

Dow Chemical's Chloracne "Incident"

In the 1960's, a "chloracne incident" occurred at Dow's 2,4,5-Trichlorophenol plant. Considering the large number of chloracne "outbreaks" that had previously occurred in several 245-TCP plants operated by other companies, the incident was somewhat unusual. After operating dioxin producing processes for approximately 30 years with an average of only one new chloracne case per year, the company was suddenly faced with an epidemic of chloracne cases.

In January, 1964, two supervisors, three trichlorophenol operators and one laboratory technician developed facial chloracne. Over the next six to seven months, nearly 50 Dow workers in the 245-TCP plant were diagnosed with chloracne. During the early months of 1964, the company tested samples taken from the process and its wastes on the shaved ears of rabbits and obtained an severe chloracnegenic reaction. Additional rabbit testing of "wipe tests" taken from equipment surfaces indicated that the plant was heavily contaminated with a "mystery" compound that was clearly chloracnegenic.

In August, the superintendent of the plant asked the main Analytical Laboratory to examine the oily wastes from the process. The superintendent had read that a compound called "TCDD" had been linked to chloracne and he wanted to determine if any TCDD was present in the process wastes that escaped from the plant's leaky pipes.

Eventually, Dow's analytical scientists confirmed that the "mystery" compound was indeed TCDD, the same chemical that a German company, C.H. Boehringer Sohn, had reported in scientific journals and in a letter to Dow some seven years earlier in 1957. In December of 1964, Dow's analytical scientists determined that the plant's oily wastes contained astonishing levels of TCDD – 6,000,000,000 to 10,000,000,000 ppt (6,000 to 10,000 ppm – 0.6 to 1.0% TCDD).

This would be the highest levels of TCDD found in chemical wastes at the Midland plant until a level of 26% TCDD was found in demolition wastes from the Ronnel insecticide plant in the 1980's.

What was extremely surprising was Dow's response to the contamination of the plant and its employees by TCDD. In retrospect, if TCDD is really as harmless to human health, as Dow would repeatedly claimed in later years, then the company's response was definite "overkill". However, in 1964, Dow may have known very little about the toxicity of this "mystery" compound except that it was extremely lethal to rabbits and caused a severe chloracne reaction in humans. The few reported cases of worker death following exposure to the "mystery" compound had not been scientifically confirmed in 1964 – at least, probably not to Dow's satisfaction.

As later sections will show, even after more than 20 years of additional research into the human health risks of TCDD exposure which Dow has claimed fail to establish any link between TCDD and cancer, the company, nevertheless, used extraordinary procedures to decontaminate dioxin contaminated equipment and buildings and prevented entry into locations that were once the site of 245-TCP plants.

At Dow's annual stockholders meeting in May 1970, H. D. ("Ted") Doan, grandson of H. H. Dow and president of the company, talked about Dow's problems and successes related to environmental concerns, "You have heard much about 2,4,5-T as a defoliant in Vietnam – less I presume, about its role increasing food production. Dow has made and sold 2,4,5-T since 1948. In 1964, we ran into difficulties with an impurity in the process, shut down the plant, identified the problem, redesigned the plant and starting producing in 1966 after spending an extra \$5 million to keep the impurity at a level considered safe, less than one part per million. ... In our opinion, Dow's 2,4,5-T does not present a hazard to health – in fact, has a large margin of safety – when used as recommended."

This definitely seems like an accomplishment that the company should be rightly proud of. However, Mr. Doan did not provide a full account of the "difficulties" nor of Dow's reaction to events.

The main "difficulty" was chloracne. There may be a misconception that chloracne is a mild skin condition similar to the blackheads and small pimples associated with teenage acne. This is true only for extremely low exposures to dioxins. Chloracne associated with higher dioxin exposure is significantly more severe and may, at times, be disfiguring.

Severe cases of TCDD exposure are characterized by boils and lesions (open wounds) on the face, neck, back and legs of exposed workers. Boils the size of an adult's thumbnails contain large amounts of pus that re-accumulate even though the boils are drained periodically. With time, the skin takes on the exaggerated appearance of the rough skin of an orange. Some exposed chemical workers have lost the tips of ears due to painful and non-healing blisters.

The number of "blackheads" (plugged sweat glands) can be so severe that the skin takes on a dark hue. Hyperpigmentation (a darkening of skin on the head, neck and hands) can range from a mild redness to a very pronounced "dark grey, intense, dusky bronzing". Dioxin related hair growth on the forehead and eyelids has been reported.

A number of the chlorophenols produced by the company were sold under the tradename, Dowicide (See Table B for more information). The chloracne experienced by the Dow's workers in these plants was labeled "Dowicide bumps" and consisted of large boils and bumps – areas of thickened skin possibly resulting from bacterial cellulitis.

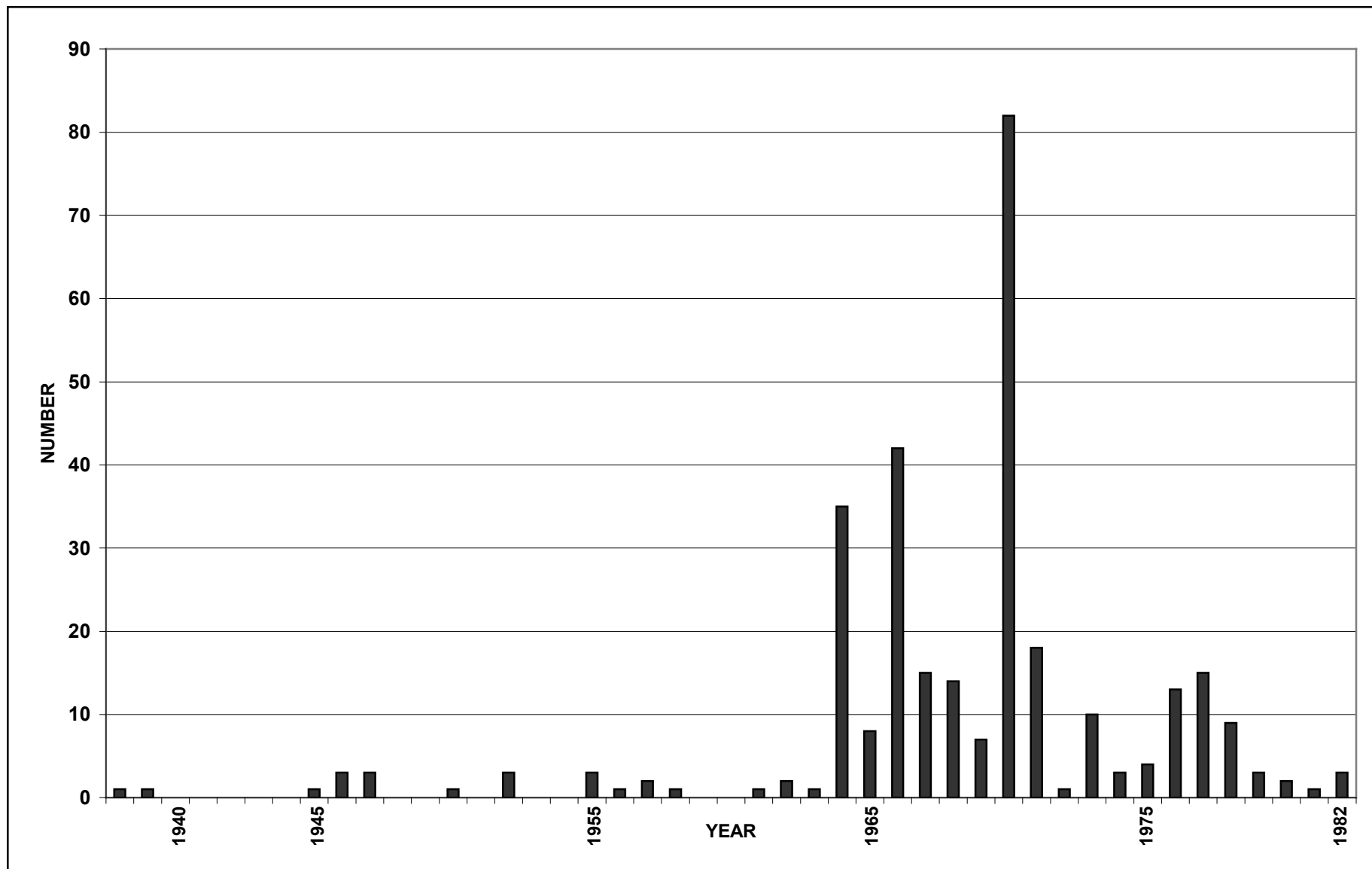
Workers that contracted chloracne also experienced a wide range of medical and psychological conditions that persisted for a number of years after exposure. A number of medical journal articles reporting on the health effects of TCDD exposure indicate that a large percentage of exposed workers developed porphyria cutanea tarda, a disease of the body's blood-forming elements characterized by a darkening of the urine by nitrogen containing compounds.

In 1964, Dow's medical director reported that TCDD exposure primarily affects the skin but in extreme exposures "a general organ toxicity can result. This is primarily demonstrated in the liver, hematopoietic [blood forming] and nervous system." The report continued, "fatalities had been reported in the literature."

Until 1964, the number of chloracne cases per year in the various chlorophenol plants, including the early 245-TCP plant, were relatively few in number. Table A on the

following page is a history of chlorophenol related chloracne as reported by the company.

Table A
Dow Chemical, Midland Plant
Chloracne Cases



It should be noted that the number of cases of chloracne from 1938 to 1964 may be understated due to the reluctance of Dow workers to report a medical condition that was an expected consequence of working in a chlorophenol manufacturing process area.

European researchers investigating the severity of chloracne events have reported that some dioxin exposed workers that failed to shower or change clothes prior to leaving work contaminated their homes. The wives, children and even dogs of these workers also contracted chloracne. Dow never reported if its TCDD investigations determined if chloracne was present in the households of its workers.

Since the initiation of the manufacture of chlorophenols in the 1920's, Dow has had a number of chemical processes that produced a wide variety of dioxins and furans.

1. The company began the manufacture of chlorophenols by the direct chlorination of phenol in the 1920's. The dioxins formed in the batch chlorination process were primarily the higher chlorinated hepta and octachlorodioxins (H/OCDD). When the principle product being produced was pentachlorophenol ("Penta"), the reactions were carried out to completion and the levels of dioxins/furans increased. For a number of years, Penta was not purified and any dioxins formed were not removed and became part of the sales product.

The exact levels of dioxins contained in the Penta product manufactured by Dow are not known with certainty. However, a 1987 study of Penta sold by a number of companies other than Dow indicated dioxin levels as high as 3,200,000,000 ppt (3,200 ppm) – 0.3% H/OCDD. The high levels of dioxin were found in commercial products sold in the 1985 to 1988 time period – more than 20 years after the hazards of dioxin exposure became widely known and manufacturers should have taken steps to reduce dioxin levels in their products. The levels of H/OCDD in Penta sold in the 1930's and 1940's is not known.

The direct chlorination process could be operated to produce a wide range of other chlorinated phenols – dichloro's, trichloro's and tetrachlorophenols. If these products were needed in large quantities, the chlorination reaction was carried out lower temperatures and at shorter reactor

residence times. During the high temperature distillation process required to separate the various chlorinated phenols, dioxins were a waste stream and were either transported to the chemical waste ponds or to the tar burner/incinerator in large metal containers called “tar boxes”. The tar boxes remained in service until the 1990’s and were used to dispose of a wide variety of waste chemicals.

2. The direct chlorination process was capable of producing **2,4,6**-trichlorophenol in large quantities. However, the **2,4,5**-trichlorophenol isomer was produced at much lower levels. When the initial Dow products (Dowicide “B” and Dowicide “2”, Dowicide “2S”) based on 245-TCP began to be sold at greater and greater quantities, the company installed a new process to produce 245-TCP.

For a number of years (192? to 194?), Dow produced 245-TCP by the chlorination of aniline followed by a diazo reaction to convert the –NH₂ group on the benzene ring to –OH. The company had practiced a number of azo reactions as part of their dyestuff businesses and had, for a number of years, successfully operated the highly reactive azo chemistry. The aniline process was installed in the Aromatics Plant (199 Building) of the chlorophenol complex.

The chlorinated aniline process is not known to be a major source of any chlorinated dioxin or furan unless high temperature purification of 245-TCP was required. Some samples of the sodium salt of 245-TCP (Dowicide 2S) have been shown to contain approximately 49 ppm (49,000,000 ppt) of total TCDD (all isomers). However, these samples were obtained in 1972 and are not representative of dioxin levels in 245-TCP produced from aniline.

3. In the mid-1940’s, the company began to commercialize 2,4,5-T herbicide and a new, higher capacity 245-TCP process replaced the chlorinated aniline process. One Dow source indicated that the new process was installed in 1942, a second Dow source indicated that the actual year was 1946. Both agree that 199 Building was the location of the new 245-TCP process. The new process was based on the hydrolysis of tetrachlorobenzene via high temperature reaction with liquid caustic and HCL. The process was very similar to the chlorobenzol process the

company had used for many years for the large scale production of phenol at the Midland plant. The 1940's 245-TCP process was a batch reaction and would remain so until 1963.

Initially, the chlorination reaction was carried out at relatively low temperatures (~155°C) and small amounts of TCDD were produced. It is not known if the low temperature of the reaction was intended to reduce reactor pressure or to minimize the amount of by-products and impurities (dioxins/furans) that would form at higher temperatures. TCDD that formed in the process was removed in the purification process that separated tetrachlorobenzene, 245-TCP and waste "tars". The number of chloracne cases associated with the new chlorobenzene 245-TCP process were small in number for a number of years.

4. In the early 1960's, the demand for 2,4,5-T (and 245-TCP) increased dramatically due to the use of Agent Orange and other 2,4,5-T herbicides in the Vietnam War. In 1963, in order to meet the demands for higher sales volumes, Dow changed the 245-TCP process from "batch" to "continuous" by connecting several chlorination reactors in series and raised the reaction temperature to ~ 225°C.

The levels of TCDD and the number of cases of chloracne increased dramatically with the increase in temperature. The TCDD formed in the new TCP was primarily 2,3,7,8-TCDD, the most chloracnegenic of all the dioxins and furans. The company has not provided any information of the levels of TCDD produced in the initial tetrachlorobenzene process. Following the chloracne outbreak in 1964, the company reported that 2,3,7,8-TCDD levels in the modified high temperature process averaged 1,818 ppm with every process sample that was taken being positive for TCDD. In 1964, concentrated waste streams from the high temperature process contained dioxin levels of 0.6% to 1% 2,3,7,8-TCDD (6,000,000,000 to 10,000,000,000 ppt-TCDD).

During this time period, the concentrated TCDD waste streams were incinerated in the company's tar burner that had built in 1957. The 1957 tar burner had been constructed without adequate air pollution control equipment and was known to both employees and Midland residents as a major source of "local air pollution" resulting from the incomplete combustion of

wastes. The 1957 unit continued in operation until replaced by a greatly improved tar burner in 1968.

5. Six years earlier, in 1957, the company had been informed by C.H. Boehringer Sohn, a German manufacturer of 245-TCP and 2,4,5-T, about the dangers of creating very high levels of TCDD when operating the chlorobenzene reaction at temperatures higher than 155°C. Boehringer wrote a letter to all the known producers of 245-TCP informing them of the high temperature problem. Dow acknowledged receipt of the information and thanked Boehringer for the information.

However, for some reason, the Boehringer information was ignored and, in 1963, Dow raised its reaction temperatures to 225°C – 70 degrees higher than the safer level suggested by the German company.

It is possible that the high levels of TCDD may have come as a complete surprise to Dow since the company has indicated that the Boehringer information was “filed and forgotten”.

It is also possible that the company’s chlorophenol scientists knew about the potential formation of TCDD but believed that their technology was superior to that of the Germans and that TCDD formation could be controlled even at temperatures higher than specified by Boehringer. Since the process changes (from batch to continuous, higher temperatures) to the 245-TCP process were significant, it is unlikely that the chlorophenol scientists would not have been involved in changing the process. Whatever the reasons, when large numbers of employees were diagnosed with chloracne, the TCDD problem was discovered.

Prior to 1964, the incidence of chloracne in the old Chlorophenol Plant was relatively rare with 1 – 2 new cases a year, if that many, being diagnosed. In 1964, Dow Medical diagnosed nearly 50 new cases of chloracne in the modified TCP plant.

Chloroacne is one of the few diseases that Dow attributes to TCDD exposure. Chloracne was first described in 1897, and was originally thought to be attributable to exposure to newly formed

chlorine – hence the term “chloracne”. With time, it was recognized as being the result of overexposure to a wide variety of chlorinated aromatic hydrocarbons, including dioxins and furans. 2,3,7,8-TCDD is the most potent chemical capable of producing the chloroacne response in humans.

With credit to Dow’s Medical and Industrial Hygiene Departments, the reason for the outbreak of chloracne was soon known : the TCP plant was heavily contaminated with TCDD. “Wipe tests” reported that the TCDD level in the plant averaged 27.3 µg/wipe ($\mu\text{g} = 10^{-6}$ gram = 1 millionth of a gram) on those surfaces that were tested. TCDD contamination on surfaces in the various chlorophenol plants not making 245-TCP was essentially non-detectable. (A wipe test consists of wiping a 10 sq. cm. area with a solvent laden filter paper and then determining the amount of contaminant picked on the filter paper through subsequent laboratory analysis).

Even process areas that should have been relatively free of TCDD were experiencing high levels of chloracne among the employees that worked in those areas. From this information, it is reasonable to conclude that TCDD had contaminated the entire plant to levels that were potentially hazardous to human health.

In 1965, just prior to the shutdown of the high temperature process, the chloracne problem was so severe that TCP plant operators were changing clothing and showering in mid-shift. The production rate had been reduced to 25% of normal in order to reduce chloracne. It is not known if the reaction temperatures were also reduced to safer levels.

Within a very short time, Dow constructed a new plant (TCP Production Plant, 804 Building) to correct the TCDD contamination problem. The company had purchased the Boehringer process for the manufacture of 245-TCP which was capable of operation without forming high levels of 2378-TCDD. The Boehringer process was based on the reaction of tetrachlorobenzene with caustic and methanol. The methanol helped to shorten reaction times with a resulting reduction in TCDD levels.

The new plant was started up in 1966 and approximately 40 new cases of chloracne were diagnosed that year – leaks and spills are part of the startup of most chemical processes. The number of chloracne cases declined to a low of 5 new cases in 1969. The problem appeared to be solved or, at least, reduced to an acceptable level.

However, in 1970, the same year in which Dow Mr. Doan reported this success to the Dow stockholders and investors, a record high number of 90 cases of chloracne were reported in the new plant. The company would continue to struggle with chloracne at its 245-TCP production plant until it was finally shutdown in 1979 – a year in which only five new cases of chloracne would be diagnosed.

6. Dow's response to the "Chloracne Incident" continues to be remarkable. For a skin condition that some have claimed is only a mild form of acne and the only proven consequence to TCDD exposure, Dow acted extremely quickly to correct the problem. The company shutdown the existing high temperature plant, invested \$5 million for a new plant based on a competitor's process and possibly lost several million dollars in reduced 2,4,5-T sales during the 12 to 18 months that 245-TCP was not produced in Midland.

Table B is a summary of typical dioxin and furan levels found in commercial samples of the various chlorophenols. In some cases, maximum levels are reported. Although the corresponding Dow Tradename is shown, none of the samples were obtained from the company. The only exception is the TCDD analysis of the waste streams found in Dow 245-TCP plant while being operated at high temperatures in 1965.

Table B
Chlorinated Phenols – Dioxin/Furan Levels
Commercial Products

<u>Chlorophenol</u>	<u>Dow Trademark</u>	<u>Total D/F</u> (ppt)	<u>All TCDD Isomers</u> (ppt)	<u>2378-TCDD</u> (ppt)	<u>Sample Date</u>
245-TCP	Dowicide 2	8,040,00 (8 ppm)			1972
245-TCP, sodium salt	Dowicide B	14,000,000 (14 ppm)			1972
246-TCP	Dowicide 2S		49,000,000 (49 ppm)		1972
246-TCP, sodium salt		60,000,000 (60 ppm)			1978
2346-TetraCP, sodium salt		182,200,000 (182 ppm)	700,000		1978
PentaCP	Dowicide 7	3,178,598,000 (3,178 ppm)	< 10,000	< 50	85 - 88
245-TCP waste stream - 199 Bldg. Midland plant				10,000,000,000 (10,000 ppm) (1%)	1965
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Mr. Doan also failed to mention that the company was so concerned about determining a “no-effect” level of TCDD exposure that it carried out testing of TCDD on the skins of prisoners in a Philadelphia county jail located in Holmesburg, PA. It is possible that Mr. Doan was not aware of the human testing although his directors of research and production must have been.

During the mid-1960's, the company developed ample information as to the levels of TCDD that would cause a chloracne response on the shaved ears of rabbits but lacked information as to the minimum TCDD exposure levels that would cause a similar result in humans.

Dow contracted with Dr. A. M. Kligman, a professor of dermatology at the University of Pennsylvania, to include TCDD in his existing research program on the response of humans to chemical exposure. The company informed Dr. Kligman that TCDD had been found to be extremely lethal to rabbits and that all TCDD solutions should be labeled with the warning: "Danger! This material is *extremely toxic*."

The TCDD testing program began in 1965 and ended in 1967. The total number of prisoners that were actually tested is unknown and estimates have ranged from 150 to 200 prisoners. Dr. Kligman was a very aggressive researcher intent on providing the company with some level of results. When low amounts of TCDD applied to the forehead and mid-back of the prisoners did not result in chloracne, Dr. Kligman continued to apply greater amounts until a maximum of 7,500 micrograms of TCDD had been applied every other day for a month to 10 new test subjects. Eight out of ten of the prisoners developed chloracne with lesions (open sores) lasting 4 to 7 months. The duration of the lesions may have been lengthened by Dr. Kligman's decision that "no effort [be] made to speed healing by active treatment."

The bio-testing also included using a group of prisoners as a control group in which varying levels of Dow's hexachloro-diphenyl oxide ("a known potent chloracne") were applied to a group of 60 prisoners.

The company did not seem concerned that the initial group of TCDD tested prisoners were primarily African-American (47 out of 56 : 83%) even though the vast majority of its own Midland workers were Caucasian. Despite this problem, Dow authorized further testing of higher levels of TCDD.

When Dr. Kligman subsequently reported that 7,500 micrograms of TCDD had been applied to the skin of 10 prisoners – Dow had specified a maximum of 16 micrograms – the company

terminated the testing program. The company failed to follow up to determine if any prisoners had any permanent health effect. Despite the discomfort and pain to the TCDD exposed prisoners, the company failed to obtain any meaningful information from the study.

Dr. Kligman was paid \$10,000 to carry out the study. That spending level should have been well within the spending authority of the Dow research director that authorized the Holmesburg Prison testing. However, the research director requested approval of the “directors of research and production” and approval was granted provided that “Dow was relieved from any liability that might be incurred by [the] experimental work.”

7. Dow’s concern about dioxin exposure is further shown in the procedures used to demolish the plant that was associated with the “Chloracne Incident”. Following start-up of the new Boehringer process in the 804 Building in 1966, the old Aromatics plant (199 Building) was demolished in 1967. All process equipment was cleaned with acid and rinsed three times with soap and water. Wipe tests were used to verify cleanliness. Laboratory reports on remaining contamination levels ranged from “Clean. Congratulations” to “Dirty. Cleanup immediately and re-test. May be hazardous over period of time.”

Cleaned process equipment and contaminated demolition rubble were buried at the Midland plant in an unknown location. One possible location is the triangular pond on the west side of the Tittabawassee River adjacent to Dow’s “T-Pond”. The Operating Permit for the Midland plant indicates that this area has been “Closed with Unknown Fill Material in Place.”

In the 1980’s, after almost 20 years of additional research on the toxicity of dioxins and their risk to human health, the company began to demolish the various buildings and processes associated with its 245-TCP and other chlorophenol products. Again, both the process equipment and buildings were cleaned and wipe tested for dioxin contamination. Some of the demolition material may have been disposed of at the Midland county landfill. Some of the equipment and construction debris that could not be decontaminated to a clean enough level was disposed of at the Midland plant. During this time period, the ash cooling pond associated with the Southside Powerhouse (500 Building) began to be filled with material, possibly dioxin

contaminated debris. The Operating Permit for the Midland plant reports, "Former Cooling Pond Closed with Unknown Fill Material in Place".

Dow's concern about this relatively harmless dioxin continues to be unusual. After the EPA banned the sales of 2,4,5-T, the 804 Building TCP plant was demolished. The ground where the plant used to stand was graded smooth and covered with blacktop. The area was enclosed with a yellow chain and several "Do Not Enter" signs were posted in the area. All of these closure provisions were enacted without any regulatory "assistance" from the EPA or DEQ and speak to the concern that the company had about further accidental TCDD exposure.

In 1988, as the EPA became more involved in Dow's areas of historic dioxin contamination, the TCP plant site was designated as LEL Site 1. "LEL" indicates Locally Elevated Levels of dioxins and furans. The EPA closure requirements may have required the installation of clay slurry walls and a clay cap to prevent further spread of dioxins by groundwater flowing to the river.

All of this extraordinary treatment of an area where a plant used to operate might lead someone to believe that Dow may know a great deal more that they have told its workers and the Midland residents about the hazards of TCDD exposure.

More than thirty years after the 1970's stockholders meeting, dioxin is still a large part of Dow's culture and various dioxin issues consumes a large part of the company's resources. All of this, over a low level impurity associated with a mild skin irritation problem.

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