1.3	Hercules	GC/ECD
3/70	2,4,5-T acid (7/07/65)*	1.5	Hercules	GC/ECD
9/13/72	2,4,5-T acid	<0.05	Dow	GC/MS
9/13/72	2,4,5-T acid	<0.05	Dow	GC/MS
9/13/72	2,4,5-T acid	<0.05	Dow	GC/MS
10/13/72	2,4,5-T butyl ester	<0.05	Dow	GC/MS
10/13/72	2,4,5-T ethyl hexyl ester	<0.05	Dow	GC/MS
10/13/72	Silvex	0.05	Dow	GC/MS
10/13/72	Silvex ethyl hexyl ester	<0.05	Dow	GC/MS
5/09/73	2,4,5-T butyl ester	0.063	Transvaal	GC/ECD
5/09/73	2,4,5-T butyl ester	0.084	Transvaal	GC/ECD
5/75	Agent Orange	<0.05	Dow	GC/MS
5/75	Agent Orange	<0.05	Dow	GC/MS
5/75	Agent Orange	<0.05	Dow	GC/MS
5/75	Agent Orange	<0.05	Dow	GC/MS
5/75	Agent Orange	<0.05	Dow	GC/MS
5/75	Agent Orange	<0.05	Dow	GC/MS
5/75	Agent Orange	<0.05	Dow	GC/MS
5/75	Agent Orange	<0.05	Dow	GC/MS
5/75	Agent Orange	0.05	Dow	GC/MS
5/75	Agent Orange	0.07	Dow	GC/MS

Table 4 (continued)
Summary of TCDD Concentrations in Products Produced at the Jacksonville Facility During During the Years of Operation
Hercules, Inc.
and
Vertac Chemical Corp.
Jacksonville, Arkansas
1965 - 1978

Date	Sample Description	TCDD conc. ug/g	Analysis Source	Analytical Method
7/78	2,4,5-T acid	0.009	Dow	GC/MS
7/78	2,4,5-T acid	0.010	Dow	GC/MS
7/78	2,4,5-T acid	0.011	Dow	GC/MS
7/78	2,4,5-T acid	0.011	Dow	GC/MS
7/78	2,4,5-T acid	0.011	Dow	GC/MS
7/78	2,4,5-T acid	0.015	Dow	GC/MS
7/78	2,4,5-T acid	0.021	Dow	GC/MS

2,4,5-T acid = 2,4,5-trichlorophenoxyacetic acid
silvex = 2(2,4,5-trichlorophenoxy) propionic acid
Agent Orange = 50% 2,4,5-T butyl ester and 50% 2,4-dichlorophenoxyacetate butyl ester
neg = negitive folliculitis response when applied to rabbit ears
ug/g = micrograms TCDD per gram of sample
Dow = The Dow Chemical Company
Hercules = Hercules Inc.
USDA/EPA = U.S. Department of Agriculture/Environmental Protection Agency
GLC = gas liquid chromatography
REFR = rabbit ear folliculitis response
GC/ECD = gas chromatography/electron capture detection
GC/MS = gas chromatography/mass spectrography
* = date sample was previously analyzed

Table 5
Summary of 2,4,5-T Acid TCDD Concentrations
ug/g
Hercules, Inc.
Jacksonville, Arkansas
1966 - 1970

Month/Year	1966	1967	1968	1969	1970
Jan.	<0.1	<0.1	<0.1	<0.1	No Mfg.
Feb.	<0.1	<0.1	<0.1	No Mfg.	No Mfg.
Mar.	<0.1	<0.1	<0.1	No Mfg.	No Mfg.
April	<0.1	<0.1	<0.1	No Mfg.	<0.1
May	<0.1	<0.1	<0.1	No Mfg.	<0.1
June	<0.1	<0.1	<0.1	No Mfg.	No Mfg.
July	<0.1	<0.1	<0.1	No Mfg.	No Mfg.
Aug.	<0.1	<0.1	<0.1	No Mfg.	No Mfg.
Sept.	0.1	<0.1	<0.1	No Mfg.	No Mfg.
Oct.	<0.1	<0.1	<0.1	No Mfg.	No Mfg.
Nov.	<0.1	<0.1	<0.1	No Mfg.	No Mfg.
Dec.	<0.1	<0.1	<0.1	No Mfg.	No Mfg.

No Mfg = no 2,4,5-T was produced for this month
ug/g = micrograms TCDD per gram of sample

Table 6
Summary of Teratogenic and Other Toxic Effects
in Charles River Mice Administered 2,4,5-T Acid
at 100 mg/kg Subcutaneously
Hercules, Inc.
Jacksonville, Arkansas
1970

	DMSO Controls	2,4,5-T (Hercules) in DMSO	2,4,5-T (Dow) in DMSO	PG Controls	2,4,5-T (Hercules) in PG	2,4,5-T (Dow) in PG
Total No. Litters	10	10	10	10	11	11
No. Fetus Mortalities	24	13	14	13	18	12
No. Fetus Examined	94	107	103	93	113	135
No. Develop. Abnormalities	1	1	3	2	3	3
Type(s) of Develop. Abnor.	1-kidney cyst	1-possible clubfoot	2-umbilical hernias 1-renal agenesis	1-clef palet 1-poss. clubfoot	1-hydrocephaly 1-epithelial defect 1-possible clubfoot	1-clef palet 1-heart defect
No. Fetus Develop. Toxic Effects	21	16	10	11	7	6

2,4,5-T = 2,4,5-trichlorophenoxyacetic acid
mg/kg = milligrams of 2,4,5-T acid per kilogram mouse body weight
DMSO = dimethyl sulfoxide
PG = propylene glycol

Table 7
EPA Process Stream and Waste Analyses for TCDD Conc.
Vertac Chemical Corp.
Jacksonville, Arkansas
1978 - 1979

Sample Description	TCDD conc.	Units
Methanol still bottoms	609	ppb
Spill from barrels in storage area (brown layer)	584	ppb
Spill from barrels in storage area (brown layer)	14	ppm
Charge to toluene still	64.9	ppm
1st cut, toluene/water distillation	<145	ppt
2nd cut, toluene/water distillation	<145	ppt
3rd cut, toluene/water distillation	381	ppt
4th cut, toluene/water distillation	6.6	ppb
5th cut, final toluene/water distillation	7.5	ppb
Toluene still bottoms (pot residue)	289	ppm
Toluene still bottoms (charge to reactor)	250	ppm
Toluene still bottoms	111	ppm

TCDD = 2,3,7,8-tetrachlorodibenzo-p-dioxin
ppb = parts per billion
ppm = parts per million
ppt = parts per trillion
Results obtained from GC-High Resolution MS analyses