NIOSH Dioxin Registry Site Visit Report
of
Givaudan Corporation
Clifton, New Jersey

Site Visit Dates
June 20, 1983, June 11, 1984,
August 25, 1986, and September 8, 1986

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DISCLAIMER

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ABSTRACT

The National Institute for Occupational Safety and Health (NIOSH) Dioxin Registry is a compilation of demographic and work history information for all U.S. production workers who have synthesized products known to be contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) 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 mortality study for which the comparison group is the U.S. male population. This study will evaluate the causes of death among workers exposed to products contaminated with 2,3,7,8-TCDD and/or HxCDD.

The Givaudan Corporation facility in Clifton, New Jersey, is included in the Dioxin Registry. Givaudan produced hexachlorophene (HCP) from 2,4,5,-trichlorophenol (2,4,5-TCP) at this site from 1945 to 1984. For the first four years of HCP production, Givaudan also produced their own 2,4,5-TCP feedstock. Presented in this report is a description of the facility, processes and the workforce taken from company documents, site visits, personnel records, and correspondence related to the site.

INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH), Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS), Industrywide Studies Branch (IWSB), is conducting an investigation of health effects resulting from occupational exposure to polychlorinated dibenzo-p-dioxins (PCDD) and in particular the 2,3,7,8-tetrachlorodibenzo-p-dioxin isomer (2,3,7,8-TCDD). The NIOSH Dioxin Registry is a compilation of demographic and work history information for all U.S. production workers who have synthesized products known to have been contaminated with 2,3,7,8-TCDD or hexachlorodibenzo-p-dioxins (HxCDD).

The Registry, initiated in 1979, was prompted by animal studies showing 2,3,7,8-TCDD to be acutely toxic and a chloracnegen, as well as a carcinogen and teratogen.[1-7] 2,3,7,8-TCDD is a contaminant found in 2,4,5-trichlorophenol (2,4,5-TCP) and/or its sodium salt, which are raw materials used to produce chemical compounds such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,2'-methylene-bis (3,4,6-trichlorophenol) hexachlorophene (HCP). Currently, there are 14 production facilities and approximately 7000 workers included in the Registry. The first use of this information is a mortality study for which the comparison group is the U.S. male population. This study will evaluate the causes of death among workers exposed to products contaminated with 2,3,7,8-TCDD and/or HxCDD.

The Givaudan Corporation has a plant in Clifton, New Jersey which produced 2,4,5-trichlorophenol from 1945 to 1949 and hexachlorophene from 1945 to 1984. Presented is a compilation of information and data from documents received from the Givaudan Corporation and from site visits conducted June 20, 1983, June 11, 1984, August 25, 1986, and September 8, 1986.

BACKGROUND

The Givaudan Corporation has operated the Clifton facility since 1924, producing flavors, fragrances, aroma chemicals, and other organic chemicals as additives for fragrances used in soaps, cosmetics, and other consumer products. Production of chemicals of interest to the NIOSH Dioxin Registry began in 1945 with the start of the 2,4,5-TCP and HCP processes. 2,4,5-TCP was produced until 1949 for use as a feedstock for the HCP process. After 1949, the 2,4,5-TCP process was shut down and purified (distilled) 2,4,5-TCP was purchased from the suppliers in Table 1. Hexachlorophene or G-11® as it was known commercially was produced until May 1984. Except for the change from on-site processing of 2,4,5-TCP to purchasing purified 2,4,5-TCP from suppliers, Givaudan made no major changes in the HCP production process. The HCP process line was dedicated solely to the production of HCP. No major accidents involving 2,4,5-TCP or HCP production occurred during their years of operation.

A layout of the plant is shown in Figure 1. HCP was produced in Buildings 58, 59, and 60, was ground in Building 47 and then packaged in Building 75. The short-lived 2,4,5-TCP process operated in Building 54. Storage of 2,4,5-TCP was in Building 52.

PROCESS DESCRIPTIONS

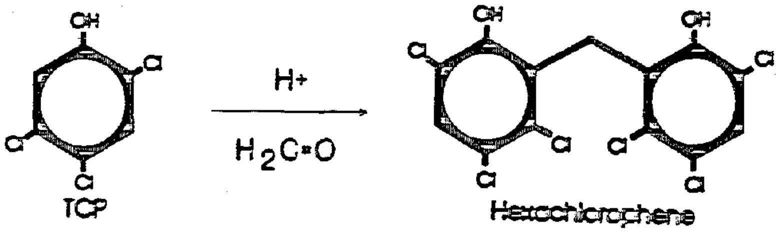
2,4,5-Trichlorophenol Process

There are insufficient records to reconstruct detailed process information for 2,4,5-TCP manufactured by the Givaudan Corporation from 1945-1949. Givaudan believes that 2,4,5-TCP was produced by the alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene with caustic soda dissolved in ethylene glycol. After the reaction was complete, the batch was neutralized with muriatic acid and the sodium chloride precipitate was removed by filtration. The filtrate was diluted with water and the 2,4,5-TCP extracted with benzene. The benzene extract was washed with water and then removed by distillation. The crude 2,4,5-TCP was distilled in a high vacuum still. Ethylene glycol was recovered by fractionation and reused in the process. After 1949 purified 2,4,5-TCP was purchased from outside suppliers, mainly from Hooker Chemical Company and Dow Chemical, U.S.A, (Table 1).

Hexachlorophene Process

Givaudan produced HCP by the condensation of purified 2,4,5-TCP and paraformaldehyde in the presence of a sulphuric acid catalyst. The HCP process was operated by six operators a shift. A typical batch used 1,500 pounds (lbs) of 2,4,5-TCP to produce 1,500 lbs. of HCP. HCP production for the years 1947 to 1984 ranged between 17,000 to 3,500,000 pounds per year. Figure 2 shows a process flow diagram for the synthesis, purification, and finishing of HCP. No significant changes were made to the process during the 39 years it was operated.

In the first step of the process, ethylene dichloride (ED) and oleum (sulfuric acid + sulfite) were charged into a glass lined reactor. Pure 2,4,5-TCP was then brought from a melt tank and added to the reactor. The reactor was heated, and paraformaldehyde was gradually added. The condensation of 2,4,5-TCP and paraformaldehyde in the presence of oleum resulted in the formation of HCP:



The finished batch in the reactor was then pumped to the First Settler, where it was refluxed and allowed to settle. The spent sulfuric acid layer was drained away and the HCP and ethylene dichloride were pumped into a treatment tank. The treatment tank was then charged with Filtrol® (bentonite clay and aluminum silicate) or other filter aids and refluxed to decolorize and to remove water. The batch was filtered through a sparkler filter and recycled back to the treatment tank where it was further refluxed until it was decolorized. When the batch was clear it was pumped through the filter into a solution storage tank. The batch was then fed into the steam still where ED and TCP were stripped off. Once the HCP was cooled it was fed into a filter press and formed into a cake. The HCP wet cake was dropped on a conveyor belt and transferred to a rotary vacuum drier.

The dried HCP was unloaded into powder carts and transferred to the grinding area where it was loaded into a hopper and fed into a micropulse grinder. The ground HCP was then packaged into 110 lb. fiber drums. The packaging and grinding operations were equipped with local exhaust ventilation.

The ED used during the process was recycled while the sulfuric acid and filtrol were waste products. ED was recovered from the spent acid layer in the acid still and also later in the process from the steam still. The distilled ED was pumped to a storage tank and subsequently recycled to the reactor. The solvent free spent acid was either pumped to the sewer or to a storage tank for reprocessing. Spent filtering agents were collected on the sparkler filter, washed with ED and vacuumed dried. The filter cartridge was removed and the filter cake shoveled into containers for disposal.

DESCRIPTION OF EXPOSURE TO 2,3,7,8-TCDD

Workers employed between 1945 and 1949 had a potential for exposure to 2,3,7,8-TCDD that was generated during the 2,4,5-TCP process. There is insufficient process information to comment on the potential degree of 2,3,7,8-TCDD contamination of the 2,4,5-TCP. The process was reported to have a distillation step, which would have removed some or essentially all of the 2,3,7,8-TCDD. The amount of 2,3,7,8-TCDD contamination of the 2,4,5-TCP that would be carried through the subsequent production of HCP would depend on process operating conditions and the degree of purification that took place in the 2,4,5-TCP process. It is unlikely that any 2,3,7,8-TCDD was formed during the production of HCP due to the process operating conditions.[1] After 1949, with the closure of the on-site 2,4,5-TCP process, exposure to 2,3,7,8-TCDD would have been limited to the amount of 2,3,7,8-TCDD contamination in 2,4,5-TCP Givaudan purchased from outside suppliers. In addition, there was potential residual 2,3,7,8-TCDD contamination in the area where the 2,4,5,-TCP process had been operated(Building 54).

2,3,7,8-TCDD Concentrations in 2,4,5-TCP

Limited analytical information on the amount of 2,3,7,8-TCDD contamination of the 2,4,5-TCP feedstock used for HCP production is available. Table 2 reports 2,3,7,8-TCDD levels that were compiled from documents supplied by Givaudan.

The Hooker Chemical Corporation supplied 2,4,5-TCP to Givaudan for 22 years between 1949 - 1971. Gas chromatography analysis results of October 27, 1970 report 3 samples of 2,4,5-TCP supplied to Givaudan were below the lower limit of detection (LOD) of 0.05 parts per million (ppm). Analysis results of March 12, 1971 report two samples below the LOD of 0.10 ppm and two additional samples below the LOD of 1.0 ppm. In the analysis of the latter two samples, the sensitivity was limited due to an interfering peak.

As a result of the 1976 accident at the ICMESA plant at Seveso, Italy which released 2,3,7,8-TCDD, the Environmental Protection Agency (EPA) required Givaudan to collect and analyze samples of 2,4,5-TCP shipments from ICMESA. The samples were collected to determine if possible process problems might have occurred before the accident that would have resulted in 2,3,7,8-TCDD contamination of the 2,4,5-TCP. A sample from each of three shipments of 2,4,5-TCP that were received from ICMESA prior to the accident were collected. EPA and Givaudan split the samples and had them analyzed. The EPA contract laboratories and Givaudan found the same results on two of the three samples, the results were less than/equal to 2 parts per billion (ppb) 2,3,7,8-TCDD. For the third sample, Givaudan reported 14 ppb while the EPA contract lab. reported the sample as non-detectable at a 2 ppb limit of detection.

The DOW Chemical Company supplied 2,4,5-TCP to Givaudan from 1976 to 1978. Certificates of analysis for 44 lots of 2,4,5-TCP reported levels of 2,3,7,8-TCDD below the 0.01 parts per million (ppm) limit of detection. In August of 1978 Celamerck began suppling 2,4,5-TCP to Givaudan. Celamerck provided Certificates of Analysis for 64 lots of 2,4,5-TCP, purchased between August, 1978 to March, 1983. The certificates reported less than 10 ppb of 2,3,7,8-TCDD for 58 of the lots. The remaining 6 lots, analyzed with a lower limit of detection, contained less than 5 ppb of 2,3,7,8-TCDD.

Givaudan had 2,4,5-TCP samples analyzed for 2,3,7,8-TCDD by California Analytical Laboratories. These results are reported in Table 3 and are also included in Table 2.

2,3,7,8-TCDD in Concentrations in Hexachlorophene

Results of analyses for 2,3,7,8-TCDD in Givaudan's hexachlorophene are reported in Table 4. The reported results were compiled from documents supplied by Givaudan.

Givaudan felt it was unlikely that 2,3,7,8-TCDD was formed during the production of HCP. Together with Hooker Chemical Corporation, Givaudan's supplier of 2,4,5-TCP (1949 - 1971), a study was conducted to investigate whether 2,3,7,8-TCDD was a possible contaminant of the HCP produced by Givaudan. The study was detailed in a Givaudan Corporation document dated August 5, 1970, entitled "Investigations concerning the possible presence of 2,3,7,8-tetrachlorodibenzo-p-dioxin in Givaudan's Hexachlorophene." Sample collection, extraction, and analysis procedures from the aforementioned report are contained in Figure 3.

Givaudan collected 6 samples, each being a bulk from 2 to 4 lots, of HCP manufactured during the second half of 1969 and 5 samples of HCP from single, random lots produced in 1970. The samples were extracted with benzene and sent to Hooker Chemical Corporation for analysis. No detectable levels of 2,3,7,8-TCDD were found in the 11 samples, the limit of detection ranged from 0.01 to 0.03 ppm. Hooker Chemical Corporation analyzed an additional HCP sample on March 12, 1971. The sample was non-detectable, with a lower limit of detection of 0.1 ppm. Givaudan began monthly sampling of random lots of HCP for 2,3,7,8-TCDD in January, 1976. Starting in mid-November, 1976, analysis was conducted on a bulked 10 gram sample of 5 grams from each of two consecutive, HCP lots that had been determined acceptable by quality control. The samples were extracted with hexane,(see Figure 4) concentrated by evaporation and sent to California Analytical Laboratories for 2,3,7,8-TCDD analysis by gas chromatography-mass spectroscopy (GC-MS). A total of 212 samples of HCP manufactured between January, 1976 and July, 1977 were analyzed. Ninety percent of the HCP sample results contained less than 1.0 ppb 2,3,7,8-TCDD. The detectable samples (n=17) ranged from 1.5 to 4.0 ppb with an arithmetic mean of 2.4 ppb. Givaudan reported in an inter-office memo dated June 22, 1983, that the higher 2,3,7,8-TCDD levels were attributed to interferences in the GC-MS analysis which probably could have been eliminated through reanalysis or additional sample clean-up. However, since the 2,3,7,8-TCDD limit at that time was established at 10 ppb, these samples were not reevaluated. The same 1983 memo reported that all samples (number of samples was not reported) evaluated after 1978 were found to contain less than 1.0 ppb.

2,3,7,8-TCDD Concentrations in Process By-Products

A sample of the sanitary sewer discharge from the Clifton facility was collected in October, November and December of 1982 and analyzed for 2,3,7,8-TCDD by Atlantic Ecology Lab., Lakewood, New Jersey. All three samples were below the 10 ppb limit of detection. Eight samples of process by-products were collected in May, 1983. The samples were analyzed for 2,3,7,8-TCDD by California Analytical Laboratories, Inc. and are reported in Table 5. Seven of the samples were non-detectable, the lower limit of detection ranged from 0.1 to 1.0 ppb. For the 8th sample, 150 nanograms per bottle was reported, however, no sample volume or concentration was given.

Three HCP process samples from Givaudan were analyzed by the EPA as part of an analytical methods development study of process wastes and related materials from plants with potential chlorinated dioxin contamination (Table 6).[1] No TCDD in excess of the minimum detectable concentrations which ranged between 50-140 ppt was found in the Givaudan samples.

2,3,7,8-TCDD Concentrations in Environmental Samples

Limited industrial hygiene data was collected that evaluated worker exposure to 2,3,7,8-TCDD. The Occupational Safety and Health Administration conducted an inspection at the Clifton plant during the period April 8, 1981, through May 14, 1981. Airborne samples were collected in all HCP areas, in Buildings

47, 58, 59, 60, and 75. The sampling was conducted with fritted glass bubblers containing xylene at flow rates between 65 and 105 cubic centimeters per minute. Seven samples were analyzed by gas chromatography with selected ion monitoring mass spectroscopy. All of the samples were below the lowest limit of detection which ranged from 1.3 to 5.2 micrograms per cubic meter.

In advance of planned soil sampling by the New Jersey Department of Environmental Protection (NJDEP) at eleven plant sites, Givaudan collected soil samples in the vicinity of the main HCP production building on approximately June 14, 1983. Results from 12 samples showed concentrations ranging from 0.94 to 11 ppb. Givaudan notified the New Jersey Department of Environmental Protection, who ordered a shut down of the entire plant including the HCP process and restricted access to the area on June 18, 1983. An environmental consulting firm contracted by Givaudan collected dust and wipe samples on July 9, 1983 under the direction of the New Jersey Department of Environmental Protection to assess the amount of 2,3,7,8-TCDD contamination present at the Givaudan facility. Wipe samples were collected with three inch sterile gauze pads saturated with laboratory grade hexane. A two foot square area in each building was wiped twice using 2 gauze pads which were then deposited into a clean glass jar. An aluminum cap was placed over the jar prior to sealing. Dust samples were collected with new natural bristle brushes. A minimum of ten grams of dust per sample was collected and placed into a new, clean glass jar, sealed with aluminum foil and capped. A new brush was used for each building. The samples were analyzed by California Analytical Laboratory. The results of the samples collected on July 9, and on additional days are reported in Table 7. The highest sample results of 6.5 nanograms 2,3,7,8-TCDD per square foot for the wipe sample and 22 parts per billion 2,3,7,8-TCDD for the dust sample were from Building 54, which had housed 2,4,5-TCP production from 1945 - 1949. The contaminated areas were solvent washed with xylol, washed again with detergent and then rinsed with water. After additional samples showed 2,3,7,8-TCDD contamination to be minimal (Table 7), the HCP process resumed operation on August 18, 1983. Operation was allowed to resume on the condition that Givaudan implement their industrial hygiene plan, (Figure 5) that had been reviewed and supplemented by the New Jersey Department of Environmental Protection (Figure 6).

DESCRIPTION OF THE RECORDS

Personnel Records

A review of personnel records maintained by the company established that they contained insufficient details to identify all of the hexachlorophene production workers. Therefore, payroll registers from 1957 to 1983, which permitted the identification of workers assigned to the hexachlorophene department were used. Company cost accounting numbers on these registers after June 1, 1957 identify the department where each individual worked. Workers employed in the hexachlorophene department after June 1, 1957 were identified from payroll records by locating the appropriate department specific, cost accounting numbers (Table 8). Workers were identified from quarterly payroll records (March, June, September and December) from June 1957 to December 1978. After that period, a computerized listing obtained from the Safety Office identified all workers who made hexachlorophene between June 1978 and May 1984, when production was terminated.

Personnel files were microfilmed for about 170 individuals identified on the payroll sheets or the computerized listing as having worked in Hexachlorophene production after June 1, 1957. From the personnel files, the employment application, summary work history cards and death notices were microfilmed. These items contained all needed demographic information as well as the job titles held by the individuals.

It was not possible to identify the maintenance workers who serviced the TCP or HCP processes. At Givaudan, maintenance workers serviced all processes in the plant and no records were retained of specific assignments to the hexachlorophene department. In addition, salaried workers could not be identified except for (four) foremen who supervised the hexachlorophene department after June 1, 1957.

It is important to note that workers employed in the hexachlorophene process from 1945 to May 31, 1957 could not be identified from the company records. Chemical operators for all of the many chemical processes at the company were listed in the personnel files only as "Production Department" employees, and the use of department specific cost accounting numbers did not begin until June, 1957. For workers still employed after June 1, 1957, it can be determined from their dates of hire whether or not they worked at Givaudan during that period, but whether they worked in the hexachlorophene process cannot be ascertained. Therefore, the length of time employed in hexachlorophene production may be underestimated for these workers. In addition it was not possible to identify workers employed between 1945 and 1949 when the company made its own 2,4,5-TCP as feedstock for the hexachlorophene process.

Medical Records

After the cohort was identified, medical and worker compensation records were microfilmed for all individuals. The Medical Department has been operated by a full-time Plant Nurse since approximately 1953. The nurse recorded notes for all visits to the health office on medical cards. Currently, a physician spends 1-2 hours each morning at the facility. Physical examinations have been offered since about 1978.

Medical and worker compensation records were microfilmed from the personnel files of some workers and from the medical files for others. Company representatives stated that chloracne was not a major problem at this plant. A letter from Givaudan's dermatologic consultant on July 2, 1970, to Givaudan, reported no cases of chloracne between 1960-1970 among the Givaudan employees referred for dermatologic evaluation.

CONCLUSION

Workers who were employed in the hexachlorophene department between 1957 and 1984 can be identified and are appropriate for inclusion in the NIOSH Dioxin Registry. Prior work in the hexachlorophene department for these individuals cannot be identified. It was not possible to identify hexachlorophene workers employed between 1945 and 1956, workers employed in 2,4,5-TCP production from 1945 to 1949 or the maintenance workers that had serviced the HCP and 2,4,5-TCP processes during their years of operation.

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Table 1
Source of Supply of 2,4,5-Trichlorophenol
Givaudan Corporation
Clifton, New Jersey

Year(s)	Supplier
1946-1949	Givaudan Corporation
1949-1971	Hooker Chemical
1971-1975	None purchased - inventories used
1975-1976	ICMESA
1976-1978	The Dow Chemical Company
1978-1983	Celamerck, GmbH & Company
1982	Linz/A.G.

Source: Givaudan Corporation

Table 2

Analysis of 2,4,5-TCP Feedstock for 2,3,7,8-TCDD
Givaudan Corporation
Clifton, New Jersey

Source of 2,4,5-TCP	Source and Date of Analysis Report		2,3,7,8-TCDD Analysis Results*
Givaudan (1947-1949)	No samples analyzed		No samples analyzed
Hooker Chemical Corp. (1949-1976)	Hooker Chem. Corp.	10-27-70 03-12-71	3 samples <0.05 ppm 2 samples <0.10 ppm 2 samples <1.0 ppm
ICMESA (Italy) (1975-1976)	EPA	11-26-76	Sample 1, 1.9 ppb (EPA) 2.0 ppb (Givaudan) Sample 2, 1.8 ppb (EPA) 2.0 ppb (Givaudan) Sample 3, <2.0 ppb (EPA) 14 ppb (Givaudan)
Dow (1976-1978)	Dow	10-76 to 12-78	44 samples, <10 ppb
	Givaudan	06-24-83	3 samples; 3 ppb, 1 ppb, <1 ppb
Celamerck, Gmbh & Co. (F.R.G.)	Celamerck	08-78 to 03-83	58 samples <10 ppb 6 samples <5 ppb
	Givaudan	06-24-83	8 samples <1 ppb
Linz (Austria)	Linz	03-24-83	8 samples <5 ppb
	Givaudan	06-24-83	2 samples; 2.9 ppb, <1 ppb

* ppm = parts per million
ppb = parts per billion

Source: Compiled from documents supplied by Givaudan Corporation, in a letter dated July 1, 1983, from Dr. M. Manowitz, Director of R&D, to Dr. Marilyn Fingerhut, NIOSH.

Table 3
Givaudan Corporation
Clifton, New Jersey

2,4,5-TRICHLOROPHENOL

ANALYSIS FOR TCDD

(2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN)

Analysis Performed by Quality Assurance

Lab #	Sample Analysis		p.p.b.
	3/17/78	Celemark T.C.P.	
		07057	<1.0
		07117	<1.0
	Sept. 1978	Celemark	
241		9517-78	<1.0
240		9516-78	<1.0
	5/11/79	Vertac T.C.P. 6995	
		1-2	<1.0
		3-4	<1.0
		5-6	<1.0
		7-8	<1.0
419	11/79	Thatcher Chem. Special Samples	
		15100-79	<1.0
449		Linz T.C.P. Special Sample	
		17989 -79	2.9
520		Filter Cake	
		50 g. S_a Reported <10	<0.2
761	12/13	Caustic Water Layer from T.C.P. Drum Washes	<1.0
762		Solids & Extract & Distillate from T.C.P. Waters	<1.0
881		Linz T.C.P. (3594-83) Drums 1 & 4	<1.0
882		Celamerck (3233 & 3244-83)	<1.0
885		Celamerck (8022-82)	<1.0
897		Celamerck #12 & #13 (4887-83)	<1.0

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Table 3
Givaudan Corporation
Clifton, New Jersey

April 19, 1983

2,4,5-TRICHLOROPHENOL

ANALYSIS FOR TCDD

(2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN)

Analysis (Extractions) Performed by Research Labs

Lab #			p.p.b.
TC 405		T.C.P. Dow 02157 (3362-77)	3
TC 466			1
TC 464		410382 T.C.P. 77	<1.0
TC 465		410383 T.C.P. 77	<1.0
TC 424	9/15/77	G-11® Mother Liquor from Crystallization	<1.0
TC 457		T.C.P. Technical MM 12017-1	<1.0
TC 462		T.C.P. High Purity Dow 9145-76	<1.0
TC 455		T.C.P. 14837-77 Celemark	<1.0
TC 445		T.C.P. MM 09027-1	<1.0
TC 434			<1.0

Source: Letter from Dr. Manowitz, Givaudan to Dr. Marilyn Fingerhut, NIOSH, dated July 1, 1983, Appendix VIII.

Table 4
Analysis Results of Hexachlorophene for 2,3,7,8-TCDD Givaudan Corporation Clifton, New Jersey

Analysis Laboratory	Date of Analysis	Sample Results*
Hooker Chemical Co.	06-08-70	1 sample <0.01 ppm 3 samples <0.02 ppm 1 sample <0.03 ppm
	07-07-70	3 samples <0.01 ppm 3 samples <0.02 ppm
	08-04-70	4 samples <0.01 ppm 6 samples <0.02 ppm 1 sample <0.03 ppm
	03-12-71	1 sample <0.1 ppm
California Analytical Laboratories	01-76 to 7-77	193 samples <1 ppb 2 samples <2 ppb 17 detectable samples mean = 2.4 ppb, SD = 0.67, range 1.5 to 4 ppb

* ppm = parts per million
ppb = parts per billion

Source: Compiled from documents supplied by the Givaudan Corporation in a letter dated July 1, 1983 from Dr. M. Manowitz, Director of R & D to Dr. Marilyn Fingerhut, NIOSH.

Table 5
Results of Samples of Process By-Products for 2,3,7,8-TCDD Analysis
Givaudan Corporation
Clifton, New Jersey

Sample ID	Sample Preparation	Nanograms /bottle	2,3,7,8-TCDD Parts per billion
867	*	150	*
867 HCP Spent sulphuric acid	100 grams neutralized & extracted	<10	<0.1
868 Filter cake for burial	Material dissolved in methanol, filtered & extracted	<10	<1.0
869 EO ethylene storage tank	100 gram sample evaporated to about 10 ml & extracted	<10	<0.1
870 HCP water from vacuum receiver from dryer	100 gram sample	<10	<0.1
871 Water recovered from catch-all tank, ethylene dichloride steamer to sewer	100 gram sample	<10	<0.1
872 Water from TCP extracted with ethylene dichloride to sewer	100 gram sample	<10	<0.1
873 Water wash from HCP filter	100 gram sample	<10	<0.1

*Not reported

Source: Compiled from documents supplied by the Givaudan Corporation in a letter dated July 1, 1983, from Dr. M. Manowitz, Director of R&D to Dr. Marilyn Fingerhut, NIOSH.

Table 6
E.P.A. Analysis Results for 2,3,7,8-TCDD in Three Givaudan Process Samples
Givaudan Corporation
Clifton, New Jersey

EPA Sample Number	Sample	Quantity of TCDD's found	Minimum detectable Concentration pg/g (ppt)*
C04130	Aqueous slurry of HCP	ND**	140
C04131	Activated clay filter cake from HCP manufacturing	ND	70
C04132	Ethylene dichloride recovery solution from HCP manufacturing	ND	50

* pg/g (ppt) = picograms per gram (parts per trillion)

** ND = No TCDD's detected in excess of minimum detectable concentration.

Source: Esposito, M.P., Tiernan, T.O. and Dryden, F.E. (1980) Dioxins, Environmental Protection Agency Publication EPA 600/2-80-197, page 154.

Table 7
2,3,7,8-TCDD Analytical Results For Wipe and Dust Samples Givaudan Corporation Clifton, New Jersey

Building Number Description	Sample Date	Sample Type	PPB*	NG/Sq. Ft.
52 2,4,5-TCP Storage	83/07/09	Wipe		1.3
	83/07/09	Composite	<.2	
54 Former 2,4,5-TCP Production	83/07/09	Wipe		6.5
		Dust	22.0	
47 HCP Grinding	84/07/25	Wipe-2 sq. ft.	0.16	0.22
		Sweep-287 sq. ft.	0.71	0.03
58 HCP Production	83/07/09	Comp dust	0.51	
		Wipe		<1.20
	83/08/11	Wipe		<1.00
	83/09/19	Wipe-2 sq. ft.		<1.00
	83/10/17	Wipe		<1.00
	83/12/01	Wipe		0.11
59 HCP Production	83/07/09	Comp dust	0.23	
		Wipe		1.90
	83/08/11	Wipe		0.75
	83/09/19	Wipe-2 sq. ft.		<1.00
	83/10/17	Wipe		<1.00
	83/12/01	Wipe		0.36
60 HCP Production	83/07/09	Comp dust	1.60	
		Wipe		4.40
	83/08/11	Wipe		<1.00
	83/09/19	Wipe-2 sq. ft.		<1.00
	83/10/17	Wipe		<1.00
	83/12/01	Wipe		0.14
75 HCP Packaging	84/07/25	Wipe-2 sq. ft.	0.23	0.34
		Sweep-209 sq. ft.	0.50	0.03

* Parts per billion (nanograms per gram of sample)
** Nanogram per square feet sample area

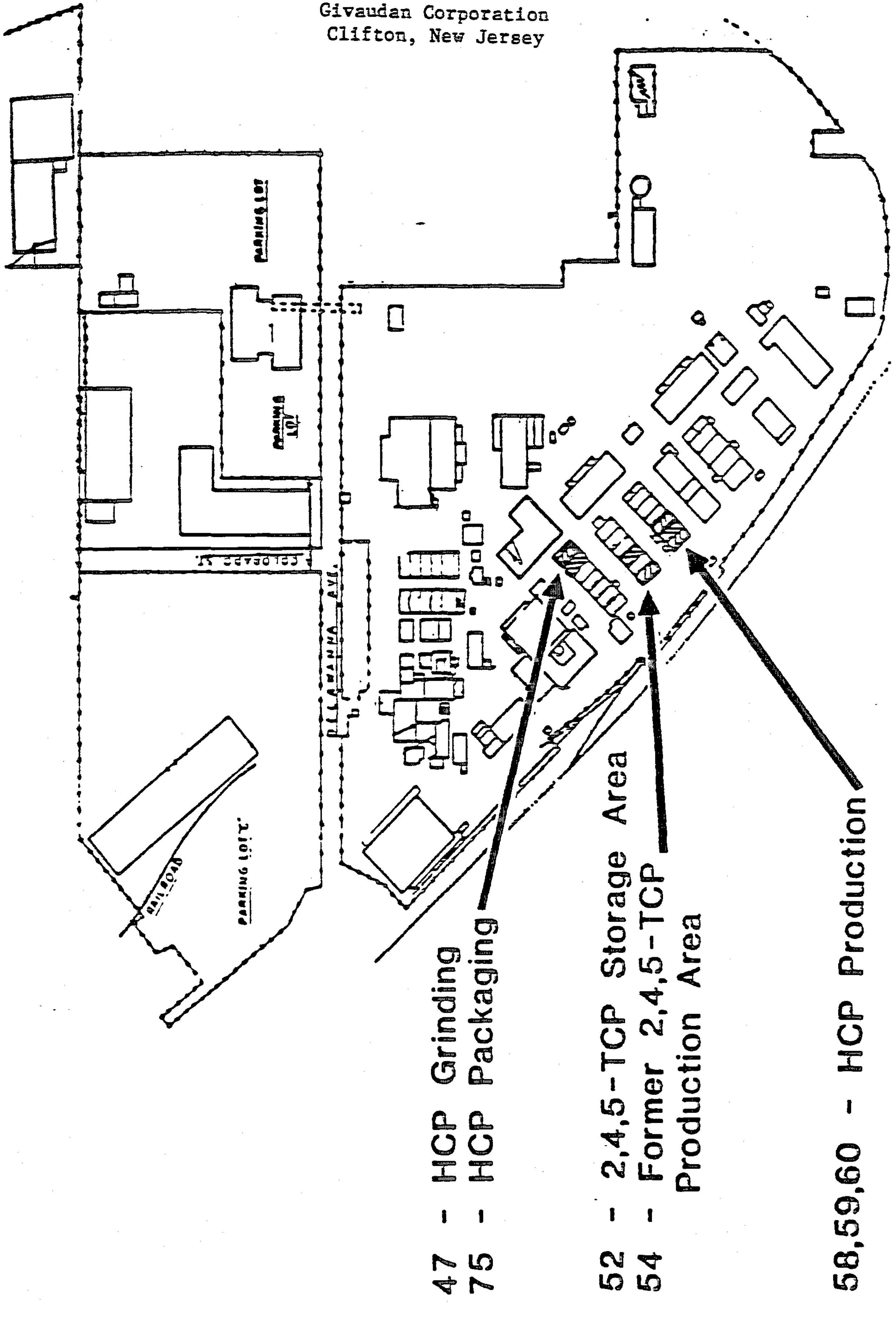
Source: Documents supplied by Givaudan

Table 8
HEXACHLOROPHENE COST ACCOUNTING CODES FROM JUNE 1957 TO JUNE 1978*
COMPUTER CODES FROM JUNE 1978 TO MAY 1984
Givaudan Corporation
Clifton, New Jersey

1957 (June-December)	8002, 8003
1958	8002, 8003
1959	8002, 8003
1960	8002, 8003
1961 (January-June)	8002, 8003
1962 (July-December)	8047
1963	8047
1964	8047
1965	8047
1966	8047
1967	8047
1968	8047
1969	8047
1970	8047, 8041
1971	8047, 8041
1972	8047, 8041
1973	8047
1974	8047
1975	8047
1876	8047
1978	8047
1978-1984**	G11

*Before June 1957, there were no cost accounting numbers in use. From 1957 to 1961, the hexachlorophene workers were assigned to 8002 and 8003; this system was renumbered in 1961, and 8047 was used for the same hexachlorophene operation. From 1970 to 1972, the process was expanded and a new building (8041) was added. This building was assigned to non-hexachlorophene processes in 1972. From June of 1978 through May 13, 1984, when the process was terminated, detailed work histories can be constructed from a computer listing generated by the company. The hexachlorophene department was identified as "G-11".

Figure 1
Plant Layout
Givaudan Corporation
Clifton, New Jersey



47 - HCP Grinding
75 - HCP Packaging

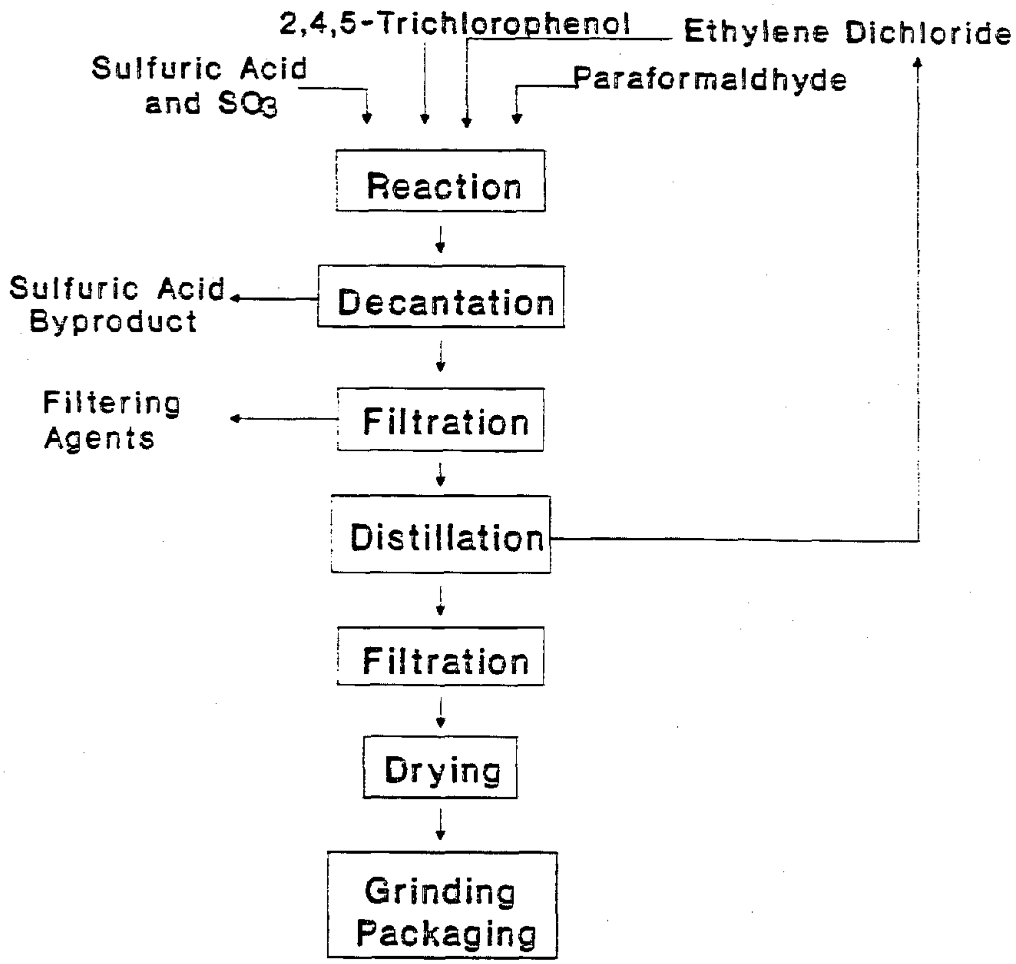
52 - 2,4,5-TCP Storage Area
54 - Former 2,4,5-TCP Production Area

58,59,60 - HCP Production

Figure 2

Hexachlorophene Process Flow Diagram

Givaudan Corporation
Clifton, New Jersey



Givaudan Corporation
Clifton, New Jersey

2,3,7,8-Tetrachlorodibenzo-p-dioxin determination in Hexachlorophene

Introduction:

The present work is a joint project by Hooker Chemical Corp. (Niagara Falls, N.Y.) and Givaudan Corp. (Clifton, N.J.). The purpose was to determine quantitatively the possible presence of 2,3,7,8-tetrachlorodibenzo-p-dioxin as an impurity in Givaudan's commercial grade hexachlorophene.

Sample selection:

The present investigation included:

(a) 5 Samples from the following lots, chosen at random, produced in 1970, with the numbers: 8857-70; 8339-70; 8743-70; 8710-70; and 8666-70.

(b) 6 Samples, each being a bulk from 2 to 4 lots, chosen at random, manufactured during the second half of 1969, with the numbers: 18089 A, 18089 B, 18089 C, 18089 D, 18089 E, and 18089 F.

Extraction procedure:

2,3,7,8-Tetrachlorodibenzo-p-dioxin is a non-phenolic substance (in contrast to hexachlorophene) and - if present - could be separated from hexachlorophene itself due to this property. It was therefore decided to carry out the planned determination with the non-phenolic impurities present in commercial hexachlorophene. That this method is proper was proven by a separate study by Hooker Chemical Corp., see report dated July 31, 1970, entitled "Extraction Efficiency in the Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Hexachlorophene" (enclosed)

The non-phenolic impurities in the samples of commercial hexachlorophene were prepared as follows:

(a) 100 g. of G-11® were dissolved in 400 ml of H_2O containing 40 g. of NaOH by heating to 45-50°C. for 3-5 minutes and agitating overnight at room temperature.

(b) The alkaline G-11 solution was extracted with benzene 3 times using 200 ml of fresh benzene per extract.

(c) The combined benzene extracts were washed with 200 ml of 10% aqueous NaOH followed by 2 successive washings with 200 ml of water.

(d) The benzene solutions were concentrated on a rotary evaporator, to approximately 25 ml for shipment. The 25 ml extracts were submitted to Hooker for analysis; it may be mentioned that they contained an average of 0.12 g material.

Analytical procedure:

(as carried out by Hooker Chemical Corp.)

At Hooker the extracts were concentrated to 0.5 ml, or as small a volume possible without precipitating solids.(1) Five μl of the concentrate were then analyzed by gas chromatography under the conditions listed on the following page.

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(1) The ultimate sensitivity of the method is a function of volume to which the extract is concentrated.

CHROMATOGRAPHIC CONDITIONS

Column	2' glass packed with 2% Versamid 900 on 60-80 mesh Chromosorb DMCS.
Detector	Flame Ionization.
Hydrogen Flow	50 ml/min
Air Flow	200 ml/min
Helium Flow	50 ml/min
Injection Port temp.	250°C.
Detector Temperature	300°C.
Column Temperature	200°C.
Chart Speed	1/2"/min
Sample size	5 µl

A standard, containing 0.2µl/µl 2,3,7,8-tetrachlorodibenzo-p-dioxin in benzene, is injected and the chromatogram compared to that of the sample.

Results:

Sample	2,3,7,8 tetrachlorodibenzo-p-dioxin	Sensitivity,(1) pp
18039 A	ND*	.01
18039 B	ND	.01
18039 C	ND	.02
18039 D	ND	.01
18039 E	ND	.02
18039 F	ND	.02
835770	ND	.03
833970	ND	.02
874370	ND	.02
871070	ND	.02
865670	ND	.01

* none detected

A. Reagents

1. Methanol, R. (Spectro Grade)
2. Hexane, R. (Mixed Hexanes)
3. Methylene Chloride, R.
4. 10% V/V Methylene Chloride-Hexane Mixture
    a. Transfer 10 ml. of Methylene Chloride into a 100 ml. volumetric flask. Dilute to volume with Hexane and mix well.
5. 2.5N Lithium Hydroxide
    a. Transfer 105 g. of Lithium Hydroxide Monohydrate (MCB LX 350) into a 1 liter volumetric flask. Add approximately 750 ml. of distilled water and mix until dissolution is complete. Dilute to volume with distilled water and mix well.
6. Alumina, Basic (Brinkman Cat. #1076)
7. Sodium Sulfate, Anhydrous

B. Special Equipment

1. Graduated 12 ml. tapered centrifuge tubes
2. Chromatographic Column
    a. Place a small piece of glass wool in the bottom of a 5-3/4" capillary disposable pipet (5 x 15 mm.).
    b. Add a small amount of sand and 1.0 g. of Basic Alumina. Pack the column by tapping several times.
    c. Dry the column for a minimum of 2 hours in a 105° oven. After removal, store in a desiccator.
3. Buchi - Rotary Evaporator (Model R or its equivalent).

<u>*SEE PRECAUTIONARY NOTES</u>

C. Procedure (This procedure is established for the analysis of a composite of two lots of G-11®.)

1. Weigh 10.0 g. of sample (5.0 g. from each lot) into a 150 ml. beaker.
2. Dissolve the sample in 50 ml. of Methanol and transfer the solution to a 1,000 ml. separatory funnel.
3. Rinse the beaker into the separatory funnel with 25 ml. of Methanol, using small increments.
4. Add 25 ml. of Lithium Hydroxide solution and swirl the contents. Add 225 ml. of distilled water to the funnel and carefully shake. <u>CAUTION:</u> The funnel should be vented frequently to prevent pressure buildup.
5. Extract this solution twice with 200 ml. of Hexane for <u>each</u> extraction.

    <u>NOTE:</u> If emulsions occur, allow the mixture to stand for an additional 5-10 minutes. If slight emulsion is still present, drain the emulsion with the aqueous layer.
6. Combine the two Hexane extracts in a 500 ml. glass-stoppered Erlenmeyer flask and dry over Anhydrous Sodium Sulfate.
7. Filter the dried Hexane solution into a 500 ml. round-bottom one-neck 24/40 joint flask. Rinse the 500 ml. Erlenmeyer flask, from Step 6, with several small portions of Hexane and transfer the rinses to the funnel, collecting the filtrate in the 500 ml. round-bottom flask. Rinse the funnel with several small portions of Hexane and collect the washes in the 500 ml. round-bottom flask.
8. Evaporate the Hexane solution to a volume of approximately 15 ml. using the Buchi Evaporator and coarse vacuum. (previous method used a steam bath)

9. Carefully transfer portions of the concentrated solution from step 8 into a 12 ml. graduated centrifuge tube partially evaporating the solution between transferring the portions. (The entire 15 ml. will not fit into the tube). Continue to evaporate the solution to a volume of 1.0 ml.
10. Transfer the 1.0 ml. of sample from step 9 to the chromatographic column (B.2.). Do not allow the column to run dry.
11. Rinse the centrifuge tube with small portions of the 10% Methylene Chloride/Hexane solution using a total of 10 ml. Do not add the washes until the liquid level is almost to the surface of the packing. Collect the effluent in a 12 ml. graduated centrifuge tube.
12. Concentrate this solution to 1.0 ml. using a water bath and a gentle stream of air.
13. Carefully transfer the 1.0 ml. of sample to a 1/8 oz. glass bottle and continue to evaporate to dryness. Cool and cap. Seal the bottle with a small piece of parafilm and label.

D. PRECAUTIONARY NOTES:

1. The extraction and separation should be performed in an efficient fume hood.
2. Disposable gloves, safety glasses and suitable clothing should be worn.
3. Worker should thoroughly wash hands prior to handling food, etc.
4. Centrifuge tubes should be regularly soaked in Chromic Acid cleaning solution for a 24-hour period.

REVISED PROCEDURE
November 7, 1977

Source: Letter from Dr. Manowitz, Givaudan to Dr. Marilyn Fingerhut, NIOSH, dated July 1, 1983, Appendix IV.

Figure 5

Industrial Hygiene Plan
Givaudan Corporation
Clifton, New Jersey

Givaudan's hygiene plan as hereby submitted is based on an important fundamental fact. This fact is that no TCDD can be formed in the hexachlorophene process and must, therefore, only come, if at all, from the raw material trichlorophenol (TCP)

1. To insure that no new TCDD contamination is possible, we will analyze all incoming TCP and use only that which shows a non-detectable TCDD level at 1 part per billion (PPB)
2. As a further check, we will analyze each production lot of hexachlorophene.
3. To insure the personal hygiene of our hexachlorophene manufacturing personnel, we will require them to:
    a. Work with long sleeves pulled down and change to freshly laundered clothes each day.
    b. Wear a fresh disposable head cover each day.
    c. Wear eye glasses with shields. Wear sealing goggles, in areas where dust could emit, should a malfunction of equipment occur.
    d. Wear sweat bands in summer in case of an accidental dust release.
4. All equipment which handles powdered hexachlorophene will be maintained to minimize dust emissions.
5. To insure complete monitoring of each worker's health, we will continue to offer each of them free annual comprehensive health examination, which includes a complete SMA 25 blood analysis. In addition, our employees can consult daily with a full-time registered nurse, and part-time doctor (each day) in a modern well-equipped medical facility.

Source: Letter from John A. Rankin, VP Manufacturing, Givaudan on August 15, 1983, to Dr. William A. Parker, New Jersey Department of Health

Figure 6

Conditions Set by the New Jersey Dept. of Environmental Protection for Givaudan to Resume HCP Production
Givaudan Corporation
Clifton, New Jersey

1. he occupational hygiene plan submitted to the Department of Health on August 15, 1983 should be implemented with the following additional provisions.

   a. Employees who work in the hexachlorophene production area should be provided with shower facilities and encouraged to shower at the end of each work shift.

   b. All personnel entering buildings 58, 59, and 60 should continue to wear disposable overboots until there is a final disposition of the outside dioxin contamination.

   c. The employee health examination should include a skin examination with special attention paid to the presence of chloracne.

2. A periodic sampling program should be conducted as outlined in my letter of August 5, 1983. This program should commence within one month of the date of this letter and monthly thereafter until further notice by this Department.

3. Based upon the results of this periodic sampling, any appropriate changes to the occupational health program as may be directed by this Department or the Department of Health shall be implemented.

4. Representatives of this Department and the Department of Health shall be provided acess to the Givaudan facility in order to determine compliance with the provisions of the administrative order issued to Givaudan on June 20, 1983, as modified by this letter or my previous letters.

Source: Letter from Michael F. Catania, New Jersey Department of Environmental Protection to Mr. William H. Hyatt, Jr., Pitney Hardin, Kipp & Szuch on August 18, 1983.