IWS - 117-18

PB85-221786

PB85221786

DIOXIN REGISTRY SITE VISIT REPORT

OF

OCCIDENTAL CHEMICAL CORPORATION
Hooker Chemical Center
Niagara Falls, New York

DATES OF VISITS:
November 1-2, 1983
February 27-March 5, 1984

REPORT WRITTEN BY:
David A. Marlow
Marilyn Fingerhut, Ph.D.

DATE OF REPORT:
August 21, 1984

REPORT NUMBER:
117.18

Industrywide Studies Branch
Division of Surveillance, Hazard Evaluations, and Field Studies
National Institute for Occupational Safety and Health
Centers for Disease Control
Cincinnati, Ohio

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	3. Recipient's Accession No. PB85 221786/AS

4. Title and Subtitle
Dioxin Registry Site Visit Report No. IWS-117-18, Occidental Chemical Corporation, Hooker Chemical Center, Niagara Falls, New York

5. Report Date 84/08/21

6.

7. Author(s) Marlow, D. A., and M. Fingerhut

8. Performing Organization Rept. No. IWS-117-18

9. Performing Organization Name and Address
Division of Surveillance, Hazard Evaluations and Field Studies, NIOSH, U.S. Department of Health and Human Services, Cincinnati, Ohio,

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C)
(G)

12. Sponsoring Organization Name and Address
Same as Box 9

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

A walkthrough survey of facilities of Occidental Chemical Corporation (SIC-2869), Niagara Falls, and Buffalo, New York was conducted in November, 1983 and February to March, 1984. The purpose of the survey was to obtain information on the manufacture of 2,4,5-trichlorophenol (95954) (TCP) and to determine if the workers should be included in the NIOSH 2,3,7,8-tetrachlorodibenzo(p)dioxin (1746016) (TCDD) registry. TCP was produced at the facility from the raw materials ethylene-glycol (107211), 1,2,4,5-tetrachlorobenzene (95943), and sodium-hydroxide (1310732) from 1949 through 1972. TCDD is a contaminant of TCP. The company maintained monthly and quarterly lists of all employees listed by job title from 1949 to 1978. Complete medical records were maintained only for workers who terminated or retired after 1967. The company had limited analytical data on TCDD concentrations in products, process streams, and residues. Such data showed maximum TCDD concentrations of 1.0 and 47 parts per million (ppm) in finished and crude product, respectively. TCDD concentations in residues were 230 to 494ppm. The authors conclude that TCP production workers and repairmen in the fine chemicals department should be included in the NIOSH dioxin registry.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms

NIOSH-Publication, NIOSH-Author, NIOSH-Survey, Field-study, Chemical-manufacturing-industry, Pesticides-and-agricultural-chemicals, Herbicides, Industrial-chemicals, Epidemiology, Disease-incidence, Medical-surveys, IWS-117-18

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages 32
	20. Security Class (This Page)	22. Price

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77) (Formerly NTIS-35) Department of Commerce

Table of Contents

PURPOSE OF VISITS:	To review the record system of the company, to discuss details of the manufacture of 2,4,5-trichlorophenol, and to evaluate the feasibility of including the trichlorophenol workers in the Dioxin Registry. To collect medical records for the cohort.
EMPLOYER REPRESENTATIVE CONTACTED:	Mitchell R. Zavon, M.D., Director Health and Safety (716) 286-3090 Kathleen Goodwin Glasgow, CRM, Manager, Records and Information Resources Jay Cull, Chemical Engineer (716) 286-3603 Elizabeth Gelfand, Nurse Supervisor David Rosenberg, Chemical Engineer, retired Vernon Lloyd, Plant Technical Director Wayne Hellman, Employee Relations Manager (716) 286-7740 David Fabrizio, Personnel Officer
EMPLOYEE REPRESENTATIVE CONTACTED:	Anthony LaMacchia, President, Niagara Hooker Employees Union (716) 278-7001 Joseph T. Reele, President, Local #57, International Federation of Professional and Technical Engineers (716) 278-7777
STANDARD INDUSTRIAL CLASSIFICATION:	2869 - Industrial Organic Chemicals

Abstract

Site visits were conducted at Occidental Chemical Corporation, Occidental Chemical Center and at the Buffalo Avenue Plant of this Corporation (formally known as Hooker Chemical and Plastics Corporation) on November 1-2, 1983 and February 27-March 5, 1984. The plant produced 2,4,5-trichlorophenol from early 1949 through June 1972. The site visits were made to determine whether this facility was suitable for inclusion in the Dioxin Registry, to obtain personnel and medical records, process information, and all available analytical data for dioxins in product and process streams of the 2,4,5-trichlorophenol process. It was determined that the trichlorophenol production workers and the repairmen assigned to the Fine Chemicals Department between 1949 and 1972 are suitable for inclusion in the Dioxin Registry.

The report includes a description for the production of 2,4,5-trichlorophenol and a summary of product, process stream, and waste analyses for 2,3,7,8-tetrachlorodibenzo(p)dioxin. Job descriptions of the trichlorophenol operators are provided and the personnel and medical records are characterized.

Acknowledgements

We wish to express our appreciation to researchers Howard Rockette, Ph.D. and Vincent Arena of the University of Pittsburgh for assisting us in the use of data which they collected for a mortality study at the Niagara plant.(1) We also thank Mitchell R. Zavon, M.D., Director, Health and Safety, Occidental Chemical Corporation, and Kathleen Goodwin Glasgow, Manager Records and Information Resources, who coordinated our data gathering activities at the Niagara plant.

Introduction

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

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

Studies of this nature are authorized under the Occupational Safety and Health Act of 1970, Public Law 91-596, December 29, 1970. NIOSH has been designated responsibility for conducting field research studies in industry, to evaluate findings, and report on these findings. Section 20(a)7 states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity.

History of the Plant

The facility in Niagara Falls, New York was founded on January 9, 1906 as the Development and Funding Company, making caustic soda and bleaching powder.[2] In 1909 the facility became the Hooker Electrochemical Company (HECO). The present facility is an aggregation of three chemical companies: HECO, the Niagara Alkali Company acquired in 1955, and the Oldbury Chemical Company acquired in 1956. In 1958 the company became the Hooker Chemical Corporation. In 1974 the company was called the Hooker Chemical and Plastic Corporation. In 1981 it became the Hooker Chemical Company with a name change in 1982 to the Occidental Chemical Corporation, a Division of the Occidental Petroleum Corporation. The Niagara plant is currently a part of the Industrial and Specialty Chemical Group of the Occidental Chemical Corporation (ISC).

Trichlorophenol production occurred in the Fine Chemicals Department from early 1949 until June 1972 in Building D7 (now demolished) of the HECO portion of the facility.

The Niagara Hooker Employee Union represents the hourly workers at the plant, except those in Area 4, the Oldbury section, who are unrepresented. The laboratory workers are represented by the Hooker Laboratory Workers Union.

Epidemiologic Study of the Hooker Industrial and Specialty Chemical Group.

A plant wide mortality study of the Niagara Plant was completed in early 1983 by Howard Rockette, Ph.D. and Vincent Arena of the University of Pittsburgh under a contract from the Occidental Chemical Corporation.(1) This study included all employees who worked in the plant for at least one year between 1949 and 1978. A major effort had been made prior to the plant-wide study to organize and validate completeness of records from the three aggregated companies.

The authors had constructed computerized alpha-numeric listing of job titles and departments at the Niagara plant which permitted identification of all TCP workers and Fine Chemical Department repairmen employed more than one year between 1949 and 1972. During a visit to the University of Pittsburgh in January 1984 personnel records were microfilmed for these workers. A manual search was made for records of workers employed less than one year during this period. No medical data was acquired by Dr. Rockette for the plant-wide study; therefore, medical and workers' compensation records were obtained for the cohort during the February visit to Niagara Falls.

Medical Records

In 1982 an extensive medical facility was constructed on the plant grounds, replacing a facility dating back to about 1943. The building houses all medical records for current and terminated employees. In the past, the company record retention policy called for destruction of employee medical records seven years after termination. Interpretation of the rule appears to have been variable, since the first microfilming of records, which occurred in 1977, included terminations from 1967. There is a list of names of persons whose records were destroyed between 1950 and 1957 in a record schedule book kept by the Nurse Supervisor. There is no information to explain the absence of records between 1957 and 1967. Log books were kept of daily visits from 1943 to 1972 in the medical facility; the books are listed as destroyed.

Two folders labeled "Chloracne" and "Trichlorophenol", prepared by the Nurse Supervisor, contain various items which have accumulated over the years. These items consisted of letters with diagnoses of chloracne by local dermatologists for workers employed in the TCP and chlorinated naphthane departments, logs of names and results of monthly "D7 checks" for TCP workers, summaries of numbers of TCP workers treated for rashes during the 1950's, and memos related to chloracne in the plant. The "D7 checks" were regular monthly medical visits for inspection and treatment of chloracne in the trichlorophenol workers of Building D7. The contents were microfilmed during the February 1984 visit.

The contents of the individual medical files include a log of the visits of the individuals to the medical facility, notations of all "D7 checks", notes from consulting physicians, workers compensation records (with diagnoses attached), medical history questionnaires, and results from company physical examinations which were begun in 1977. The files of current employees were microfilmed during the February 1984 visit. Photocopies were made for all terminees for whom there were medical files on the company microfilm.

The following medical files were obtained:

	Current Employees	Terminated and Retired Employees	No Medical Records	Total
TCP Operators	32	41	65	138
Repairmen	44	80	79	203
Persons Employed Less Than One Year	0	0	34	34
Total	76	121	178	375

In summary, complete medical records exist for all employees who terminated or retired after 1967. Incomplete information also exists which describes "D7 checks" and chloracne diagnoses for some individuals.

From about 1942 until October 1975, the Hartford Indemnity Insurance Company of Buffalo was the insurance carrier. It is not known whether the carrier has retained records on the Hooker employees.

Record Retention

In 1962, the company instituted an organized system for record retention and destruction. A Records Center was located at the plant, under the supervison of Mr. Edward Rossi. In 1982, a commercial firm was hired to conduct this activity. All stored records and microfilms are now located at Commercial Archives, 305 Niagara Street, Buffalo, N.Y.

Personnel Records

Five filing categories are utilized by the personnel office: active, retired alive, retired deceased, exits (terminated), and summer exits (summer help). The original personnel files for all hourly current employees and for all retired employees (hourly and salaried) are maintained in the personnel department in approximately 25 file drawers. Original personnel files for "exits" (terminated persons who did not retire) which remain in the Personnel Department seem to date back about ten years. Older files, which were microfilmed, are stored in the Commercial Archives Building.

A typical retired or exit personnel record includes a "bucket card" (See Figure 1), rate change cards, attendance cards, and application for employment. Bucket cards for current employees are maintained in the Accounting Department. The bucket card contains demographic information as well as the detailed work history for the individual. The department in which the person worked and the job title are listed. These cards are used as the basis for seniority and are accurate reflections of the complete work activity of the individual.

The Personnel Department has a complete photocopied set of bucket cards compiled for the recent company-wide epidemiologic study, and Dr. Rockette has a second set. It is believed that each set contains a card for every individual for whom there existed a personnel file either in hard copy or on microfilm at the time of record review for Dr. Rockette's plant-wide mortality study in 1978, whether or not the individual worked longer than one year. The current cohort for the Dioxin Registry was compiled using Dr. Rockette's set of bucket cards located at the University of Pittsburgh. During the visit to Hooker on February 1984, a 5% sample of the Hooker set of bucket cards was examined for TCP workers. No additional persons were found.

"Force Lists"

The company generates monthly and quarterly force lists, which list by job title the individuals employed in each department. Lists from 1949 to 1978 were used in the recent company-wide epidemiologic study to validate completeness of employee personnel files. During the visit of February 1984, Force Lists were reviewed for TCP workers and repairmen in the Fine Chemicals Department. All monthly lists were examined for 1949-1959, and all quarterly lists were reviewed for 1960-1972. The collection of force lists was complete for most years. Incomplete sets which were examined are listed here:

1956 - January to November examined
1957 - February, May and November examined
1958 - February, August and November examined
1959 - February, May, June, July, September and October examined

Six individuals were identified in the review of these lists who had not been included in the cohort obtained from the University of Pittsburgh records.

Salaried Workers

Only two salaried individuals, both of whom who held the job title Process Foreman, worked in the TCP department.

Maintenance Workers

Some maintenance workers are assigned to a central pool which services the entire plant; none of these individuals who may have worked in the TCP area can be identified. Other maintenance workers held the title Repairmen and were assigned to the Fine Chemicals Department. These workers are identifiable from the Force Lists. The company representatives stated that these workers had a high probability of working in the trichlorophenol building, but they also would have worked in the other areas of the Fine Chemicals Department.

The company knows of no way to precisely arrive at the average amount of time worked by repairmen in the 2,4,5-trichlorophenol process. One estimating approach suggested by the company is to assume that during a given year a repairman could have worked on approximately 10 different processes in the Fine Chemicals Department. If it is also assumed that overtime work was counter-balanced by vacation and holidays, then the average potential exposure time would be 208 hours per year for a given repairman. This number is conceivably high, since repairmen also spent time in various repair shops away from the 2,4,5-trichlorophenol process. It does, however, reflect work on small equipment taken from the 2,4,5-trichlorophenol process for repair in the shops.

Process Description for the Production of 2,4,5-Trichlorophenol

The production of 2,4,5-trichlorophenol (TCP) used the following raw materials: 1,2,4,5-tetrachlorobenzene (TCB), ethylene glycol and flake caustic soda (NaOH). Other materials used in the process included ethylene glycol as a solvent, nitrogen gas to keep the process anhydrous, and anhydrous hydrogen chloride for neutralization purposes. All raw materials, with the exception of ethylene glycol, were produced at the Niagara Plant. Table 1 shows the specification that the raw materials had to meet in order to be used in the production of TCP. A flow diagram of this process is provide in Figure 2.

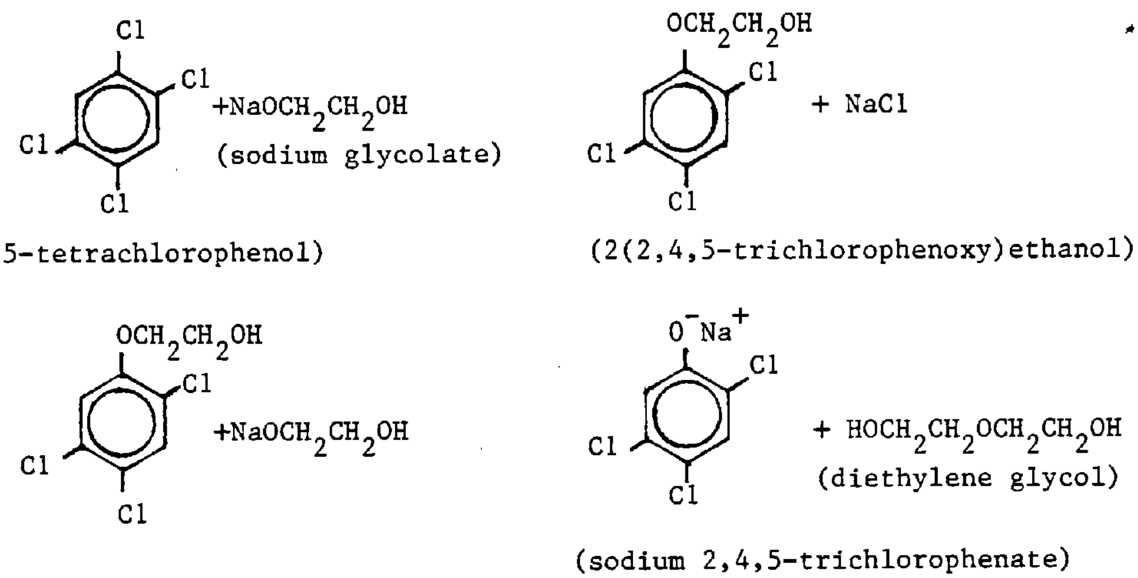
Throughout the years of production, no changes were made in the basic method for producing TCP. The changes made were the addition of equipment to increase production capacity and efficiency. Table 2 lists the changes made and the dates the changes took effect.

The first step in the process took place in the glycolate reactor. Ethylene glycol and flake caustic soda were added to the reactor. Nitrogen gas was purged through the system to keep the reaction anhydrous. The reaction that took place between the ethylene glycol and NaOH was as follows:

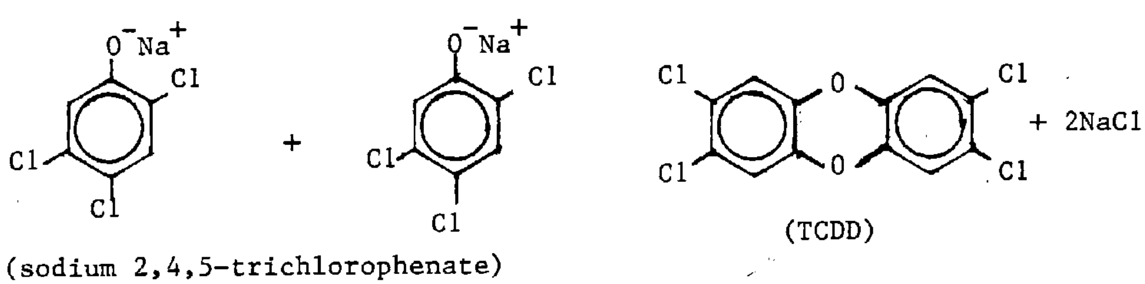
$$\underset{\text{(ethylene glycol)}}{HOCH_2CH_2OH} + NaOH \longrightarrow \underset{\text{(sodium ethylene glycolate)}}{NaOCH_2CH_2OH} + H_2O$$

Ethylene glycol was used in excess of a 1:1 stoichiometric ratio with NaOH, and the sodium ethylene glycolate formed was dissolved in the excess ethylene glycol. The water vapor formed in the reaction was driven out of the reactor by the nitrogen gas and went to the glycol-water storage tank. Once the reaction was completed, the sodium ethylene glycolate solution was pumped to the 5000 gallon glycolate storage tank. Nitrogen gas was kept in the glycolate storage tank to keep the solution anhydrous by preventing water vapor from entering the system.

The next step in the process took place in the TCP reactor vessel. This reactor vessel was a 500 gallon closed agitated jacketed nickle reactor. TCB and sodium ethylene glycolate, in excess of a 1:1 stoichlometric ratio with TCB, were pumped into the reactor. Although the exact reaction mechanism was never investigated by the company, one possible reaction mechanism could be as follows:

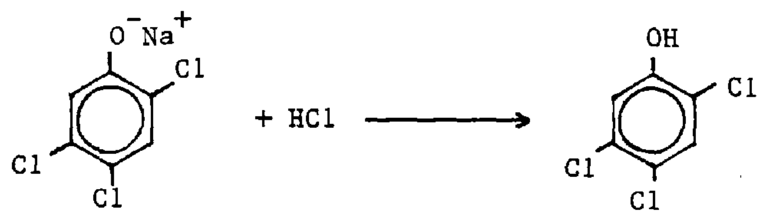


The reaction temperature was generally maintained between 165° and 175°C while the pressure was approximately 35 pounds per square inch gauge (psig). The reaction time was approximately 8 hours and was determined to be complete if no TCB could be measured. Diethylene and triethylene glycols, as well as dioxane were also formed as by-products during this reaction. Table 3 lists the chemical structure of these by-products. Another unwanted reaction which occurred at a much lower rate during this step was of the formation of the contaminant, 2,3,7,8-tetrachlorodibenzo(p)dioxin (TCDD). The reaction mechanism for the TCDD formation is written as follows:



The resulting solution contained, in weight percent, 36.5% ethylene glycol, 4.5% sodium ethylene glycolate, 12.0% diethylene glycol, 0.3% sodium diethylene glycolate, 1.0% triethylene glycol, 0.3% dioxane, 1.6% unknown low boiling organic compounds, 7.0% water, 8.4% sodium chloride, 25.4% sodium 2,4,5-trichlorophenate and 3.0% unknown high boiling organic compounds. A fraction of the unknown high boiling organic compounds would have contained TCDD. This solution was pumped to a 6500 gallon TCP reaction storage tank.

The next step in the process, the neutralization step, was conducted in the a 500 gallon HCl neutralization tank. A portion of the contents in the TCP reaction storage tank was then pumped to the HCl neutralization tank. Anhydrous hydrogen chloride was then bubbled into the solution and the following principal reaction took place:



(2,4,5-trichlorophenol)

This step continued until a pH in the range of 3 to 4 was reached. The temperature was kept at approximately 70°C and the pressure was atmospheric during this step.

After the neutralization step, the resulting solution was referred to by the company as "crude" TCP and had a chemical composition, by weight percent, of 37.2% ethylene glycol, 11.4% diethylene glycol, 0.9% triethylene glycol, 0.3% dioxane, 1.5% unknown low boiling organic compounds, 6.6% water, 18.6% sodium chloride, 21.3% 2,4,5-trichlorophenol, and 2.2% unknown high boiling organic compounds.

The next step in the process was the removal of the solid NaCl from the "crude" TCP with an Oliver filter in a continuous filtration step. The "crude" TCP was pumped from the HCl neutralization tank through the Oliver filter to a 1000 gallon extractor feed tank. The solid NaCl collected on the Oliver filter which was back flushed with hot water to remove the salt. The resulting brine was then pumped to the brine settling tank. Brine collected in the settling tank was then pumped to the sewer. Periodically "crude" TCP was drained from the bottom of the brine settling tank and pumped to the extractor feed tank.

The next step in the process involved feeding the "crude" TCP in the extractor feed tank to a continuous counter current extraction column. In the extraction column, the "crude" TCP was contacted with hot water at approximately 70°C and at atmospheric pressure in order to remove the various glycols present as well as the remaining NaCl.

The resulting solution which came from the extraction column contained, by weight percent, 0.4% ethylene glycol, 0.6% diethylene glycol, 0.9% triethylene glycol, 0.6% dioxane, 3.7% water, 4.0% 2,5-dichlorophenol, 82.3% 2,4,5-trichlorophenol, and 7.0% unknown high boiling organic compounds. From the extraction column, the "crude" TCP was transfered to the "crude" TCP storage tank, a 2000 gallon tank.

Following the extraction step, to remove the various glycols from the "crude" TCP, the next step in the process was the purification of the "crude" TCP by fractional distillation under a vacuum. The "crude" TCP was pumped from the "crude" TCP storage tank to the batch TCP still, a closed jacketed heating vessel with an associated packed distillation column. In the TCP purification, a portion of the overhead after being condensed was recycled back to the batch TCP still as reflux. The remaining overhead was separated into three fractions or cuts. The cuts were the low boiling cut, the intermediate cut, and the main or product cut. The cuts were determined by the temperature of the overhead coming from the batch TCP still.

The first cut (the low boiling cut) contained, by weight percent, 3.2% ethylene glycol, 0.4% diethylene glycol, 0.8% dioxane, 0.9% water, 31.1% 2,5-dichlorophenol, 62.5% 2,4,5-trichlorophenol, and 1.0% unknown high boil organic compounds. The low boiling cut was routed to the low boiling cut storage tank, a 1000 gallon tank. From the low boiling cut storage tank, the low boiling cut was pumped to the extractor feed tank for use in the next production run.

The second cut (the intermediate) contained, by weight percent, 1.0% ethylene glycol, 9.3% dichlorophenol, 89.4% trichlorophenol, and 0.3% unknown high boiling organic compounds. This cut was routed to the intermediate cut storage tank, a 1000 gallon tank. From the intermediate cut storage tank, the intermediate cut was pumped to the batch TCP still for use in the next production run.

The third cut (main or product) contained, by weight percent, 0.2% diethylene glycol and 99.8% 2,4,5-trichlorophenol. This cut was taken at a temperature in the range of 160 to 180°C and under a vacuum in the range of 30 to 40 mmHg. The main cut was transfered to the main cut storage tank, a 1000 gallon tank. From the main cut storage tank, the main cut was pumped to the 1000 gallon TCP flaker storage tank.

Remaining in the TCP still after distillation were residues or "still bottoms." The "still bottoms" consisted of, by weight percent, 3.0% diethylene glycol, 9.0% triethylene, 0.9% water, 18.4% 2,4,5-trichlorophenol, and 68.7% unknown high boiling organic compounds. The "still bottoms" were drained from the bottom of the batch TCP still and pumped to the residue storage tank. The "still bottoms" were periodically drained from the storage tank into drums which were disposed of at waste sites. Table 4 lists the estimated amount of waste and TCDD disposed of for each year of operation.

The final step in the process was the flaking of 2,4,5-trichlorophenol. The main cut in the TCP flaker storage tank was high purity 2,4,5-trichlorophenol, in a molten liquid state. The high purity TCP in the TCP flaker storage tank was then transferred to a pan in the flaker. A water cooled nickel drum rotated through the molten TCP causing the TCP to solidify on the surface of the drum in a layer 2-4 mm thick. As the drum rotated, the TCP was scraped off the drum surface. The TCP flakes then fell into fiber drums, 32 gallon size containing 200 pounds TCP net.

The water from the extraction step was separated by continuous distillation from the glycols and recycled back to the extraction step. The remaining glycol rich steam was then sent to a batch vacuum recovery still where the ethylene glycol fraction was recovered and the high boiling fraction (water soluble polyglycols and NaCl) was sent to the sanitary sewer. The recovered ethylene glycol was then recycled back to the glycol feed tank available for the use in the production of the next batch of sodium ethylene glycolate.

Supplemental Information about the Operation at this Facility

Most of the 2,4,5-trichlorophenol produced was the high purity product used mainly as a raw material by others for hexachlorophene manufacture. Starting in 1962, however, small amounts of TCP were sold as a technical grade material. Estimates are that this amount was normally less than 5% of the total production. The company was unable to provide information indicating what quantity of this technical grade material was used for the manufacture of pesticide derivatives. Table 5 gives a list of TCP customers and indicates the customers most likely to have received technical grade material.

The production of technical grade TCP was essentially the same as the production of high purity TCP. The only difference was that for technical grade TCP two fractions or "cuts" were made instead of three in the batch fractional distillation step of the process. The two fractions or "cuts" made when technical grade TCP was being produced were the low boiling cut and the main or product cut. There was no intermediate cut taken when a technical grade batch of TCP was produced.

A company representative stated that one incident occurred in the 2,4,5-trichlorophenol process in August 1956. The representative declared that no records were found but that company discussions with various personnel associated with the process indicated that an extra charge of sodium hydroxide had been inadvertently added to a TCP reactor. (In 1956 a separate glycolate reactor did not exist). This addition of extra sodium hydroxide then caused a rapid build-up of pressure which the safety seal was not capable of venting. Damage to the roof of the buidling, as well as to near-by lines and equipment, resulted. The representative believes that little TCDD was released since the accident occurred before the main reaction between tetrachlorobenzene and sodium ethylene glycolate took place.

Environmental, Product, and By-Product Analyses for TCDD

Hooker has no documents related to the analysis of TCDD in ground water, surface water, ambient air, or any other environmental media at their Niagara facility.

Hooker, beginning in 1965, had the capability to analyze their products, process streams, and process wastes for TCDD. The analysis of TCDD was not a routine requirement for product sale. TCDD was analyzed by the company by gas liquid chromotography with flame ionization detection. A compilation of all TCDD analytical information which Hooker was able to provide is listed in Table 6. Table 6 lists the TCDD analyses in chronological order with a description of the kind of sample analyzed. The company states that the data presented used analytical procedures which would be unacceptable by today's standards. From Table 6, Table 7 was constructed and summarizes the TCDD analytical data according to the point in the TCP production process where samples were taken. These various points in the TCP production process can be found on Figure 2, the TCP flow diagram. High purity TCP can be found following the flaker; technical grade TCP can be found at stream number 34; "crude" TCP can be found at stream number 16; intermediate fraction can be found at stream number 33; the main (product) fraction can be found at stream number 35; and residue ("still bottoms") can be found at stream number 32.

Job Descriptions for Trichlorophenol Process

The TCP process operated for 3 eight hour shifts per day, seven days per week. On the first and second shifts there were two workers who ran the TCP production process, the TCP still operator and the TCP reactor operator. On the third shift there were three workers, the TCP still operator, the TCP reactor operator and the TCP glycolate-flaker operator. Table 8 lists the duties of these operators.

The TCP production process was a part of the Fine Chemical Department and was located in Building D-7. Repairmen were also assigned to the Fine Chemical Department and therefore routinely worked in the TCP production area (Building D-7). The job titles for the repairmen were Repairmen A, B, and C. Table 8 also lists the duties of the repairmen.

Based on the process description and the analytical data there are particular duties found in Table 8 which represented the greatest potential for exposure to TCDD to the TCP operators. The duties of collecting freeze point samples from the TCP batch still overhead, collecting final product samples, and draining the residue or "still bottoms" from the residue storage tank to drums represented the greatest potential for exposure to TCDD to the TCP Still Operator. The duties of collecting samples from the TCP reactor vessel and the testing of the pH in the HCl neutralization tank represented the greatest potential for exposure to TCDD to the TCP Reactor Operator. The duties of operating and cleaning the flaker and the packaging of the TCP product represented the greatest potential for exposure to TCDD for the TCP Glycolate-Flaker Operator.

Aside from the duties described in Table 8 for each of the job titles, all the workers who worked in Building D-7 had to follow a special set of procedures to work in this building. Table 9 gives a description of these procedures.

Conclusions

The trichlorophenol production workers and the repairmen assigned to the Fine Chemicals Department between 1949 and 1972 are suitable for inclusion in the NIOSH Dioxin Registry. Identification of all workers employed more than one year was obtained by using records collected for the recent company mortality study. Manual identification of workers employed less than one year was accomplished by use of force lists, bucket cards and microfilmed records.

Medical records are complete only for persons who terminated or retired after 1967, although some incomplete information exists describing examinations of individuals for chloracne between 1949 and 1967. Worker's Compensation records are contained in the medical files of each individual. The company does not retain copies in the medical office for more than seven years. It is not known whether the insurance carrier or the New York State Disability Office retained compensation records for Hooker employees.

The process for the production of 2,4,5-trichlorophenol had no changes in the basic method of production over the years of operation. The duties of the workers were clearly defined in documents obtained from the company. There is some limited analytical data on 2,3,7,8-tetrachlorodibenzo(p)dioxin analyses of product, process streams and wastes. Based on this information a worker exposure estimate for each job title is possible.

References

1. Rockette, Howard E. and Arena, Vincent C. Mortality Patterns of Workers in the Niagara Plant, June, 1983.

2. DiFraglia, David. Site Visit Report - Hooker Chemical Company, September 9, 1977.

3. Kushner, E.J. On Determinating the Statistical Parameters of Pollution Concentration From a Truncated Data Set. Atmospheric Environment Vol. 10, pp. 975-979.

Figure 1

"Bucket Card"
Occidental Chemical Company
Hooker Chemical Center
Niagara Falls, New York

OUT

NAME

ADDRESS						TEL. NO.	
DATE HIRED		SENIORITY DATE		S. S. NO.		SEX	
HEIGHT	WEIGHT	COLOR HAIR	COLOR EYES	MARITAL STATUS	DEPENDENTS CHILDREN OTHERS		
PHYSICAL DEFECTS					BIRTHPLACE		
BIRTH DATE AND PROOF				CITIZEN	WHEN AND WHERE NATURALIZED		
HMBA	ADD INS.	PENSION	HOSPITALIZATION	LOCKER NO	PARKING NO	UNION MEMBER	CLOCK NO.

POSITION AND RATE CHANGES

DEPARTMENT	WORK	REASON	RELEASED	YEAR	DATE	RATE
Research Mfg	Tetrachlorobenzene Oper			1950	11/3	1.40
					12/4	1.50
				1951	1/1	1.55
		Change in Hiring Rate			1/22	1.65
					1/29	1.70
					2/26	1.75
					3/26	1.78
		General Increase 4¢			9/3	1.82
	TTP Operator			1952	2/4	1.86
		General Increase 5¢			3/10	1.91
		General Increase 2¢			10/6	1.93
	Sulfene Operator				11/17	1.91
		Gen Inc 3¢ Retroactive to	10/6/52	1953	2/9	1.94
F-28	Sulfene Operator				6/1	1.94
		General Increase 5¢			8/3	1.99
		Job Evaluation		1954	3/1	2.00
		General Increase 4¢			8/2	2.05
		General Increase 10¢		1955	8/1	2.15
	DDM Still Operator				8/1	2.15
	DDM Burner Operator	Temp		1956	2/20	2.17
	DDM Burner Operator				6/18	2.17
		General Increase 12¢			10/1	2.29
		General Increase 14¢		1957	10/1	2.43
	DDM Reactor Operator				12/2	2.45
	DDM Still Operator			1958	4/21	2.41
	FBHC #3 Operator				8/4	2.39
		General Increase 9¢			10/1	2.48
	DDM Still Operator	Temp			12/29	2.50
Area #3	Shipping Laborer			1959	1/26	2.29
Research & Dev	Pilot Plant Oper C				2/18	2.50
	Pilot Plant Operator B				8/31	2.56
		General Increase 11¢			10/1	2.67
Fine Chem.	B T F Operator #1			1960	7/1	2.67
		General Increase 8¢			10/1	2.75
	TCP Flaker Operator	Hold Rate for 13 wks		1962	8/27	2.75
		General Increase 7¢			10/1	2.82
					11/26	2.68
	1 BTF Operator			1963	5/6	2.82
		General Increase 6¢			10/1	2.88

PL 104163 A
VISIforms Div.
SO. NORWALK, CONN.
HOOKER CHEMICALS & PLASTICS CORP. PERSONNEL RECORD NIAGARA FALLS, N. Y. 8 x 10 - 1 186

Figure 2

Flow Diagram for 2,4,5-Trichlorophenol Production
1949-1972

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

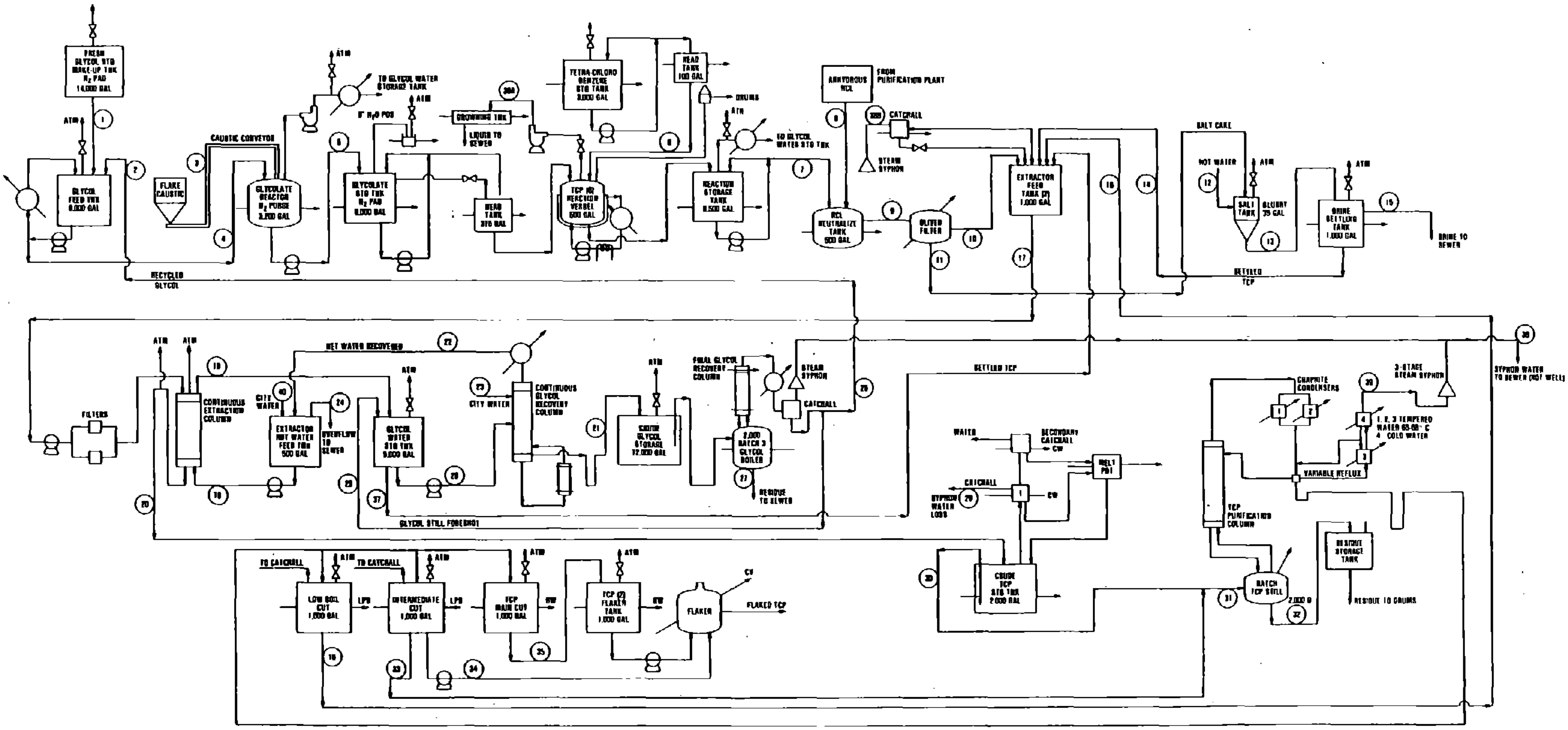


Figure 3

2,4,5-Trichlorophenol Production Process Material Balance
1949-1972

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

MATERIAL		Stream 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
ETHYLENE GLYCOL	1	14319	24300		38619	24659		24519		26841	25314	1521		1527		1527	81	25315	2094	27399
Na ETHYLENE GLYCOLATE	2					18915		3060												
DIETHYLENE GLYCOL	3		2277		2277	1641		8097		8256	7785	471		471		471	9	7794		7674
Na ETHYLENE GLYCOLATE	4					768		192												
TRIETHYLENE GLYCOL	5							675		675	636	39		39		39		636		456
DIOXANE	6							186		186	99	6		6		6	21	120		
UNKNOWN (LOW BOILING)	7							1062		1062										
H_2O	8	60	384		444	4605		4749		4749	4263	258	98882	99140		49940	24	4287	71431	74928
Na OH	9			9243																
NaCl	10							5643		13467	4350	9117		9117		9117		4350		4350
HCl	11								4881											
1,2,4,5-TETRACHLOROBENZENE	12						18900													
2,5-DICHLOROPHENOL	13																795	795		
2,4,5-TRICHLOROPHENOL	14									15310	14469	876		876	726	150	1596	17091	504	1314
Na 2,4,5-TRICHLOROPHENATE	15							17106												
UNKNOWN (HIGH BOILING)	16							2007		1611	1618	93		93		93	27	1545		150
TOTAL (LBS)	17	14319	26961	9243	41340	50583	18900	67356	4881	72237	58834	12387	98882	6269	126	60943	2553	62013	71037	86271

MATERIAL		Stream 20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38 A	38 B
ETHYLENE GLYCOL	1	90	31305	3099		1005	1005	24300		79404		90	117		27			9		15	
Na ETHYLENE GLYCOLATE	2																				
DIETHYLENE GLYCOL	3	120	8085				411	2277	5397	8095		120	120	60		24	27				
Na ETHYLENE GLYCOLATE	4																				
TRIETHYLENE GLYCOL	5	180	456						456	456		180	180	180							
DIOXANE	6	120										120	120					99		[illegible]	91
UNKNOWN (LOW BOILING)	7																			[illegible]	[illegible]
H_2O	8	798	5768	89349	14805	45456	5484	384		80112	708	90	90	18				48		[illegible]	[illegible]
Na OH	9																				
NaCl	10		4350						4350	4350											
HCl	11																				
1,2,4,5-TETRACHLOROBENZENE	12																				
2,5-DICHLOROPHENOL	13	795										795	1047		252						
2,4,5-TRICHLOROPHENOL	14	16281	300	714		210			300	1014	21	16260	18690	366	2430	498	13650	160	300		15
Na 2,4,5-TRICHLOROPHENATE	15																			18	
UNKNOWN (HIGH BOILING)	16	1395	150						150	150		1395	1404	1368	9						
TOTAL (LBS)	17	19119	50514	93162	14805	46611	12900	26961	10653	128871	729	19050	21768	1912	2118	522	13677	306	300	[illegible]	[illegible]

(1) Streams 36 and 39 were equal and therefore 39 was eliminated from the figure. Only TCP was measured in the "hot well" and it was assumed to come from the batch TCP still. Glycol losses undoubtedly occurred, but were not measured.

(2) In line 7 unknown low boiling, Dioxane losses were measured. Unidentified low boilers (greater than Dioxane) were on the gas chromotograph scans. The magnitude of these unknowns was adjusted in order to have agreement between the total and the sum of the individual measurements.

(3) In line 16 unknown high boiling, it was assumed that this unknown was a diphenol formed in the reaction step in the process by the use of excess caustic soda (NaOH) which may have removed more than one mole of chloride ion per mole of 1,2,4,5-tetrachlorobenzene. As shown in Table 9, the unknown also contained on the average 362 ppm TCDD. This is based on limited analytical data.

(4) Stream measurement 40 was eliminated. It was water, 27546 lb. per one day's operation.

Table 1

Raw Material Specification for Use in the Production of 2,4,5-Trichlorophenol*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

1. Material - <u>Tetrachlorobenzene - 1, 2, 4, 5 - Hooker</u>
   Description - White flakes
   Color - (Molten in a 1 inch test tube, ASTM colorimeter) 1 Maximum
   Clarity - (Insolubles in benzene) 0.05% maximum
   Melting point - 137.5°C Minimum

2. Material - <u>Ethylene Glycol - Carbide and Carbon Co</u>
   Sp Gr - 20/20°C 1.1151-1.1156
   Boiling range - °C at 760 mm 193-210
   Ave wt/gal - lb @ 20°C 9.28
   Max acidity as acetic acid - % by wt 0.01
   Max water content - % by wt 0.30
   Max color - P + Co scale 15

   Material - <u>Ethylene Glycol - Dow Chemical Co</u>
   Sp Gr - 25/25°C 1.112-1.115
   Boiling range - @ 760 mm Hg 5-95% 194-200°C
   Acidity as acetic acid - 0.01% maximum
   Inorganic chlorides as Cl^- - 0.001% maximum
   Water - 0.05% maximum
   Color (APHA) - 15 maximum

3. Material - <u>Sodium Hydroxide - Hooker</u>
   Sodium Oxide - 75.45%
   Sodium Hydroxide - 96.76%
   Sodium Carbonate - 0.70%
   Sodium Chloride - 2.05%
   Sodium Sulfate - 0.10%
   Sodium Chlorate - None
   Silicon - 0.03%
   Aluminum - 0.001%
   Calcium - 0.0015%
   Magnesium - 0.002%
   Iron - 0.0015%
   Manganese - 0.0005%
   Copper - 0.0002%
   Nickel - 0.00002%

* Table 1 was constructed from documents received from the company

Table 1

Raw Material Specification for Use in the Production of 2,4,5-Trichlorophenol*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

4. Material - <u>Anhydrous Hydrogen Chloride - Hooker</u>
   Hydrogen Chloride - 98.0% Min (By Vol)
   Chlorine - 0.02% Max (By Vol)
   Nitrogen and Hydrogen - 2.0% Max (By Vol)
   Water - 0.05% Max (By Vol) (Dew point of + 7°C)

5. Material - <u>Nitrogen - Linde Air Products Co</u>
   Commerical Nitrogen - 99.7% purity: Impurities consisted mainly of oxygen with traces of atmospheric rare gases.

Table 2

2,4,5-Trichlorophenol Production Process Changes*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

The changes listed below represent the best available information found for increasing the production rate. Essentially, more efficient utilization of the existing equipment plus a rigorous preventive maintenance program was in great part responsible for increasing the rate.

<u>1949 - Rate 50 tons/month</u>
Utilized 1 reactor   1 TCP still   1 glycol still

<u>1950-1955 - Rate 100 tons/month</u>
a) Added 2 reactors for a total of 3
b) Added 1 TCP still for a total of 2
c) Added 1 glycol still for a total of 2

<u>1964-1968 - Rate 150 tons/month</u>
a) Installed additional extractor feed storage capacity
b) Installed additional reactor storage capacity

<u>1968-1972 - Rate 200 tons/month</u>
a) Installed the sodium glycolate reactor
b) Added 3 reactors for a total of 6

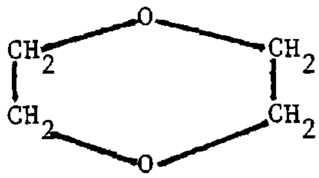
* Table 2 was constructed from documents received from the company

Table 3

Chemical Structures of By-Products Produced in the Production of 2,4,5-Trichlorophenol

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

1. Dioxane; 1,4-Diethylene dioxide ($C_4H_8O_2$)
   M.W. = 88.10



2. Diethylene Glycol; 2,2'-Oxybisethanol; 2,2'-Oxydiethanol ($C_4H_{10}O_3$)
   M.W. = 106.12

$HOCH_2CH_2OCH_2CH_2OH$

3. Triethylene Glycol; 2,2'-[1,2-Ethanediylbis(oxy)] - bisethanol; 2,2'-ethylenedioxybis(ethanol) ($C_6H_{14}O_4$)
   M.W. = 150.17

$CH_2OCH_2CH_2OH$
|
$CH_2OCH_2CH_2OH$

Table 4

The Amount of 2,4,5-Trichlorophenol Produced, the Estimated Amount of Residue Generated and the Estimated Amount of TCDD in the Residue*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

Year	Tons 2,4,5-TCP** Produced	Estimated Tons Residue	Estimated Pounds*** of TCDD in Residue
1949	348	87	35- 87
1950	552	138	55-138
1951	624	156	62-156
1952	432	108	43-108
1953	648	112	45-112
1954	540	135	54-135
1955	732	180	72-180
1956	1056	259	104-259
1957	396	97	39- 97
1958	504	116	46-116
1959	348	80	32- 80
1960	588	135	54-135
1961	600	138	55-138
1962	864	175	70-175
1963	924	139	56-139
1964	1548	164	66-164
1965	1752	193	77-193
1966	1632	180	72-180
1967	1512	166	66-166
1968	2045	219	88-219
1969	2216	260	104-260
1970	1893	208	83-208
1971	2388	209	84-209
1972	988	96	38- 96
Total	25,130	3750	1500-3750

Disposal Locations (total pounds of TCDD estimated)

Hyde Park	1302-3254	Love Canal	98-245
S-Area	98-244	Chem-Trol	3-7

* The columns, year, tons 2,4,5-TCP produced and estimated tons residue, were provided in documents from the company.

** Total production, high-purity and technical grade TCP

*** This column was generated by NIOSH. This column was based on very limited analytical data that TCDD content in the residue was estimated to be in the range from 200 to 500 ppm. The company points out that the analytical procedures used at the time of analysis would be totally unacceptable today for either a qualitative or quantitative determination of TCDD.

Table 5

2,4,5-Trichlorophenol Customers*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

Customer**	Address
Burgess Cellulose (T)	Freeport, Illinois
Magna Corporation (T)	Sante Fe Springs, California
Hamlet & Hayes (T)	Salem, Massachusetts
Sanford (T)	Elk Grove Village, Illinois
Economics Labs (T)	St. Paul, Minnesota
General Aniline (T)	New York, New York
Acid Products (T)	Chicago, Illinois
Betz Labs (T)	Philadelphia, Pennsylvania
Enjay (T)	Maspeth, New York
Givaudan Corp.	Clifton, New Jersey
Apex Chemical	Elizabeth, New Jersey
Uniroyal Ltd. (T)	Elmira, Ontario, Canada
Vinings Chemical Co.	Marietta, Ohio
Norwich Pharmaceutical	Norwich, Connecticut
B. C. Chemical Company	Barkersfield, California
Dow Chemical Company (T)	Midland, Michigan
Nash Chemical Company	Fort Lauderdale, Florida
Drew Chemical Corporation	Kearny, New Jersey
Pace National Chemical	Kirkland, Missouri
Park Davis & Company	Detroit, Michigan
Petrolite Corporation	Tulsa, Oklahoma
Textilana Corporation	Hathorne, California
Merck & Company, Inc.	Rahway, New Jersey
National Aniline (Allied)	Buffalo, New York
American Hoechst	New York, New York
International Corp. (T)	Chicago, Illinois

* Table 5 was constructed from documents provided by the company.

** Hooker was unable to determine precisely which firms purchased technical grade material. Those firms with a (T) are the ones most likely to have received such material.

Table 6

All Available Measurements for TCDD
in Products, Process Streams, and Residues*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

Date	Type of Sample Analyzed	TCDD (ppm)
4/13/65	"Crude" TCP	47
4/15/65	"Crude" TCP	40
4/15/65	"Crude" TCP, Run #136	20
4/15/65	"Crude" TCP, Run #151	13
4/15/65	"Crude" TCP, Run #166	< 1.0
4/15/65	Low, Low boil fraction, Run #151	< 1.0
4/15/65	Low boil fraction, Run #136	< 1.0
4/15/65	Low boil fraction, Run #151	< 1.0
4/15/65	Low boil fraction, Run #166	< 1.0
4/15/65	Low boil fraction, Run #?	< 1.0
4/15/65	Main or Product Fraction, Run #136	< 1.0
4/15/65	Main or Product Fraction, Run #151	< 1.0
4/15/65	Main or Product Fraction, Run #166	< 1.0
4/15/65	Main or Product Fraction, Run #?	< 1.0
5/06/65	Technique Grade TCP, Lot #1	< 1.0
5/06/65	Technique Grade TCP, Lot #2	< 1.0
5/06/65	Technique Grade TCP, Lot #10	< 1.0
5/06/65	Technique Grade TCP, Lot #11	< 1.0
5/06/65	Technique Grade TCP, Lot #16	< 1.0
5/06/65	Technique Grade TCP, Lot #19	< 1.0
5/06/65	Technique Grade TCP, Lot #22	< 1.0
5/06/65	Technique Grade TCP, Lot #26	< 1.0
5/06/65	Technique Grade TCP, Lot #47	< 1.0
5/06/65	Main or Product Fraction	< 1.0
5/06/65	Low Boil Fraction	< 1.0
5/06/65	Intermediate Fraction	< 1.0
5/06/65	High Purity TCP, Lot #123	< 1.0
5/06/65	High Purity TCP, Lot #124	< 1.0
5/06/65	High Purity TCP, Lot #56	< 1.0
5/06/65	High Purity TCP, Lot #47	< 1.0
5/06/65	High Purity TCP, Lot #45	< 1.0
6/09/65	High Purity TCP, Cut #2	< 1.0
6/09/65	Low Boil Fraction, Run #136	< 1.0
6/09/65	Intermediate Boil Fraction, Run #136	< 1.0
6/09/65	Main or Product Fraction, Run #136	< 1.0
6/09/65	"Crude" TCP charged to #2 Still	20
6/09/65	"Crude" TCP charged to #2 Still, Run #151	13
6/09/65	Low Boil Fraction, Run #151	< 1.0
6/09/65	Intermediate Boil Fraction, Run #151	< 1.0
6/09/65	Low Boil Fraction #2 Still, Run #151	< 1.0
6/09/65	Main or Product Fraction #2 Still	< 1.0

Table 6

All Available Measurements for TCDD
in Products, Process Streams, and Residues*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

Date	Type of Sample Analyzed	TCDD (ppm)
6/31/65	TCP Still Bottoms or Residue	494
6/31/65	"Crude" TCP, Run #166	< 1.0
6/31/65	Low Boil Fraction, Run #166	< 1.0
6/31/65	Intermediate Boil Fraction, Run #166	< 1.0
6/31/65	Main Fraction, Run #166	< 1.0
2/16/70	High Purity TCP, Lot #50	< 1.0
1/14/70	High Purity TCP, Lot #8	< 1.0
2/06/70	High Purity TCP, Lot #38	< 1.0
2/21/70	High Purity TCP, Lot #58	< 1.0
1/17/70	High Purity TCP, Lot #14	< 1.0
1/22/70	High Purity TCP, Lot #20	< 0.2
3/02/70	High Purity TCP, Lot #65	< 0.2
1/07/70	High Purity TCP, Lot #4	< 0.2
3/09/70	High Purity TCP, Composite of lots #42, 25, 30, 19, 36	< 1.0
3/09/70	High Purity TCP, Composite of lots 61, 64, 26, 37, 21	< 1.0
3/09/70	High Purity TCP, Composite of lots 50, 8, 38, 58, 14	< 1.0
3/18/70	Extractor Feed Water	< 0.01
3/18/70	Extractor Feed (TCP from Oliver Filter)	3.0
3/18/70	Crude Glycol from Batch Glycol Boiler	< 0.01
3/19/70	Crude TCP charged to Still	12.0
3/18/70	Oliver Filter Salt	< 0.04
3/14/70	Oliver Filter Salt	< 0.04
3/30/70	Technical Grade TCP, Lot #3	< 0.05
3/25/70	TCP Still Residue	230
3/25/70	Glycol Still Residue	< 0.03
3/25/70	Crude Glycol from Extractor Column	< 1.0
3/25/70	Reactor Discharge Tank	< 0.10
3/25/70	Low Boil Fraction	< 0.03
3/25/70	Intermediate Boil Fraction	< 0.03
2/04/72	Technical Grade TCP, Composite of Lots #7, 9, 11	< 0.09
2/04/72	Technical Grade TCP, Composite of Lots #10, 12	< 0.08
2/04/72	Technical Grade TCP, Composite of Lot #8	< 0.03
2/04/72	Technical Grade TCP, Composite of Lot #13	< 0.05
2/04/72	Technical Grade TCP, Composite of Lot #14	< 0.05
4/12-4/15/71	High Purity TCP, Composite of Lots #110-118	0.008 (L.O.D. 0.008)**
4/19-4/23/71	High Purity TCP, Composite of Lots #119-127	0.032 (L.O.D. 0.016)**

Table 6

All Available Measurements for TCDD in Products, Process Streams, and Residues*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

Date	Type of Sample Analyzed	TCDD (ppm)
4/24-5/2/71	High Purity TCP, Composite of Lots #128-139	< 0.016
5/3-5/7/71	High Purity TCP, Composite of Lots #140-146	0.012 (L.O.D. 0.012)**
5/10-5/14/71	High Purity TCP, Composite of Lots #147-155	< 0.009
5/17-5/21/71	High Purity TCP, Composite of Lots #156-164	< 0.011
5/24-5/28/71	High Purity TCP, Composite of Lots #165-174	< 0.010
6/1-6/4/71	High Purity TCP, Composite of Lots #175-183	< 0.011
6/4-6/11/71	High Purity TCP, Composite of Lots #184-193	< 0.022
6/14-6/18/71	High Purity TCP, Composite of Lots #194-202	< 0.010
6/21-6/25/71	High Purity TCP, Composite of Lots #203-210	< 0.011
6/28-7/5/71	High Purity TCP, Composite of Lots #211-222	< 0.022
7/7-7/9/71	High Purity TCP, Composite of Lots #223-226	0.022 (L.O.D. 0.022)**
7/9-7/15/71	High Purity TCP, Composite of Lots #227-236	< 0.017

* Table 8 was constructed from documents provided by the company

** L.O.D. = limit of detection

Table 7

Summary of TCDD Measurements in Products, Process Streams, and Residues*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

TCDD found in Chemical Compound	Dates	# of Sample	# of Non-detectable Measurements	Range (ppm)
High Purity TCP	5/6/65 - 3/9/70	18	18	< 0.2 - 1.0
High Purity TCP	4/12/71 - 7/15/71	14	10	< 0.009 - 0.032
Technical Grade TCP	5/6/65 - 2/4/72	15	15	< 0.03 - 1.0
"Crude" TCP	4/13/65 - 3/19/70	9	2	< 1.0 - 47
Low Boiling Fraction	4/15/65 - 3/25/70	11	11	< 0.03 - 1.0
Intermediate Fraction	4/15/65 - 3/25/70	9	9	< 0.03 - 1.0
Main (Product) Fraction	4/15/65 - 6/31/65	8	8	< 1.0
Residue ("still bottoms")	6/31/65 - 3/25/70	2	2	230 - 494

* Table 7 was constructed from documents provided by the company

Table 8

Job Descriptions of Workers Involved in 2,4,5-Trichlorophenol Process**

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

A. The Duties of the TCP Still Operator
   1) Coordinated and acted as trouble-shooter for the complete process.
   2) Assisted TCP glycolate-flaker operator when necessary.
   3) Brought fresh ethylene glycol from tank farm to TCP process.
   4) Separated crude TCP from glycols.
   5) Vacuum distilled crude TCP, which included taking freeze point samples to determine when the various "cuts" or fractions were to be made.
   6) Operated Dowtherm boilers.
   7) Tested main or product cut and transferred it to the flaker tank.
   8) Discharged TCP batch still residue and drum the residue.
   9) Operated the continuous crude glycol still.
   10) Operated batch crude glycol stills.
   11) Occasionally assisted glycolate preparations, and flaking operations.
   12) Made minor repairs.
   13) Kept area clean inside and outside Building D-7.
   14) Checked extraction of crude TCP to assure minimum product loss.
   15) Checked glycol still operation to assure minimum ethylene glycol loss and recovered dry ethylene glycol.
   16) Checked final still operation to assure maximum yields, good quality, to prevent freeze-ups and possible decomposition.
   17) Cleaned out equipment.

B. The Duties of the TCP Reactor Operator
   1) Operated the TCP reactors.
   2) Charged the reactor with one or more of the following compounds: sodium glycolate; 1,2,4,5-tetrachlorobenzene (molten or flake); flaked caustic soda; ethylene glycol.
   3) Heated reactor to proper temperatures and maintained desired pressure.
   4) Tested reactor product, streams if necessary, and discharged when 1,2,4,5-tetrachlorobenzene content was low.
   5) Neutralized product to the desired pH and tested it frequently.
   6) Operated Oliver filter to remove salt from the neutralized TCP.
   7) Operated salt slurry system to recover crude TCP.
   8) Charged recovered TCP to melt tank as needed.
   9) Assisted the TCP still operator and the TCP glycolate-flaker operator as needed.
   10) Made minor repairs to keep operation running smoothly.
   11) Kept area clean inside and outside Building D-7.
   12) Unplugged pipes, opened vessels, steamed lines, cleaned the Oliver filter as necessary.
   13) Checked the neutralized TCP with pH paper.
   14) Cleaned out equipment.

Table 8

Job Descriptions of Workers Involved in 2,4,5-Trichlorophenol Process**

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

C. The Duties of the TCP Glycolate-Flaker Operator
   1) Charged ethylene glycol and flake caustic soda to make up sodium ethylene glycolate solution for the TCP reactors.
   2) Operated flakers to flake out TCP and 1,2,4,5-tetrachlorobenzene.
   3) Assisted other operators where needed on other phases of the process.
   4) Cleaned all equipment routinely.
   5) Performed minor repairs on equipment.
   6) Painted equipment.
   7) Kept area clean inside and outside of Building D-7.
   8) Charged recovered TCP to melt tank.
   9) Analyzed each batch of sodium ethylene glycolate to assure good process control.
   10) Was responsible for accurate weighing and labeling of materials flaked.

D. The Duties of Repairmen A, B*, and C*
   1) Under general supervision they made necessary repairs to all types of piping systems and operating equipment throughout the Fine Chemical Department.
   2) Sometimes installed new equipment and facilities.
   3) Planned and directed the work of B and C Repairmen (Repairman A only).
   4) Instructed men and did rigging as required.
   5) Sometimes entered vessels to make repairs or to clean vessels.
   6) Performed temporary rough insulation as required.
   7) Worked on glass-lined vessels.
   8) Used chain hoists, power-driven threader, and similar equipment.

* Repairmen B and C are more junior levels than Repairman A. Repairman C never worked alone.

** Table 8 was constructed from documents received from the company.

Table 9

Company Recommended
Procedures for Work in Building D-7 (TCP)
(TCP Production)*

Occidental Chemical Corporation
Hooker Chemical Center
Niagara Falls, New York

Anyone about to work in Building D-7 for the first time would be have sent to the Plant Hospital for a skin check and to receive protective cream, cleansing solution, basic soap and instructions. The initial visit to the Plant Hospital would have been sufficient for maintenance men, unless there was a need for more protective cream, cleaning solution or basic soap.

People who worked regularly on the TCP process (Building D-7) would have had a monthly skin check at the Plant Hospital.

Coveralls were to be worn and changed at least every other day. If clothing was contaminated by an unusual concentration of fumes or any liquid or phenol compounds were spilled on clothing, the clothes were removed as quickly as possible and skin was washed thoroughly on an every other day basis.

For hand protection, "Grabbit" gloves were to be used; however, if there was a liquid hazard, approved rubber gloves were to be worn.

Anyone working over 4 hours, or on a particularly dirty job was to take a shower at the end of the work day. This being an important procedure, an extra 15 minutes was allowed to insure adequate use of cleansing solution on face and a thorough shower.

Work Permit would specify the following requirements:

1. Visit the plant hospital
2. Coveralls
3. Rubber Gloves
4. Early Shower

* Table 9 was constructed from documents provided by the company