

Monsanto

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CS7J

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CC:

Nitro

SUBJECT : CEA 9247, 2,4,5-T Overview

REFERENCE :

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Attached for your use is the "2,4,5-T Overview" document.


D. L. Weber

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2,4,5-T OVERVIEW

Following pilot plant testing Monsanto commercial production of 2,4,5-T began at the Nitro Plant in October 1948. Manufacture of NaTCP centered about a 500 gallon autoclave in Building 41. All reactants were manually charged to the autoclave in total prior to heat-up and reaction. The 2,4,5-T production was in Building 34 which included equipment for recovering the excess methanol from the crude NaTCP, reaction of the NaTCP with MCA, separation and purification of the NaTCP salt, dissolving and acidification, and separation of the 2,4,5-T crystals. Drying of the product was done in a number of locations with the product returned to Building 34 for packaging. The initial capacity was targeted at 600,000 pounds per year. The operations were basically manual and operator exposure was high. Close to 40 routine manual operations involving operator exposure were included.

At this time one of the unit operations was the filtration of NaTCP batches. This filtration would have removed a substantial portion of the TCDD present but was a high area of operator exposure. The presence of TCDD was unknown.

The 2,4,5-T product was shipped in drums to the J. F. Queeny Plant where it was converted to various salts and esters. The Queeny process was a simple batch reaction, stripping of excess alcohol and filtration. Blends were also made by mixing various 2,4-D and 2,4,5-T products.

On March 8, 1949 a violent reaction and decomposition in the NaTCP autoclave at Nitro caused a discharge of its contents throughout the area. Cleanup operations resulted in heavy exposure and many cases of chloracne, some quite severe. Chloracne appeared in persons working in the area within a few days. A dermatology expert was called in. He recommended treatments and suggested methods for cleanup of the building.

Production of NaTCP was suspended until August 1949 while the cause of the decomposition was investigated. TCP was purchased to sustain the 2,4,5-T operations. When NaTCP production was resumed the operation was changed to reduce the amount of unreacted TCB in the autoclave at any given time. This lower TCB concentration might have also had a side benefit of lessening TCDD formation.

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2,4,5-T OVERVIEW

In the Summer of 1950 a new NaTCP production unit was started up in Building 51. A 2,500 gallon autoclave was used and capacity was 2.7M pounds per year. Worker exposure and TCDD formation were likely not significantly improved since the new unit employed essentially the same unit operations. In 1951 new cases of chloracne continued to be reported. It became obvious that these cases were not related to the March 1949 incident but were arising out of exposure to the NaTCP/2,4,5-T operations.

By late 1952 a "tarry component" present in the TCB hydrolysis step was implicated as responsible for chloracne. Tests at Mellon Institute showed that TCP distillation could remove much of the chloracnegen, which was concentrated in the distillation residues. However, distillation was never incorporated in the manufacturing operation. Instead steps were taken to reduce operator exposure.

By way of contrast it should be noted that Dow Chemical Company produced a purified NaTCP from the earliest production in 1946. This predates any knowledge of TCDD. Dow separated a "caustic insoluble oil" layer which was incinerated. The NaTCP was then acidified and distilled. As a result Dow 2,4,5-T always had a much lower TCDD content.

In January 1953 new 2,4,5-T facilities were started up in Building 34. Capacity was rated at 2.4M pounds per year. In the new operation process equipment was closed wherever possible. All equipment was equipped with positive ventilation through a wet dust collector. Routine manual operations were reduced by about one-third. Labor intensive operations, such as the use of tray dryers, were replaced with more modern facilities.

The period from 1953 through 1962 was characterized by repeated attempts to improve the Nitro operations, both from a cost/capacity standpoint and also for improved industrial hygiene. Numerous attempts were made to optimize condensation reaction conditions to improve yields.

The first comprehensive environmental survey was conducted in April 1953. It highlighted areas of greatest operator contact: digging out centrifuges; rodding the hopper feeding the rotary dryer; filling and weighing drums at the Rotex; the Alsop filters for 2,4,5-T and the filter press for NaTCP. Within the next few years action was taken on virtually all these items: a mechanical arch breaker was installed in the dryer feed hopper;

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2,4,5-T OVERVIEW

additional exhaust ventilation was provided, particularly in the packaging area; and both the Alsop filters and the NaTCP filter press were eliminated. These last items were especially significant. Eliminating the filtration steps would have had a very beneficial affect on operator exposure. However, any TCDD formed in the NaTCP autoclave would now pass through the entire process and be present in the 2,4,5-T product. The filtration steps likely removed a high percent of any TCDD formed.

Test work in the mid 1950's both by Monsanto and at the University of Cincinnati tended to confirm that pure 2,4,5-T as well as TCA were non-toxic. An unidentified high boiling impurity was suspected but not identified. The possibility of distilling NaTCP as a solution to the chloracne problem continued to be discussed. However, a major concern was disposal of the still residue. Monsanto did not have an incinerator at the Nitro Plant. As a result emphasis remained on industrial hygiene improvements.

During the 1950's research was also done on alternate processes for production of TCP. However, none proved economically attractive.

By 1956 a second environmental survey reported major improvements to rectify areas cited in the 1953 survey. However, overall levels of dust and vapor in the building were not significantly changed. Hence, the need for additional work was indicated. Steps taken included replacing a Tolhurst centrifuge with a lower exposure Fletcher unit, reducing fume problems by making a more dilute NaTCP solution, installing a centrifuge plow, and reslurry tanks under the centrifuges to eliminate the cake conveying step. By 1958 the number of routine manual operations involving operator exposure had been reduced to 16; by 1962 to 13.

The first isolation of TCDD from a TCB hydrolysis process was reported in the literature by Kimming and Schulz in 1957. The first evidence of Monsanto's receipt of this information was in 1959. By 1961 further work, reported in the literature, related TCDD to chloracne and liver damage.

A new Agricultural Ester Plant was started-up in 1961 at the W. G. Krummrich Plant. The process was not significantly different from the Queeny operation except for capacity. Major steps involved the pre-slurrying of 2,4-D or 2,4,5-T in an alcohol, batch reaction in the presence of H₂SO₄ catalyst, neutralization and filtration. Blends of various products were made by mixing in storage tanks or shipping containers. Some limited production continued at the Queeny Plant to supplement Krummrich capacity.

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2,4,5-T OVERVIEW

In August 1963 a new integrated facility for NaTCP and 2,4,5-T was started-up. Capacity was 4M pounds per year. The new unit was highly automated. Only 7 routine manual operations involving worker exposure were required as compared to 13 in the old plants. The frequency and severity of new chloracne cases was greatly reduced in the new plant.

The new 2,4,5-T facility had a number of start-up problems resulting in high costs and a poor quality product. Correction of these problems received priority attention through the remainder of 1963 and most of 1964.

Also in 1963 Monsanto began working with the U.S. Army Biological Laboratories to set specifications and physical properties for planned purchases of ester mixes. One such mix was a 50:50 blend of the butyl esters of 2,4-D and 2,4,5-T designated "Orange". Government sales began in 1963 and increased sharply in 1964.

By late 1964 the 2,4,5-T plant was coming under pressure to increase capacity. As production rates were increased quality problems, particularly color, moisture level, and salts became more significant. Also changes rendered much of the instrumentation unusable thereby increasing manual operations and worker exposure.

Monsanto received from Dow in 1965 an analytical procedure for determining TCDD levels in NaTCP and 2,4,5-T. The method was sensitive to 1 ppm. Normal Nitro production of NaTCP analyzed in the 5-12 ppm TCDD range. This compares to the 1 ppm maximum which Dow was achieving. It is noteworthy however, that while Dow apparently had chloracne complaints from customers there is no evidence that Monsanto ever did. Hence, with chloracne in the new Nitro facility apparently under control there would have been no compelling motive for any major investment to remove TCDD. However, a detailed laboratory study was undertaken to study the chemistry of TCDD formation and possible changes in autoclave conditions to reduce the amount of TCDD formed.

By late 1965 demand pressure from the government was so great that additional ester capacity was required. This was met by two production runs on butyl 2,4,5-T in the ROUGE^(R) facility at Nitro. The esters produced at Nitro were shipped to Krummrich for blending and shipment.

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2,4,5-T OVERVIEW

Government demands for "Orange" reached the limit of industry capacity by mid 1966. Industry was asked to dedicate all 2,4,5-T capacity to meet government needs. Most producers including Monsanto took steps to debottleneck their equipment to increase capacity.

Most projects executed from 1964 to 1968 were designed to increase capacity. Work also continued to improve quality and yields. Attempts were made to insure no deterioration of industrial hygiene by maintaining or improving dust control and ventilation systems. As a result chloracne, while a continuing problem at Nitro, was limited to mild cases. For the first time however, a limited number of cases appeared in the ester operations at Krummrich and Luling. Routine analysis of 2,4,5-T product for TCDD began in 1967.

In 1968 equipment was installed to charge the methanol and NaOH to the NaTCP autoclave under pressure. The reason for this change was to reduce cycle time and hence, increase capacity. However, the reduced cycle time also had the side affect of halving the TCDD level of formation.

The results of the research study into TCDD formation were published in January 1969. Recommended changes called for essentially doubling the methanol TCB molar ratio and some increase in NaOH:TCB ratio. These changes were implemented in the plant and the TCDD level in NaTCP was reduced from over 10 ppm to about 3 ppm. By mid 1969 this had been reduced to 1-3 ppm normal in NaTCP and less than 1 ppm in 2,4,5-T. However, 2,4,5-T production was terminated in August 1969 so little of the higher quality material was actually produced.

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