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National Institute for
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Robert A. Taft Laboratories
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Cincinnati, OH 45226

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January 8, 1982

Mr. Evan E. Cambell
Manager Industrial Hygiene
Diamond Shamrock Tower
717 North Harwood Street
Dallas, Tx. 75201

Dear Mr. Cambell:

On December 16, 1982 a meeting was held with the Special Peer Review Committee to review the protocol for the NIOSH Dioxin study. All members are supportive of the draft research plan. During the day-long meeting many suggestions were made, and we are currently working on some modifications of the protocol.

I am sending a copy of the draft protocol to all companies and unions to invite your suggestions. Please note that this is a draft document which will be modified following our consideration of comments we receive. I would appreciate receiving your suggestions before February 15.

If you have any questions, please feel welcome to call me at (513)684-3346.

Sincerely yours,

Marilyn Fingerhut

Marilyn Fingerhut, Ph.D.
Dioxin Activity
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1 Enclosure

CAMPBELL
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Report Prepared by Review of Documents
Received from

Diamond Shamrock Company
Newark, New Jersey

April 1, 1983

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Introduction

This report was prepared by reviewing documents sent to NIOSH by the Diamond Shamrock Company. Table 1 lists the abbreviations used in this report to refer to the chemicals produced by Diamond Shamrock.

History of the Plant (From "Attachment #8" sent to NIOSH by Diamond Shamrock)

The Kolker Chemical Works Inc. operated a plant at 80 Lister Avenue, Newark, New Jersey, from February 1946, until Diamond Shamrock acquired it by an exchange of stock in August 1951. Diamond Shamrock owned and operated the facility until March 1971, when the property and equipment were sold to ChemicalLand Corporation. Production at the plant ceased earlier, on August 1, 1969.

Ray Guidi, former employee of Diamond, accepted an offer of the purchaser to run the Newark plant on March 15, 1970.

Personnel Information

1. Microfilm of Personnel Records

The microfilmed personnel files contain an application form, an employee status report of hire, medical reports, workers' compensation reports, change of address notices, an attendance sheet, and an employee status report noting termination. Most useful to NIOSH are the employee status reports which list job titles. On some employee status reports, a job location is noted under "Work Location" (e.g., Newark - 2,4-D Unit). Other documents which note job title are the physician's reports ("Classification"), and the application form ("Position Desired" or "Job Interest").

Unfortunately, the microfilmed personnel files do not permit reconstruction of work histories. There are very few employee status reports noting job changes, and the attendance sheets list only dates and check marks.

2. Master List

This is an alphabetic listing of all hourly and salaried Newark employees which was compiled by the company. It includes date of birth, date of hire into Diamond (without distinguishing whether Newark or another facility), date of termination, date of death (if deceased) and social security number.

3. Primary and Supplemental Personnel Card Files

These two (photocopied) card files provide social security number, job title and date of birth, hire, and termination. Most cards list only one job title for an individual (e.g., first class chemical operator) but others list a progression of jobs (e.g., fourth to first class operator). It is unclear whether these cards contain a complete accounting of job title changes of each worker. If so, they might be suitable for a reconstruction of work histories.

Diamond Shamrock Units and Operating Conditions

The Newark facility had eight production units:

TCP Unit	2,4,5-T Unit
Ester Unit	Amines Unit;
Formulations Unit	2,4-D Unit
MCA Unit	HCl Unit

The maintenance for the units was provided regularly by Diamond maintenance personnel, although a contractor was utilized occasionally.

Monthly reports, which were given to NIOSH, are titled Summary of Vacancies, Operating Data, and Operating Comments (Production, Maintenance and Utilities, and Plant Technical). The reports cover the periods January 1966 to December 1968. They provide a detailed review of monthly costs and production figures, as well as a commentary on equipment changes and production problems. Beginning in January 1967, comments on operating conditions were added to the monthly report. The data provided each month for each product are as follows:

TCP: Average and maximum temperatures in the autoclaves;
Maximum temperature in the anisole still;
Product assay (including "p-dioxin" check).

2,4,5-T: Average cooking time and temperature;
Average TCP conversion in the reactor;
Average assay of acid packaged.

Esters: Average, short, and long esterification temperature and time;
Average product assays.

Table 2 presents mean values for measurements reported during the period January 1967 - December 1968.

Diamond Shamrock Facilities - 1967 Expansion of 2,4-D and 2,4,5-T Acid Production

A company report dated June 22, 1966 details expansion plans for 2,4-D and 2,4,5-T. A total budget allotment of \$1,168,000 is requested to install a 12 million lbs/year 2,4-D acid facility, convert the existing 2,4-D facility to 2,4,5-T acid production, install TCP purification facilities and build a warehouse addition. The report notes that the effort would increase the capacity for 2,4,5-T acid production from the existing rate of 1,800,000 lbs/year of wet cake product to 3,000,000 lbs/year of a more desirable dry flake product. The production of 2,4-D would rise from the existing rate of the successful dry flake acid of 7,200,000 lbs/year to 12,000,000 lbs/year of the same dry flaked acid.

The report also noted that the supplemental processing equipment for the TCP unit is intended "to remove the chloracne and eliminate one of the objections to the Diamond T-acid (and)...result in better working conditions-reduced chloracne at the Newark facility". The equipment, a new mixer, filter, glass-lined acidification tank, glass-lined decanter, stainless steel neutralization tank and 10,000 gallon surge tank, would be installed in a new building adjacent to the existing TCP process building. The report also states that "present T-acid facilities are old (15 years) and beyond the point of economical repair."

The monthly reports state that on July 4, 1967, the "T" Unit was shut down and the area turned over for construction of the new "D" Unit. All "T" acid operators were assigned to training in the Melt Unit and reactions. On September 18, "T" acid production was resumed in the revised old "D" Unit. Many problems with line plugging occurred.

The TCP pilot carbon column ran substantial volumes of TCP for the first time in September 27, 1967.

Products and Years of Production

The products and their periods of production were provided to NIOSH as Attachment #7 on August 1, 1980. We have added dates for these products, which we found in other documents. See Table 1. Our review of other Diamond documents also indicates that additional products were made. These are listed in Table 3.

Levels of Production at Diamond Shamrock

The company provided NIOSH with pages that seem to be copied from The Pesticide Review 1968, USDA. Annual U.S. production figures and Diamond production figures are given for 2,4-D and 2,4,5-T. The Diamond figures from 1960-1968 are summarized in Table 4. From 1960 to 1968, 2,4,5-T production constituted from 10 to 25% of total phenoxy acetic acid production. This amounted to an annual production total of 2,4,5-T ranging from 600,000 lbs to 2.9 million lbs.

Monthly reports required by the U.S. Department of Commerce and a summary report (Form BDSAF-797) detail the production levels from January 1966 through January 1969. The amounts are summarized in Table 5. The data indicate that the heaviest production time extended from April 1967 through October 1968 when the plant produced about 200,000 lbs of 2,4,5-T and 700,000 lbs of 2,4-D each month. Most of the 2,4,5-T during this period was devoted to military use as a component of Agent Orange, but the 2,4-D was utilized for both military and domestic use.

The monthly breakdown data of Table 6 indicate that 56,000 lbs of 2,4,5-T were produced monthly from January 1966 through March 1967, but this constituted only 8% of total acid production. The production of 2,4,5-T

increased by a factor of 3.5 during the period April 1967 through October 1967, and constituted 22% of total acid production. Production of both 2,4-D and 2,4,5-T decreased somewhat during the period November 1968 through January 1969, but the monthly production of 156,000 lbs of 2,4,5-T still constituted 22% of the total acid production at Diamond.

A copy of a Western Union telegram of December 17, 1968, states that the government terminated the contract for Agent Orange as of January 1969.

Plant Layout

No layouts were provided. References in various documents suggest that there were two buildings at the facility with the following arrangement of activities.

<u>Bldg. 1</u>	<u>Bldg. 2</u>
TCP	T acid
Office	D acid
Maintenance	DCP
	Esters
	Formulations

It is not clear where DDT production, chlorination, or amine production occurred. Detailed layouts must be obtained from the company, as well as a description of how the buildings changed due to the 1960 and 1967 construction efforts.

A publication by Poland et al (1) states that in February 1969 a building separate from the production area housed administrators, technical help, engineers, business office workers, laboratory technicians and janitorial help. This does not coincide with the description of Building 1, above, and may indicate that the TCP unit was moved during one of the construction periods.

A report of October 2, 1968, to a G.L. Pratt, Cleveland, from F.G. Steward, Newark entitled "Ester Plant Replacement" states that the equipment requires replacement because it was installed in the late 40's and early 50's, was poorly arranged and required much maintenance. The report noted that the unit includes five 1000-gallon esterifiers used for batch processing, and that "the Dacamine reactor is in the middle of the 'T' ester area." A recommendation was also made to renovate the Formulations Building and equipment which "is also old and has close proximity and a close working relationship with the Ester unit."

1. Poland, A., Smith, D., Merter, G. and Possick, P., A Health Survey of Workers in a 2,4-D and 2,4,5-T Plant. Arch. Environ. Health 22:316-327, 1977.

A memo of February 14, 1968 from F. Gordon Steward to R.R. Wirmartin states that TCP mother liquor is recovered batchwise in the recovery area in the 2,4-D unit, and requests planning to permit switching mother liquor recovery from that location to the TCP purification unit. This indicates possible exposure of "D" area workers to TCP. It is unknown whether the same or separate workers were responsible for the "D" and "TCP recovery" activities.

Personnel

Some references suggest the following arrangement of workers. However, it is not clear whether this description fits all periods (separated by indicated times of construction) 1951-1960, 1961-1967, and 1967-1969.

A.) Hourly workers

One or two men per shift worked the TCP process, 2 men per shift worked on 2,4,5-T, and 32 men over 4 shifts were responsible for the 'D' and 'T' esters and other products. There were about 20 mechanics at anyone time, plus 3 lab technicians, 12 persons in the offices, and 3 or 4 men in the yard.

Some references suggest that the 2,4-D and 2,4,5-T and ester workers shared a common area, but formulations workers were in another section of the same building.

The company will be asked to describe worker assignment patterns and locations and to assist in defining the work areas where the various products were made. The job titles for hourly workers are listed in Table 7.

B.) Salaried Workers

Job titles for salaried employees were abstracted from personnel records. These are listed in Table 8. The company will be requested to assist in determining which job titles indicate a routine presence in production areas.

Accident at Diamond Shamrock

An explosion and fire occurred at noon on February 20, 1960. The autoclave pressure and temperature rose rapidly and the manhole cover blew, releasing methanol fumes which ignited and caused the explosion. One man walking nearby was killed. References indicate that the plant was shut down until a new plant was built. It reopened in 1961 with the same 2,4-D equipment but all new TCP equipment. It is unclear, however, whether one or both buildings were damaged and/or replaced, and whether the location of the TCP unit was changed by the reconstruction.

Chloracne at Diamond Shamrock

Dermatitis problems occurred during the period January 1951 and January 1952 when the company was producing tetrachlorobenzene by chlorination of monochlorobenzene. The problem cleared up when the company began to purchase tetrachlorobenzene from Hooker in January 1952.

In 1955, several TCP workers developed chloracne. This occurred 6 months after a 1954 change in the TCP process which initiated a steam distillation step. Chloracne continued to occur from time to time among TCP, and 'T' workers and mechanics.

No chloracne cases were reported as being caused by the explosion in the TCP process which occurred on February 20.

Production was increased to supply Agent Orange during the 1960's. Chloracne problems continued to arise. Information obtained from the monthly reports indicates that chloracne continued to be a problem in September, 1968 and that industrial hygiene measurements were made in the plant about that time. The December 1968 report states that no dioxin was found in the plant.

Published Reports of Chloracne

The two reports are described because they contain descriptions of process location and worker assignments. In a publication by Bleiberg et al, entitled "Industrially Acquired Porphyria,"⁽²⁾ a medical evaluation was presented for 29 workers employed at Diamond. This study involved 18 individuals having chloracne and 8 without the condition, and concluded that hyperpigmentation and hirsutism were proportional to the severity of chloracne in these individuals. Eight of the 29 workers and three additional hospitalized individuals with chloracne had evidence of porphyria cutanea tarda, but this was not proportional to the severity of chloracne. The authors concluded that some intermediate or products were responsible for both chloracne and porphyria cutanea tarda. This was the first published report relating porphyria cutanea tarda to chloracne or to industrial exposure.

Poland, et al,⁽³⁾ studied all male volunteers among the workers employed at Diamond in February 1969. Emphasis was placed on observations of chloracne, porphyria cutanea tarda, hepatotoxicity, and neuropsychiatric

2. Bleiberg, J., Wallen, M., Brodtkin, R., et al. Industrially Acquired Porphyria. Archives of Dermatology 82:793-797, 1964.
3. Op. cit.

symptoms. Seventy-three men were divided into four groups: 1) (n=20) administrators, technical and clerical help, lab technicians and engineers housed in a building separate from the production area; 2) (n=11) supervisors, foremen spending most of their time in the production area; 3) (n=28) on-line production area workers; and 4) (n=14) maintenance workers, some confined to the shop and some frequently in the production area. The total group included 55 white and 18 black employees, with an average duration of employment of 8 years.

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

Identification of the Chloracnegen

A report was written by John Cort, Jr. on March 24, 1965, which describes a meeting of representatives of Dow, Hooker, Hercules, and Diamond. Dow announced the identification of the chloracnegen as 2,3,7,8-tetrachlorodibenzo-p-dioxin (dioxin), and the development of an analytic technique with a sensitivity of 1 ppm. Wipe tests at Dow had confirmed the presence of dioxin on tool handles, benches, instruments, etc. Dr. Holder of Dow described the chloracne which occurred in Dow workers in 1964 and a secondary symptom of a fatigue reaction. Dow analyzed materials from other companies, including Diamond, and found amounts as high as 10 ppm in 2,4,5-T acid and 20-30 ppm in sodium 2,4,5-trichlorophenolate. Using results of rabbit ear tests Dow concluded that 1 ppm with repeat exposure can cause a real problem. The analytical results on Diamond products were to be forwarded to the company.

Dioxin Measurements

Analysis of the dioxin content in trichlorophenol (TCP) is provided in some monthly reports. The first recorded value was 115 ppm in April 1967, and the amount in May was 71 ppm. The reports from June through October do not

state any measured values, but reference is made to successful operation of a substantial volume of TCP through the pilot carbon column on September 22, resulting in less than 1 ppm contaminating "p-dioxin." The November 1967 level of dioxin was 1.7 ppm. The reports suggest that no TCP was produced due to annual shutdown and construction from July 24 to early or mid-September, 1967.

A report entitled "p-Dioxin Review" of December 23, 1969, reviews the plan for treatment of trichlorophenol to remove "p-dioxin." The carbon absorption technique for purification of TCP was initiated in September 1967 and "continued until plant operations were suspended in August 1969." Table 9 summarizes the dioxin measurements provided in this report.

An interim report dated March 23, 1966, from W.A. Goodloe is referenced in F.G. Steward's memo of March 23, 1969, as providing a description of Diamond efforts to remove "p-dioxin." The report of March 23, 1966, was not contained in the Diamond documents forwarded to NIOSH.

A report of September 18, 1967, to F.G. Steward entitled "Regeneration of a Carbon Column with 20 Be-HCl" describes the laboratory testing of extraction of the carbon column with HCl and benzene. He concluded that benzene extraction required too much handling and was not safe. He suggested draining the HCl and water into the sewer line, but noted that the insolubility of dioxin in water might cause a buildup in the local line. This report seems to be a pretesting of the TCP purification system installed at Diamond with the new construction in 1967. It is unclear what final method of disposal was selected. It is also unclear how the disposal of the charcoal with bound dioxin was to be handled.

A report of September 19, 1967, to F.G. Gordon, entitled "TCP Purification - Pilot Column" states that the pilot column, in operation since September 8, 1967, had purified 20,000 gals of 15% TCP. The average concentration of dioxin in the first 17,900 gals passed was 1.4 ppm. (Twenty-one of 42 samples had less than 1 ppm.) The report notes that this average of 1.4 exceeds the "present safe limit of 1 ppm" because an incorrect flow rate was used. The column would be regenerated when the pressure drop required it or when the columns no longer extracted dioxin below the 1 ppm level.

Diamond Alkali Laboratory reports show that various samples were analyzed for dioxin. The reports provided are from the period September 25, 1967 to November 18, 1967, and all measurements are under 1 ppm. However, because these are separate sheets, there is no way to know whether other measurements were also made and might have been high. Figure 1 is a copy of a laboratory procedure which may have been the method of analysis used.

Confounding Exposures

Some confounding exposures must be considered in evaluating the Diamond workers. A dermatitis problem existed during the period when tetrachlorobenzene was made from monochlorobenzene from January 1951 to January

1952. Trichlorophenol and 2,4,5-T were also made at this time, but the company began to purchase tetrachlorobenzene from Hooker in January 1952, at which time the dermatitis cleared up. This suggests that the dermatitis problem during this period may have been associated with the chlorination of monochlorobenzene.

Hexachlorobenzene production occurred from February 1946 to August 1969 and a variety of other chlorinated benzene substances were produced. The locations of use of production of all chlorinated benzene substances must be evaluated.

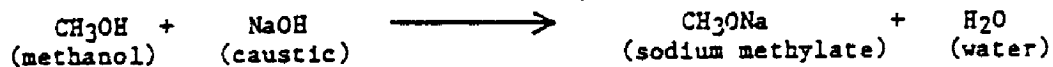
Additional possible confounding must be investigated by determining the years and locations of DDT production. References indicate that the production of hexachlorobenzene and chloral, a DDT intermediate, occurred in the TCP building and that DDT production occurred in the 'D' and 'T' Building, but in an area removed from these processes.

The components of the Dacamines are unknown and must be evaluated for possible confounding.

Process Description For The Production Of Sodium 2,4,5-Trichlorophenate

The Diamond Alkali Company produced an aqueous solution of sodium-2,4,5 trichlorophenate (NaTCP) using the following raw materials: 1,2,4,5-tetrachlorobenzene (TCB), flake caustic (NaOH), and methanol (MeOH). Methanol and water were also used as solvents. A flow diagram of the process is shown in Figure 2.

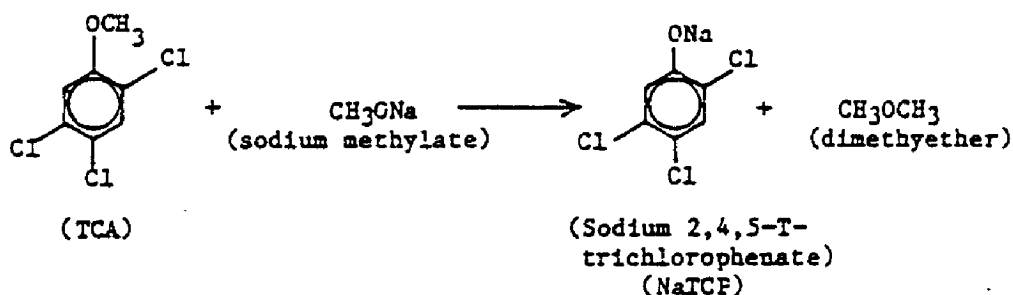
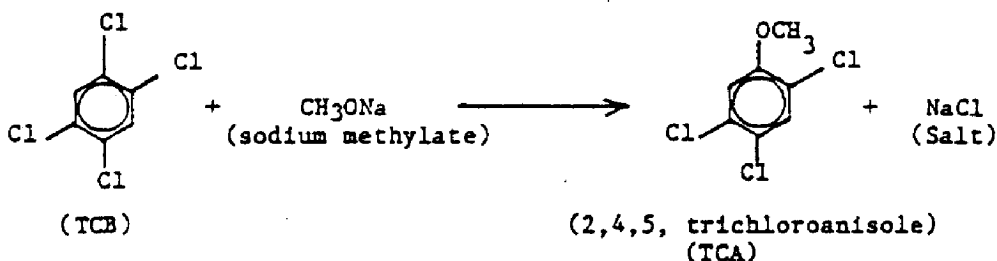
In the first step of the process, methanol is pumped into the methanol-caustic mix tank. The methanol is charged from the methanol recovery tank and supplemented with fresh (unused) methanol to make up a desired amount. Flake caustic is dumped from 50 gallon drums into the methanol-caustic mix tank which contains methanol. Sodium methylate is formed by the following reaction:



Methanol is added in excess in this reaction with mole ratio of 4 moles methanol per mole caustic. The sodium methylate solution is pumped to a drop tank where it is heated to 60°C.

TCB is stored in steel tanks and heated to 165°C to keep it in a molten liquid state. The TCB is pumped to a drop tank and fed to an autoclave reactor, a closed pressure vessel. Once the TCB has been charged to the reactor the sodium methylate solution is pumped to the reactor in a gradual controlled flow rate with constant agitation. A mole ratio of 6 moles sodium methylate solution per mole TCB is present in the reactor. Once all

the sodium methylate has been added the temperature of the reactor is raised to 165-175°C at a pressure of 350-375 pounds per square inch gauge (psig). The following reactions take place:



Following a digestion period of 3-5 hours, the reactor is allowed to cool down to 50-60°C at a pressure of less than 25 psig. During the cool-down period the dimethyl ether is allowed to outgas into the atmosphere through vents. After the reactor has cooled, the temperature of the reactor is raised to 90-100°C to distill off the unreacted methanol. The distillation of methanol is complete when the temperature of the reactor reaches 120°C.

The methanol vapors that come off during distillation are collected in the crude methanol condenser and pumped to the crude methanol storage tank. The crude methanol solution is pumped to the crude methanol redistillation still. The crude methanol is purified with the vapors piped to a series of two condensers and from there to the redistilled methanol receiver. The recycled methanol is now ready for reuse in the preparation of sodium methylate.

Once the majority of the methanol is removed, the crude sodium 2,4,5-trichlorophenate (NaTCP) is pumped from the reactor to the crude NaTCP holding tank. Six batches of NaTCP are made in this manner and stored in

the crude NaTCP holding tank. After six batches are in the crude NaTCP holding tank, the contents are pumped to the anisole still. In the anisole still, the crude NaTCP is steam stripped to remove TCB, TCA, and unrecovered methanol. The distillate is condensed and collected in the anisole receiver; at a later time, when sufficient material has been collected, a batch of NaTCP is made from this material. A batch of this type occurs, on the average, once a month. The process to make NaTCP from recovered, unreacted materials is the same as the process just described with the exception that less methylate solution is added to the TCB in the autoclave reactor.

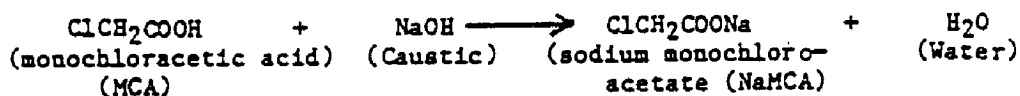
The steam stripped NaTCP is then pumped from the anisole still through the Monel screen filter which removes salts. The finished product, 36% NaTCP, is then pumped to a finished product holding tank, where it is either diluted with water to 25% concentration NaTCP for use in the production of 2,4,5-trichlorophenoxyacetic acid, or acidified to produce 2,4,5-trichlorophenol for sale.

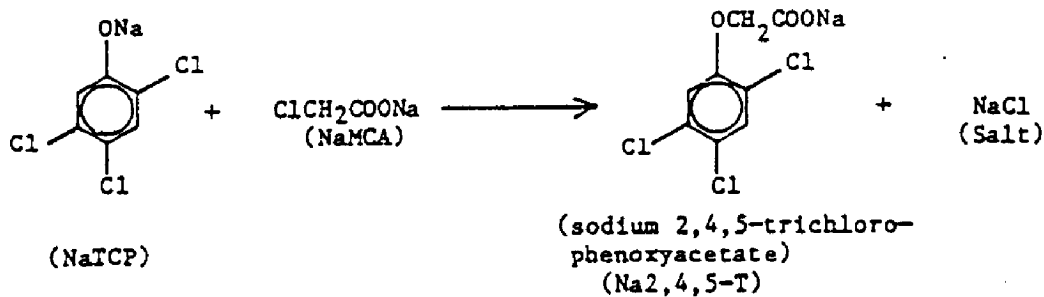
In 1967 a purification tower was added to the process to help remove contaminants from the NaTCP. This tower was filled with activated charcoal. The tower was in line after the Monel screen filter.

Process Description For The Production Of 2,4,5 Trichlorophenoxyacetic Acid

Diamond Alkali produced 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) using the following raw materials: aqueous sodium 2,4,5-trichlorophenolate (NaTCP), aqueous caustic soda (NaOH), monochloroacetic acid (MCA), sulfuric acid (H₂SO₄), and water as a solvent. A flow diagram of the process is shown in Figure 3.

In the first step in the process, NaTCP is pumped to a drop tank and then charged to the condenser reactor. Cooling water is applied to the reactor's jacket and agitation is started. An automatic pH meter used to determine acidity of the reactor contents should read between 12 to 13. Sulfuric acid is pumped to the reactor until the pH is adjusted between 9.5 and 10. Next, MCA is pumped to the reactor. The reactor temperature should be about 70-80°. A second drop tank is charged with NaTCP and pumped to the reactor. The mole ratio is 1.24 moles MCA per mole NaTCP, and the pH should read approximately 4. Upon the completion of the second charge of NaTCP, caustic soda is pumped until the pH is adjusted to 9.5. The batch is now ready to be cooked. The batch is cooked at 95-100°C for 2 1/2 hours at approximately 20 psig. The following reactions take place:

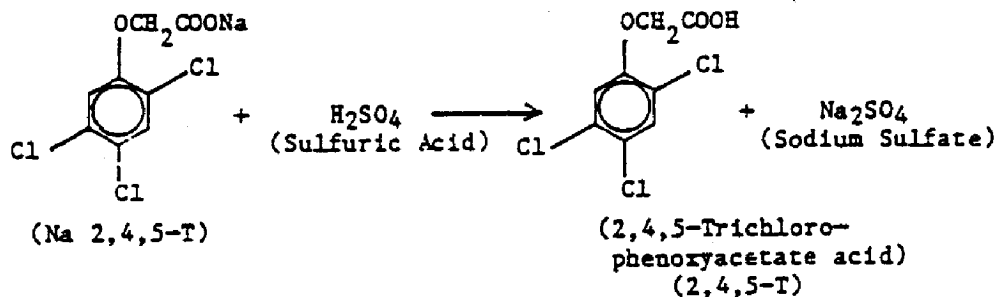




During the cooking period the pH is checked periodically. Caustic soda is added if the expected reading of 9.5 is not obtained. If the pH meter does not respond to the addition of caustic soda, water is added to thin the batch solution until the meter responds. After the cooking period a sample is taken, and the batch is pumped to the filter holding tank.

Na 2,4,5-T is held in the filter holding tank at 70°C and 15-16 psig with constant agitation. Caustic soda is sometimes added to maintain a pH of 9.5. From the filter holding tank, the Na 2,4,5-T is pumped to the 6'x6' filter feed pan and then to the filter where any unreacted Na 2,4,5-T-trichlorophenate and water soluble impurities are removed using sodium sulfate wash sprays. The Na 2,4,5-T is pumped from the filter to the slurry tank. In the slurry tank, the Na 2,4,5-T is heated to 70-100°C under a pressure of 15-16 psig. When a specific amount of Na 2,4,5-T has been added to the slurry tank, it is then pumped to the primary acidification tank.

In the primary acidification tank, acidification of the Na 2,4,5-T is started. The partially acidified mixture of 2,4,5-T and water then overflows into the secondary acidification tank where the acidification process is completed. The acidification tanks are kept at 120°C and 15 psig. The reaction that takes place in these tanks is as follows:



The molten mixture of 2,4,5-T and water overflows from the secondary acidification tank into the decanter where it is allowed to settle into two layers, water and 2,4,5-T. The water layer (still containing some unreacted Na 2,4,5-T) overflows to the settling tank. The 2,4,5-T layer is pumped to the decanter (procedure is described later).

The settling tank is used to recover Na 2,4,5-T from both the decanter and wash column overflows. The overflow enters the settling tank and is cooled to 40-50°C. Water is sometimes added to help the cooling process. Cooling the overflow results in a considerable amount of solids precipitating out of solution. The solids are recovered in the pressure filter, through which the cooled overflow is pumped into the sodium sulfate makeup tank. Solids recovered from the pressure filter are periodically flushed into the slurry tank for use in future 2,4,5-T batches. In the sodium sulfate makeup tank, caustic soda is added to recover sodium sulfate used as spray wash in the filter which is in line to the slurry tank, described earlier in this section.

The molten 2,4,5-T is pumped from the bottom of the decanter to the top of the wash column where it is washed with a countercurrent flow of hot water at 120°C. The washed molten 2,4,5-T comes out the bottom of the wash column and collects in the washed acid receiver while the wash water overflows from the top of the wash column to the settling tank where it is cooled for further recovery of 2,4,5-T. The washed 2,4,5-T is pumped from the washed acid receiver either to the dryer, where it is dried at 155-160°C, or to the amine makeup tank where the 2,4,5-T is mixed with triethylamine to make amines of 2,4,5-T. The dried molten 2,4,5-T is collected in the dry acid receiver where it is maintained at 160-165°C and 70-80 psig. The molten 2,4,5-T is pumped to either the flaker system to be bagged for sale or via the ester drop tank to the esterification unit to be used for production of esters of 2,4,5 T.

Major Process Changes, With Notations About Chloracne

Table 10 summarizes the major process changes initiated during the period of Diamond ownership. The list was compiled from a review of many of documents received from Diamond.

The "NaTCP Patent Application" of April 21, 1969, from F. G. Steward to R. Chonoles describes a new TCP process of gradual addition of caustic methanol which would lower the temperature increases and decrease the chloracnegens. It refers to the old TCP process as essentially the same as the Timbrol (Australian) 1951 patent process - producing high temperatures, chloracnegens and runaway conditions difficult to control. The report states that the old process was used until the explosion of 1960, but it does not indicate whether or when the new process was initiated.

Summary

This report describes production processes, personnel information and the history of the Diamond Shamrock Newark plant relevant to the production of sodium 2,4,5-trichlorophenolate and 2,4,5-trichlorophenoxyacetic acid. All information was contained in written materials sent to NIOSH by the company.

Attached to this report are questions which the company is requested to answer in order to provide NIOSH with additional information not contained in the materials sent by the company.

TABLE 1

Kolker and Diamond Products and Periods of Production(Attachment #7)

<u>Number</u>	<u>Product</u>	<u>Chemical Name</u>	<u>Years of Production</u>
1	2,4,5-T	2,4,5-trichlorophenoxyacetic acid	2/46 - 8/69
2	2,4-D	2,4-dichlorophenoxy acetic acid	2/46 - 8/69
3	TCP	2,4,5-trichlorophenol	2/46 - 8/69
4	TCP	2,4,6-trichlorophenol	2/46 - 8/69
5	DCP	2,4-dichlorophenol	2/46 - 8/69
6	MCA	Monochloroacetic acid	2/46 - 8/69
7	HCB	Hexachlorobenzene	2/46 - 8/69
8	DDT	dichlorodiphenyl trichloroethane	2/46 - 2/51
		Overex, Multicide	
9	KI01	p-chlorophenyl-p-chlorobenzene sulfonate	2/46 - ?/57
10	Compound 923	2,5-dichlorophenyl-p-chlorobenzene sulfonate	2/46 - ?/57
11	Chloral	1,1,1-trichloroacetaldehyde	2/46 - 8/61
12	BSC	benzenesulfonyl chloride	2/46 - ?/59
13	PCBSC	p-chlorobenzenesulfonyl chloride	2/46 - ?/59
14	PCBSA	p-chlorobenzene sulfonamide	2/46 - ?/59
15	44-DDS	4,4-dichlorodiphenylsulfone	2/46 - ?/59
16	PAABSC	p-acetylamino benzene sulfonyl chloride	2/46 - ?/59
17	PMBSC	p-methoxy benzenesulfonyl chloride	2/46 - ?/59

TABLE 2: Means and Ranges of Values Reported
for Various Operating Conditions at Diamond
January 1967 to December 1968

<u>TCP</u> (n=22)	<u>Mean</u>	<u>Range</u>
Average Temperature in Autoclaves	168°C	163-172°C
Maximum Temperature in Autoclaves	173°C	169-178°C
Maximum Temperature in Anisole Still	105°C	105-108°C
p-dioxin and related impurities (n=15)	15.4 ppm	0-115 ppm
<u>2,4,5-T</u> (n=20)		
Average Cooking Time	3.6 hr	2 - 8 hr
Average Cooking Temperature	101°C	97-105°C
<u>Esters</u>		
<u>Butyl-T</u> (n=24)		
Average Reaction Temperature	145°C	135-152°C
Average Cycle Time	23.5 hr	18.5-25.6 hr
<u>2 EH-T</u> (n=8)		
Average Reaction Temperature	153°C	150-159°C
Average Cycle Time	19.0 hr	15.8-24.6 hr

TABLE 3

Diamond Products and Periods of Production
(not identified in Attachment 7)

<u>Number</u>	<u>Product</u>	<u>Period of Production</u>
18	tetrachlorobenzene	1/51 - 1/52
19	2,4-D amines Please specify each one	? - 8/69
20	2,4,5-T amines Please specify each one	? - 8/69
21	2,4 D esters ethylhexyl butyl	? - 8/69 ? - 8/69
22	2,4,5-T esters ethylhexyl butyl	? - 8/69 ? - 8/69 ? - 8/69
23	Dacamine	? - ?

TABLE 4: Diamond Production Levels
Adapted from Source: 1968, The Pesticide Review, USDA

Production(millions of lbs)

<u>Year</u>	<u>Total Acid</u>	<u>2,4-D</u>	<u>% of Total</u>	<u>2,4,5-T</u>	<u>% of Total</u>
1960	5.8	5.2	89.7	0.6	10.3
1961	5.6	4.4	78.6	1.2	21.4
1962	6.7	5.4	80.6	1.3	19.4
1963	6.5	5.0	76.9	1.5	23.1
1964	7.5	6.2	82.7	1.3	17.3
1965	7.0	6.3	90.0	0.7	10.0
1966	8.6	7.9	91.9	0.7	8.1
1967	7.8	6.3	80.8	1.5	19.2
1968	12.9	10.0	77.5	2.9	22.5

TABLE 5: Summary of Production Levels at Diamond.
Figures are Average Monthly Production Amounts

<u>Time Period</u>	<u>TCP</u>	<u>2,4,5-T(lbs)*</u>	<u>2,4-D(lbs)*</u>	<u>Orange (gal)**</u>
1/66-3/67	ND	56,000	641,200	ND
4/67-10/68	177,726	195,596	701,208	31,897
11/68-1/69	84,207	156,213	571,126	0

*lbs refer to acid equivalents

** 1 gal Agent Orange requires 4.2 lbs of 2,4,5-T (acid equivalent) and 4.5 lbs of 2,4-D (acid equivalent).

TABLE 6: Relative Production Levels of 2,4,5-T and 2,4-D

<u>Time Period</u>	<u>Total Acid</u>	<u>2,4,5-T</u>		<u>2,4-D</u>	
	<u>lbs/mo</u>	<u>lbs/mo</u>	<u>% of Total</u>	<u>lbs/mo</u>	<u>% of Total</u>
1/66-3/67	697,200	56,00	8.0	641,200	92.0
4/67-10/68	896,804	195,596	21.8	701,208	78.2
11/68-1/69	727,339	156,213	21.5	571,126	78.5

TABLE 7

Job Titles of Hourly Workers (from Card Files)

Operator (1st,2nd,3rd,4th class)	Maintenance (1st,2nd,3rd,4th cl.)
Operator Trainee	Maintenance Leader
Head operator	Maintenance Helper
TCP Operator 2nd, 3rd class	Maintenance Helper
TCP Operator trainee	Mechanic(3rd cl.,1st cl. special)
Production Helper	Welder-Mechanic
*Platform operator	Janitor
*Centrifuge Operator/Ester 2,4,D Trainee	
	Lab assistant
*Flaker Operator	Lab technician
*Melt Operator Trainee	DDT Helper
*Whse sol. oper. 3rd cl.	*Painter
*Production	*Lubrication man
*Material Handler	
*Stockroom Helper	
*General Worker	
*2,4-D Centrifuge	

* These titles were found only on one or two cards.

TABLE 8

Job Titles of Salaried Workers:

A) Possibly had routine presence in production areas;
Clarification Requested.

Plant manager
Superintendent-Newark plant
Process engineer
Technical superintendent
Production and maintenance superintendent
Operations superintendent
Shift supervisor
Maintenance Foreman
Design engineer
Engineering trainee
Development engineer
Production supervisor
Hourly operations clerk/Relief Shift Supervisor
Summer Trainee
Chemist, Jr. Chemist, Ag Chemist, Chief Chemist,
Tech Staff Chemist
Lab Technician
Manager, Technical Staff
Field Supervisor Hourly
Personnel and Safety Supervisor

B) Clerical Workers, assumed to have no presence
in production areas; clarification requested

Office Manager
Clerk
Employee Relations (Personnel) Supervisor
Receptionist
Admin. Secretary
Acct. Dept.
Shipping and Billing Clerk
Payroll

TABLE 9: p-Dioxin Measurements Reported
 In Diamond Document "p-Dioxin Review", Dec. 23, 1969
 by F.G. Steward

<u>Date</u>	<u>Sample</u>	<u>Dioxin Content(ppm)</u>
May 1965	40% TCP Solution	25 - 40
	40% TCP Solution (diluted and filtered)	None
	Recovered trichloroanisole	73
	Recovered methanol	None
	'T' acid (7 lots)	under 10 (3 lots) 11-40(4 lots)
June 1965	Plant streams	80-140
June 1965	Filtration	"markedly reduced"
Sept. 1965	'T' Acid Sample	
	Lot 123	13
	Lot 124	26
	Lot 281	7
	Lot 282	7
Jan.-Mar. '68	2,4,5-TCP	3.8
Apr.-June	-	0.9
Jul.-Sept.	-	0.2
Oct.-Dec.	-	9.0 *
Jan.-Mar. '69	-	3.2
Apr.-June	-	1.7
Aug. '69	Plant suspended operations	

*(Due to labor dispute which delayed column cleaning)

TABLE 10

Major Process Changes, With Notations About Chloracne

Jan. 1951	Initiated production of tetrachlorobenzene (TCB) from monochlorobenzene. Chloracne occurred.
Jan. 1952	Terminated TCB production. Initiated purchase of TCB from Hooker. Chloracne ceased.
(Month?) 1954	TCP process change made from water purification plus filtration to a steam distillation technique. Chloracne appeared 6 months later.
Feb. 20, 1960	Explosion in TCP autoclave. No chloracne. TCP Building destroyed. Production ceased.
(Month?) 1961	New TCP unit opened, with new equipment. Melt process for T-acid initiated.
Sept. 1967	Charcoal filtration unit installed for removal of dioxin from TCP
(Month?) 1967	Newly constructed 2,4-D unit opened.
August 1967	2,4,5-T production switched to old 2,4-D equipment and locations.
April 21, 1969	A report to R. Chonoles from F. Gordon Steward is entitled "NaTCP Patent Application".
August 1969	All production terminated.

Laboratory Procedures

FIGURE 1

ANALYSIS OF TCP FOR p-DIOXIN

PROCEDURE:

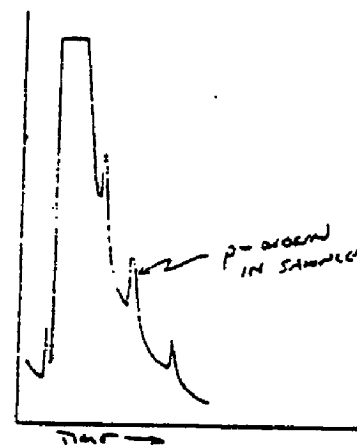
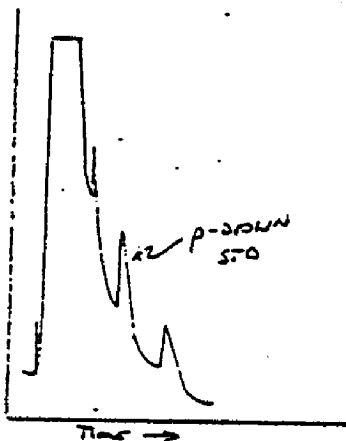
An equivalent of 50 grams of 100% TCP (example: 250 grams of 20% TCP = equivalent of 50 grams of 100% TCP) is weighed into an iodine flask (500 ml) and 50cc of benzene are added. This mixture is agitated for 2 hours and the mixture transferred to a separatory funnel. The bottom (TCP) layer is discarded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

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

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

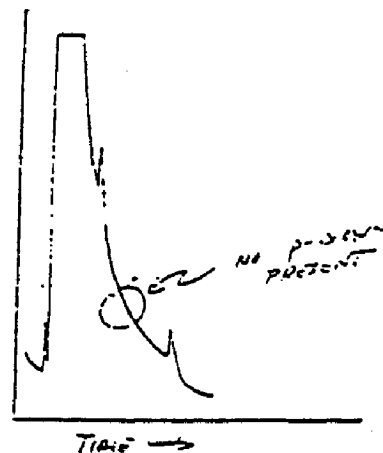
CONDITIONS:

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



CONDITIONS:

NaTCP (After purification column)
No p-Dioxin present
Condition:
C = 5' 5% SE 30
A = 10/8
S = 1.0 μ l
T = 245° on proportional controller
Gas Rates:
Air = 11.5 on rotometer
Helium = 9.5 on rotometer
Hydrogen = 6.0



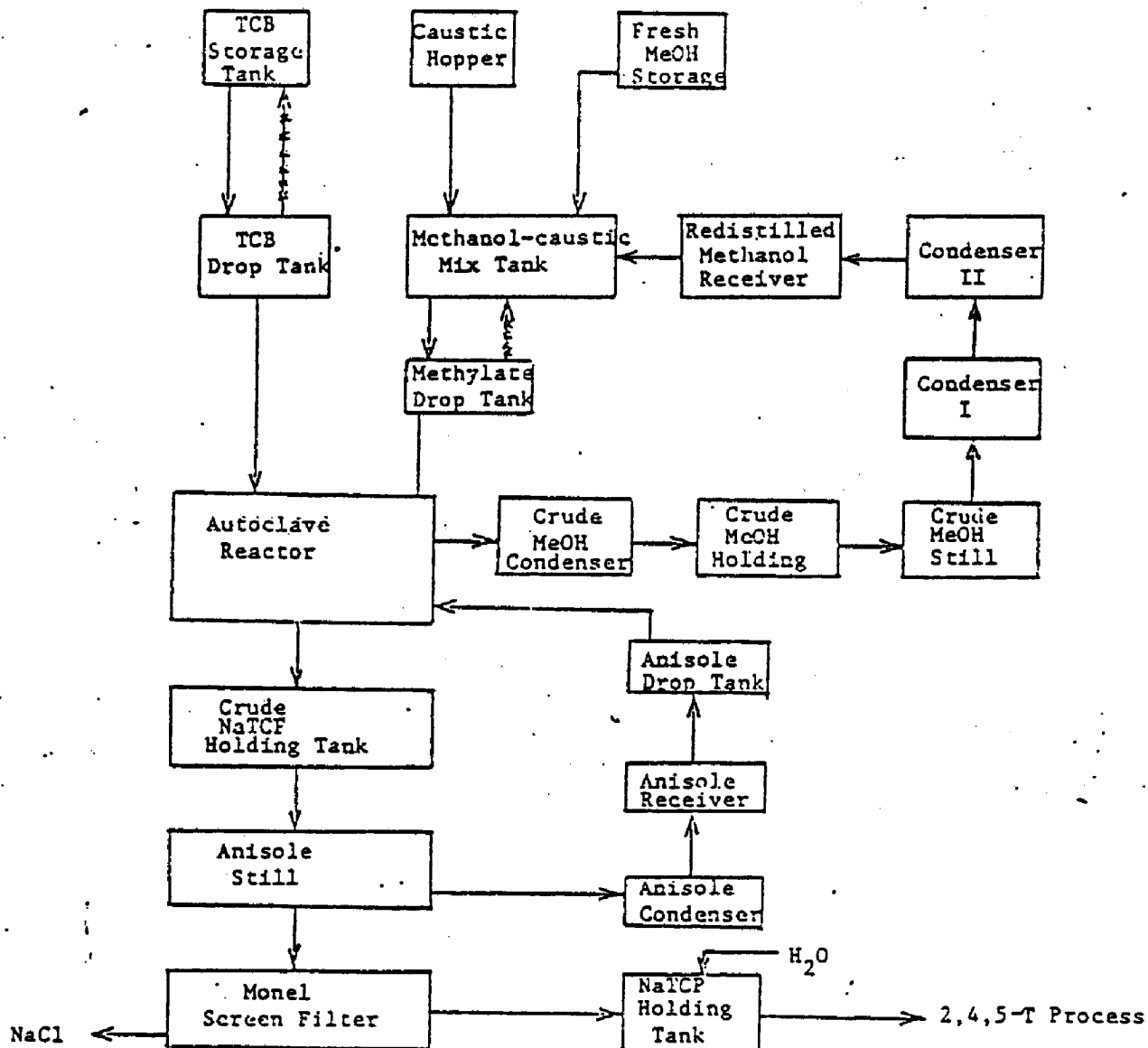
DS 00000226

D

57126

FIGURE 2

NaTCP PROCESS FLOW DIAGRAM



~~-----~~ Overflow lines

FIGURE 3

2,4,5-T Process Flow Diagram

