Original/Box #3 on #7
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cc: ~~F. P. [illegible]~~
W. S. [illegible]
J. P. [illegible]
4.

VERTAC CHEMICAL CORPORATION
24th Floor • 5100 Poplar • Memphis, TN 38137 • 901-767-6851

REPLY TO: P. O. BOX 69
JACKSONVILLE, AR 72076
(501) 982-9481

February 16, 1981

Ms. Roxanne Jayne
Hercules Incorporated
910 Market Street
Wilmington, Delaware 19899

Dear Roxanne:

Enclosed is a copy of the information you requested in our phone conversation last Friday.

Hope this will be of help to you.

Sincerely yours,

VERTAC CHEMICAL CORPORATION
Jacksonville Plant

A. E. Sidwell

A. E. Sidwell, Ph.D.
Director of Research

AES:ew

Enclosures: (History of Trichlorophenol and 2,4,5-T Acid Manufacture at Jacksonville, Arkansas - 9/17/76)
(Chemistry of 2,4,5-T Production - 9/17/76)
(TCDD Content of Soil and Liquid Samples - Memo, A.E.S. to T. Bennett, Jr. - 10/27/76)

EXHIBIT
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OLP 7-23-87

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FEB 23 1981

HISTORY OF TRICHLOROPHENOL AND 2,4,5-T ACID MANUFACTURE AT JACKSONVILLE, ARKANSAS

Trichlorophenol and 2,4,5-T acid have been manufactured in Jacksonville, Arkansas, for the past nineteen years. Another phenoxy-herbicide, 2,4-D acid has been made for a longer period at the same location. However, this is written to provide a history of the production of 2,4,5-trichlorophenol and 2,4,5-T acid. Both of these materials have been the subject of recent and continuing public interest.

As a result of the unfortunate accident in Italy, all manufacturers of 2,4,5-TCP have been reviewing the safety aspects of their operations. The facility in Jacksonville, Arkansas, has safely produced TCP for many years. The chemistry design and operation at this facility is considerably different from that in Italy. Although safety controls and operations here are demonstrably believed to be adequate, additional controls will be installed. These controls will totally contain all safety pressure releases from the TCB reactors and water wash all reaction materials from the released vapors. The added control measures will consist of an additional automatic pressure relief on each reactor, a high pressure blowdown or catch tank, and a water scrubbing tower.

REASOR-HILL CORPORATION

The plant in which these materials are produced in Arkansas was originally a part of the Jacksonville Ordnance plant which was built and operated for the Government in the 30's and, early 40's. The Reasor-Hill Corporation, established in late 1946 by Dr. Lyle O. Hill, a native of Russellville, Arkansas, and the late Mr. Gerald Reasor, then a Chicago business executive, purchased the site from the Government. The corporation first began production of cotton insecticide dust, it later expanded to other types of insecticide production and finally began making the herbicide, 2,4-D acid and esters, in a well isolated portion of the plant to avoid cross contamination.

Production of 2,4,5-T acid was begun in October 1957 after about a year of laboratory work on the method. Although both 2,4,5-T and 2,4-D are made by an essentially similar process from monochloroacetic acid and an appropriate chlorophenol, 2,4,5-trichlorophenol, from which 2,4,5-T is made, is more difficult to prepare than 2,4-dichlorophenol used in making 2,4-D.

LABORATORY STUDY

Laboratory work by the author and co-workers was concentrated on the preparation of 2,4,5-trichlorophenol as its sodium salt. Though other companies already were engaged in the manufacture of 2,4,5-T acid at that time, relatively little information was available in the form of published chemical literature. However, since one reasonably economical, direct route to prepare the needed trichlorophenol involves the treatment of symmetrical tetrachlorobenzene (TCB) with caustic (NaOH) in methyl alcohol (CH_3OH), this reaction was studied extensively.

Most of the work was done using a Parr laboratory pressure reactor. The reaction needs heat to get started, then requires cooling to control the heat and pressure generated while the primary reaction takes place. Various weight ratios of TCB, NaOH and methyl alcohol were mixed and heated to start the reaction in the Parr reactor. The resulting temperatures and pressures developed during the reaction by the different mixtures were noted. Various lengths of time were employed in ageing after the reaction had subsided to ensure completion. The information obtained was then used to design a method for larger scale manufacture which would minimize potential danger due to temperature and pressure and maximize safe operating conditions and useful product.

It was decided to limit the amount of material to be produced in a plant reactor to a quantity which could be heated to start the reaction but which also could be cooled successfully in controlling the heat produced during the reaction. Essentially this meant that the reaction vessel must have a volume to internal surface ratio sized to either add or remove heat rapidly in order to insure safety.

INSTALLATION

As a result of the experimental work and consideration of safe operation, Reasor-Hill purchased a 500 gallon vessel designed at 350 PSI and actually tested at 525 PSI. The normal operation proceeded at pressures well below the design pressure. The vessel was fitted with a relief valve to release small amounts of vapor should the pressure exceed the normal working pressure. After the heat generated by the reaction has subsided, which can be controlled by cooling, the material must be aged about five hours. During aging the compound first formed (a methyl ether of TCP) reacts slowly with the alkaline methyl alcohol to form the sodium salt of trichlorophenol, at the same time producing volatile dimethyl ether. Most of the dimethyl ether dissolves in the liquid mixture under pressure, but it has a low boiling point and slowly exerts increased pressure at the temperature employed during the aging process. (Currently the pressures are controlled well below 350 PSI during the aging process, and the dimethyl ether vapors are absorbed in a water scrubber and discharged to waste during distillation, being decomposed by bacteria in the city sewage treatment plant.)

The vessel was also provided with a rupture disc designed to relieve well below the vessel test pressure. This permitted sudden reduction of pressure within the reactor should the pressure during initial reaction rise unduly above the normal working pressure. The pressure reduction allowed rapid evaporation of methyl alcohol which has the effect of sudden cooling of the reactor mass. Such sudden cooling in addition to forced external cooling by water immediately drops the temperature of the reacting mass. The drop in temperature prevents the reaction from continuing.

In addition to the necessary tanks, pumps and piping the vessel was fitted with recording temperature and pressure measuring devices. These recorders were placed so that the operator could know what conditions were present within the reactor at all times after the reaction mixture had been charged to the vessel and fully prepared by checking all valves and bolted closures. The reactor was situated within one of three bays having reinforced concrete walls. The recorders and all operating steam and water valves were placed in the bay furthest away from the reactor.

After a reaction was complete and ageing finished, the reactor was allowed to cool down from the ageing temperature. The pressure thus was reduced so that dissolved dimethyl ether could be vented. The reactor product then could be pumped to a still for the removal of methyl alcohol while adding an equivalent mass of water. When the methyl alcohol had been completely removed, the water solution of sodium trichlorophenate together with sodium chloride and excess caustic was permitted to cool to a temperature that would allow it to remain liquid. This liquid was then pumped to a heated storage tank.

HERCULES INCORPORATED

This reactor and equipment was used by Reasor-Hill without trouble and by Hercules Powder Company (now Hercules Incorporated) who purchased the plant in December, 1961, for several years thereafter. After Hercules bought the plant all insecticide production was stopped at the site. Production was limited to phenoxy-herbicides and various production improvements were made.

Sometime in 1965 Hercules made a decision to increase the capacity of the plant for the production of 2,4,5-T acid. This meant that the capacity for making trichlorophenol had to be increased.

Hercules reviewed the production history of safety and efficacy of the existing procedure for making trichlorophenol. After consideration by their Engineering and Safety Departments two additional reactors of the same design as the original one were installed. These reactors often were operated round the clock especially during the period that the Government was requiring the material called 'Orange'. ('Orange' was a mixture of about 50-50% by weight of the butyl esters of 2,4-D and 2,4,5-T used by the military to effectively defoliate areas around their installations in Vietnam.) Since that period, as the demand for 2,4,5-T has dropped to that of the domestic and foreign markets, all three of the reactors have been continued in use as required.

TRANSVAAL, INC.

Transvaal, Inc. purchased the plant on October 1, 1971. Under these owners the original method of processing has been continued, with improvements in the handling of potential air or water pollution.

DIOXIN ANALYSIS

The discovery in 1970 that formulations of 2,4,5-T from various sources contain variable amounts of a highly toxic contaminant, TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin), prompted the cessation of its use in Vietnam. The use of 2,4,5-T was restricted and a total ban on the use of 2,4,5-T having a "high" dioxin content has been imposed by the U. S. Environmental Protection Agency.

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Fortunately investigations by the Aerospace Research Laboratories, U. S. Air Force, published in May 1975, indicate that the dioxin content of 'Orange' supplied to the military from this plant show an average of less than 0.05 parts per million of dioxin. Averaged analyses of samples of 'Orange' from other manufacturers mentioned in the ARL report ranged from 0.12 ppm to 14.2 ppm dioxin. The work done by Aerospace Research employed gas chromatograph-mass spectrum analysis capable of lower concentration determinations than by chromatographic method alone.

This appears to confirm work done in our laboratory covering analysis of pooled retained samples of 2,4,5-T acid produced during the period January 1966 through May 1970. Our findings reported in a letter to Hercules Management dated

January 27, 1971 (copy attached) were to the effect that all samples examined for dioxin by a gas-liquid chromatograph method contained less than 0.1 part per million. However, as a precaution we have continued routine examination of pooled batch samples of 2,4,5-T acid and have never found dioxin present in amounts greater than 0.1 ppm. (After the acid has been converted to an ester the dioxin content should drop because of the increase in mass of the ester.)

Samples of our 2,4,5-T acid examined as a courtesy by a competitive company have also been reported to have TCDD content below 0.1 ppm.

DIOXIN SOURCE

It is the writers firm belief that the source of the dioxin or related dioxins present in the 2,4,5-T acid is the reaction by means of which the trichlorophenol used is formed. Most experts and the Report of the Panel on Herbicides of the President's Science Advisory Committee confirm this view. Our method does not appear to produce dioxin in significant quantity. However we have under way tests of various waste materials and recycled liquors to determine if these might concentrate dixoin and thus be a hazard.

EFFECTS OF EXPOSURE

The writer has worked for twenty years with various phenoxy herbicides both in the laboratory and in the plant. No ill effects have ever been noted. Occasional instances where accidental skin contact with the alkaline sodium trichlorophenate solution, or with raw trichlorophenol dissolved in recycle liquors, has produced local chemical burns on arms or hands. These tend to heal within a short time and the skin appears to be quite normal after healing. This is also true of many plant workers who have from time to time over the years been 'burned'.

A.E. Sidwell

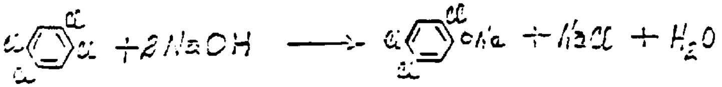
Dr. A. E. Sidwell
Director of Research

September 17, 1976

CHEMISTRY OF 2,4,5-T PRODUCTION

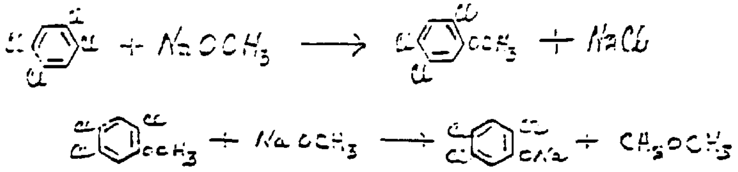
The manufacture of 2,4,5-T starts with production of 2,4,5-trichlorophenol from 1,2,4,5-tetrachlorobenzene, ideally by removal of one chlorine atom substituting an hydroxyl radical in its place, with generation of a molecule of sodium chloride.

Thus, on paper,



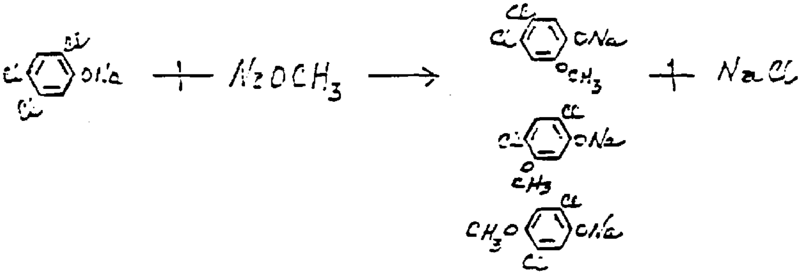
However, the reaction must be carried on in a solvent (methanol or a glycol) which will permit the materials to interact. It is necessary to heat the mixture to effect solution of the two reacting substances. At the temperature where the tetrachlorobenzene melts, the caustic has largely dissolved in the alcohol. This condition permits an intimate mixture of the ingredients, promoting interaction.

Study of the reaction shows that in reality caustic reacts with methanol (and glycol) to produce some $NaOCH_3$ (or $NaOCH_2$-CH_2OH) and water. The $NaOCH_3$ then reacts as follows:



Once the reaction is started, heat is developed. This heat must be removed or the pressure developed, as also temperature of the reacting mass, will rise rapidly. With high temperatures many side reactions other than that desired can and do occur.

Some of the side reactions may be illustrated as follows:



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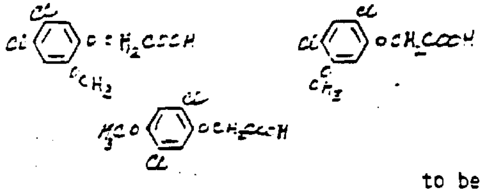
where any one of the other chlorine atoms may be lost and substituted by a methoxyl group. This permits of variable small amounts of

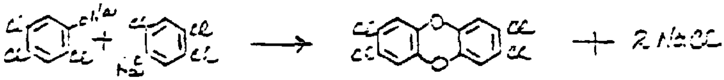


and

to be present with a major amount of the desired product.

Vanishingly small amounts of further products of dechlorination are to be expected.

If temperature and/or concentration are too high, further reaction may result in the formation of 2,3,7,8-tetrachlorodibenzo-p-dioxin:



If the temperature or concentrations employed are too high, or if the temperature rises out of control, this reaction and autoxidation of the mass can take place.

2,4,5-T acid results from the reaction of $ClCH_2COOH$ and 2,4,5-TCP as sodium salts to form the sodium salt of 2,4,5-T. The free acid is obtained by acidification. Since the other sodium salts of secondary dechlorination products couple to varying extents with monochloroacetic acid, such related materials will be present as minor impurities in the 2,4,5-T acid. Several of such impurities have been shown to have biological activity similar to 2,4,5-T.

AESidwell:ew
September 17, 1976

TRANSVAAL

October 27, 1976

TO: MR. THURMAN BENNETT, JR.

FROM: A. E. SIDWELL

SUBJECT: TCDD CONTENT OF SOIL AND LIQUID SAMPLES

REPLY REQUESTED BY

Several samples were taken and assayed for 2,3,7,8-tetrachlorodibenzo-p-dioxin.

Sample No.	Type	Location	Amount Taken	TCDD Content
1	Liquid	Effluent from city stabilization ponds	2,250 ml.	Not detected
2	Liquid	Plant effluent at V notch	2,300 ml.	0.2-0.6 ppB
3	Solid	Sludge from lime pH adjusting pit	150 gm.	14 ppB
4	Solid	Earth from site 40-50 ft. from TCP operation	197 gm.	2.9 ppB
5	Solid	Earth from culvert head (drainage from TCP area)	160 gm.	8 ppB
6	Solid	Sweepings from concrete diked area at TCP operation	200 gm.	57 ppB

Samples #1 and #2 were continuously extracted via liquid-liquid extractor for 24 hours.

Samples #3, #4, #5, and #6 were first dried in air at 55° C., then the weights shown were extracted for 24 hours in Soxhlet apparatus.

A. E. Sidwell

A. E. Sidwell

AES:ew

cc: Mr. R. A. Guidi - Vertac - Memphis
Mr. Jarrell Southall - Arkansas Pollution
Control and Ecology Commission