

ATTORNEY WORK PRODUCT.
ATTORNEY-CLIENT PRIVILEGE

2,4,5-T PRODUCTION, NITRO

AREAS OF HIGHEST OPERATOR EXPOSURE

(NA = Not Applicable)

Operation	Estimated PPM TCDD			
	Plant 1	Plant 2	Plant 3	
	1948-1952	1953-1955	1956-1969	1963-1969 ⁸
A. Cleaning NaTCP Filter Press ¹ <i>main filter</i>	30-60 ⁷	20-40 ⁷	NA	NA
B. Digging out cake from Na 2,4,5-T Centrifuges ²	5-10 ⁷	5-10	10-20	NA
C. Cleaning out Na 2,4,5-T Slurry Filters ¹	1-5	1-5	NA	NA
D. 2,4,5-T Filtration Operation ³	1-10	NA	NA	5-25
E. Digging out cake from 2,4,5-T Centrifuge ²	NA	1-5	5-10	NA
F. Cleanout of Settling/Storage Tanks - <i>since 1958</i>	5-10 ⁷	1-5 ⁷	15-30 ⁷	35-70
G. Rodding hopper feeding rotary dryer ⁴	NA	1-5	5-10	5-25
H. Assisting cake conveying operations ⁵	1-5	1-10	10-20	NA
I. Drying of Product on Tray Dryers ⁶	1-10	NA	NA	NA
J. Packaging of 2,4,5-T Product	1-10	1-5	5-10	5-25

- 1 Operations eliminated by 1956.
- 2 Plows added by 1958. No centrifuging in Plant 3.
- 3 High exposure applies to Plant 1 only. Plant 3 filter was automated thus low exposure.
- 4 Mechanical arch breaker (vibrating device) added by 1956.
- 5 Conveyors eliminated by 1960.
- 6 Tray dryers used in Plant 1 only. Rotary dryer used in Plants 2 and 3 thus low exposure.
- 7 Concentrations are for inlet stream. Actual cleanout operations would have resulted in exposure to cakes/residues/tars with a much higher TCDD content.
- 8 Exposure levels for Plant 3 are pre-1969. For the last eight months of operation (Jan.-Aug., 1969) changes were made in processing conditions which dramatically lowered TCDD levels; most product lots in the 1-3 ppm range.

Hygiene practices improved over the years

005080

HCG/DLW
7/28/83

B. HYDROLYSIS OF TCB

5. Recognition of TCDD in NaTCP: A Chronology

e. Chronology of the Recognition of TCDD

- 3/8/49 A runaway reaction in the TCB hydrolysis autoclave at Nitro discharged its contents throughout the area.^{5,6,7} Skin disorders appeared in persons working in the area within a few days.
- 5/8/49 A dermatology expert (L. Schwartz) visited the site and examined 25 cases of dermatitis which he diagnosed as chloracne.²⁵¹ He cited existing literature reports on such cases. He recommended treatments and suggested methods for further cleanup of the building. He also recommended patients be examined for liver disfunctions.
- 5/23/49 Report was issued by Nitro Research Dept. on lab investigation of the runaway reaction.²⁰¹ They were unable to duplicate the runaway but made recommendations for safer operation of the autoclave, particularly for feeding TCB over a period of time to the autoclave after it had been heated to the reaction temperature.
- 8/5/49 A second visit to the plant by Dr. L. Schwartz showed 52 new cases of chloracne since the May 8 visit.²⁵² All were less severe than the early cases. Most of the early cases showed improvement. He made recommendations for further building cleanup and a number of personnel protective steps: clothing, showering, medication, etc.
- Summer 1950 New TCB hydrolysis unit in Building 51.^{5,12} went into operation. Design features reduced worker exposure to process streams (see Section VIII, Chronology of Events, this date).
- 6/16/50 Laboratory attempts were made to identify a tarry material, water insoluble, in NaTCP.²⁵³ They noted that it was produced occasionally when autoclave temperature was on the high side. A portion of the tarry material was a very high melting solid.

Comment: This may well have been, at least in part, TCDD. It would have been partially removed from the process when NaTCP filtration was being practiced.

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1950- Samples were being taken for evaluation at Mellon
1952 Institute (see below).

10/7/52 Dr. R. E. Kelly feels a tarry component in TCB
hydrolysis step is responsible for chloracne. 254
Engineering control, not medical control, is the
important factor in controlling chloracne.
Manufacturing equipment must be designed to avoid all
exposure, or the tarry component must be removed from
the process. It is his impression that Dow does the
latter and has avoided chloracne.

11/52 Results of the "rabbit ear test" on 44 samples
submitted in previous months to Mellon Institute were
reported.²³ While there were anomalies, a
reasonable summary of these results is:

Mild Reaction: NaTCP from distilled TCP or Dow
TCP;
2,4,5-T from regular production;
2,4,5-T recrystallized.

Marked Reaction: Production or pilot plant NaTCP;
TCA, some samples.

Severe Reaction: NaTCP from recovered TCP;
Tar from NaTCP filter;
Residues from TCP distillations;
TCA, several samples;
2,4,5-T from recovered TCP.

Comment: The Mellon studies showed that TCP
distillation could remove much of the chloracnegen,
which was concentrated in distillation residues. TCA
was also implicated as the chloracnegen. Memos of
transmittal of the samples to Mellon are not
available, so exact sample preparations are not
known. It is reasonable to assume that most of the
TCA samples were prepared by extracting NaTCP
solutions with TCE (trichloroethane or
trichloroethylene, not specified) and removal of the
solvent. Such a procedure would have also extracted
the then-unrecognized TCDD which would be left in the
TCA. This assumption makes the test results generally
consistent.

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Laboratory results at this time indicated that TCP distillation might be economically feasible since distilled TCP gave better 2,4,5-T yields than the current process, offsetting the distillation losses.²² Various laboratory investigations aimed at TCA reduction were then proposed.^{23,24} These studies were threefold:

- a) Acidifying NaTCP and distilling TCP for 2,4,5-T production with residue disposal to be determined;
- b) Extraction or steam distillation of TCA from NaTCP solution and return of TCA to the autoclave for further reaction to NaTCP;
- c) Further examine the autoclave reaction to reduce amount of TCA made.

Comment: Distillation of TCP would have removed most of the TCDD, and residue disposal would have been a problem. Extraction or steam distillation of TCA and return to the autoclave would also have returned TCDD to the process, and would not have been a forward step.

- 1/6/53 New 2,4,5-T facilities started up.^{6,27} Closed operations and improved ventilation were designed to lessen worker exposure.
- 4/14/53 An environmental survey conducted at the plant identified areas for improvement of working conditions.³⁰
- 1953 Literature reports of acute toxicity studies of 2,4-D and 2,4,5-T in dogs gave an oral LD₅₀ of approximately 100 mg/kg.²⁴⁶
- 10/3/53 Final report on lab investigations of TCB hydrolysis noted increase in NaOH:TCB molar ratio gave definite reduction in TCA content (TCA thought to be the chloracne).²⁶ No cases of chloracne in NaTCP production at W. G. Krumrich plant were noted in late 1952 and early 1953. Report recommended minimum contact with process materials.

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- 12/31/53 Research report issued on 2,4,5-T yield improvement studies.³⁶ Report recognizes chloracne concentrated in recovered TCP, and work undertaken to increase yields sufficiently to permit economical discard of recovered TCP. Results were not successful.
- 6/8/54 State Department of Health air sampling defined some areas where 2,4,5-T concentrations were highest.³⁴
- 7/1/54 Report from Kettering Laboratories of University of Cincinnati (Dr. R. S. Suskind) reported failure of TCA or 2,4,5-T to cause chloracne on rats or human skin.³ Further work proposed. (The rabbit ear test was not used as it was not considered by Suskind to be realistic or reproducible.²⁵⁵)
- Comment: Failure of human skin tests to show chloracne may have been use of too low a concentration. See entries for 11/3/55 and 6/22/56 below.
- 1954 Literature report of acute toxicity of 2,4-D and 2,4,5-T and their various derivatives in rats, mice, guinea pigs and rabbits gave an oral LD₅₀ in the range of 300-1000 mg/kg.²⁴⁷
- 7/27/54 Dr. R. E. Kelly, recognizing further basic research (chloracne testing) will be lengthy and uncertain, recommends improvement in department's exposure potential be made.²⁵⁶
- 4/8/55 "Arch breaker" installation in 2,4,5-T dryer feed hopper eliminates exposure in manual rodding operation.³⁹
- 11/3/55 Dr. Suskind (Kettering Labs) was able to induce chloracne in human skin tests with Halowax 1014 (penta- and hexachloro-naphthalenes) but not with recrystallized 2,4,5-T.^{257,258} No liver disfunctions were noted with either substance.
- 11/17/5 Results of Dr. Suskind's work in attempting to identify chloracnogens were presented to the Workmen's Compensation Commission in Charleston, W.Va.²⁶⁰

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11/18/55 Further testing by Suskind is proposed.²⁵⁹

12/7/55 Memo from R. E. Soden recognizes chloracne problem has not been solved at Nitro and is outstanding problem in dealing with hourly personnel.²⁶¹ He is convinced that Monsanto, Dow and Diamond Alkali experience indicates distillation of TCP will alleviate the problem. Recommends Dr. Suskind's laboratory be engaged to verify whether distillation will solve the problem. Samples were then set to Suskind's Lab.²⁶²

1/10/56 A second environmental survey of the Nitro plant identified further areas needing improvement in reducing worker exposure.⁴⁰

6/12/56 E. P. Wheeler reported on a visit with Dr. H. Oettel and others at BASF (Badische Anilin-und Soda-Fabrik).²⁶³ BASF had on 11/17/53, a TCB hydrolysis autoclave runaway reaction. Chloracne cases developed. The chloracne was accompanied by fatigue, vertigo, painful joints, etc. Cases seemed worse than those experienced at Nitro. Rabbits exposed in cages in the area died shortly of liver necrosis.

They found liver necrosis in rabbits exposed to the following doses of various substances:

15-20 mg. pentachloronaphthalene (e.g. Halowax);
1 mg. chlorinated diphenyl ether;
0.1 mg. residue from TCP distillation;
0.01 mg. highest boiling fraction of the residue from TCP distillation.

Dr. Oettel had no faith in animal skin tests for chloracne, but BASF tested raw material TCP with animal liver function tests using bromsulphophthalein²⁶⁴ before using it for 2,4,5-T production.

BASF was also able to reproduce the hydrolysis runaway reaction in the laboratory, but Wheeler did not get details.

Comment: These results apparently were published in 1957 as noted below.²³²

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6/22/56 New Kettering Lab (Suskind) results were discussed.
228 All tests used NaTCP applied to human skin compared to Halowax. Tests showed NaTCP produced from distilled TCP or a Diamond Alkali dilution - filtration - precipitation procedure were far less chloroacnegenic than plant NaTCP. No liver disfunction was discerned. The reference also stated that examination of Nitro people in 1949 showed minimal liver damage, and in 1953 none was noted in 35 people examined.

Comment: TCDD would have been present in the plant NaTCP. It would have been largely removed by acidifying, separating and distilling the TCP (remaining in the distillation residue). No adequate description of the Diamond Alkali procedure was found. Presumably the NaTCP solution was diluted and filtered (TCDD probably largely filtered out), and TCP then precipitated by acidification. Some of the remaining TCDD may not have been precipitated with the TCP. Unfortunately, this is speculative without further data.

1957 First published synthesis of TCDD was reported.²⁶⁵ Dibenzo-p-dioxin and several other chlorinated isbenzo-p-dioxins had been synthesized previously, and generalized procedures for their preparation were known.

1957 Kimmig and Schulz published an investigation of chloracne cases resulting from TCB hydrolysis.²²² (Chemical Abstracts publication in early 1958). Using the rabbit ear test they showed that pure TCP was not chloracnegenic while the commercial product was. They isolated TCDD from the reaction by-products (details lacking) and showed it to be a potent chloracnegen.

1957 H. Th. Hofmann described (apparently) the BASF incident described previously²²³ (Chemical Abstracts article in early 1958). Extracts from the carbonized residue of the runaway hydrolysis reaction, and from commercial TCP, produced severe liver damage in rabbits at low dosages. Of chlorine-containing compounds tested for comparison, various chlorinated dibenzo-p-dioxins showed similar toxicity.