EXHIBIT
MULHOLLAND
2
3-14-84 mjt

NAUGATUCK CHEMICALS
DEVELOPMENT DEPARTMENT

"DIOXIN" and DOW Midland

2,4,5-Trichlorophenol

August 10, 1965

SUMMARY

1. Ross Mulholland arranged and conducted a highly satisfactory tour of Dow's Midland Bioproducts Division for THE on August 3. Problems of "DIOXIN" were discussed very freely.

2. H&T should investigate Dow's (Midland) GLC methods for determination of "DIOXIN" using samples of "DIOXIN" to be received from Midland.

3. THE will maintain contact with Ross Mulholland and Dow (Midland) re "DIOXIN". Dow suggests that no 2,4,5-T products containing "DIOXIN" should be sold.

4. This problem should not be discussed outside this Division, at present.

J 3761

INTRODUCTION

The Biochemical Research Department of Dow (Midland) is a comparatively new building, #1701, in the main plant. We were accompanied by Douglas Johnston, a young Scotsman who is Development Manager for Herbicides at Dow, Sarnia. Our chief contact at Midland was Lawrence Silverstein, a chemist with considerable background in radio and tracer techniques. An M.D. with about twenty-five years as a general practitioner, and now employed at Midland for about a month, also took part in the discussions.

Effects of Dioxin

Folliculitis

This is an inflammation of the hair follicles which eventually causes them to enlarge and bleed. Scab formations continue, depending on the severity of the contact of the Dioxin. Eventually necrosis and death of the animal will occur. Apparently, this folliculitis is not more prevalent with humans with "sensitive" skins or those with a history of acne. The effect of Dioxin is systemic and is not connected with the point of contact on the victim. The development of acne is symmetrical and was described as "thousands of blackheads on the back, as if the person had been shot with a shotgun". Face, arms, legs, etc can also be effected.

Dow (Midland) has had a few employees suffering from folliculitis. These were not workmen engaged in normal 2,4,5-T production, but rather those who were working with 2,4,5-T residues. Dow (Midland) has detected no liver damage in their workmen, and those with folliculitis

were able to return to work without too long an absence However, the plant was closed down for some period of time. Dow (Midland) has not only investigated the presence of Dioxin throughout the process and in their 2,4,5-T (CP) residues but also in dusts which might be polluting the factory air, etc. They have, of course, considered the solvent effect of TCP or of T-acid on possible Dioxin action, and the health hazards of these products are discussed in data sheets which are intra-Dow only.

Dow (Midland) has discussed Dioxin problems with German and with French producers of TCP. In Germany (Hoechst) two workmen died, presumably due to exposure to Dioxin. The German Companies didn't seem to be very concerned. One autopsy was inconclusive, and the other was not performed. Some workmen who survived showed evidence of liver damage for five years, but, apparently, these Germans feel that one only needs about 25% of one's liver functioning for normal existence.

Isomers

Dioxin is 2,3,7,8-tetrachloro-dibenzodioxin. Separation of various isomers has been carried out using thin layer chromatographic techniques. The 1,3,7,8-tetrachloro-analog is relatively inactive, and Dow (Midland) is not sure about the 1,2,7,8-. The octachloro-analog (previously prepared by MX) is not very active but Dow is repeating this work to assure the absence of Dioxin. German work has shown that if there are less than three chlorines in a dibenzo furane derivative, it is comparatively inactive physiologically, but is active with more than three chlorines.

[illegible] Ears

... were shown a number of rabbits whose ear had been treated with benzene (or chloroform) solutions of Dioxin. These showed various stages of folliculitis from mild to severe, depending upon the concentration of Dioxin solution administered and the number of applications. Rabbit ears might receive one application or a number of daily applications for a five-day week or for several five-day weeks. As treatments persisted or dosages increased, rabbit ears became swollen, thicker [illegible] formed; eventually, the ear might be penetrated, and if treatment was sufficiently severe the rabbit would die. Dow (Midland) felt that animals were more susceptible than humans. However, one application with a solution of 10 ppm Dioxin would have a noticeable effect on the ear of a rabbit as would repeated doses of [illegible] ppm.

[illegible]

A number of graphs were presented and discussed. These usually showed as ordinate total dosage and as abscissa concentration of individual application. There was, of course, variation among individual rabbits but generally speaking it was possible to obtain areas on the graphs where folliculitis was prevalent and other areas where it did not occur. Sometimes there was not much distinction between two applications and four applications, or between seven and fifteen. There were some anomalies but in general the message was quite clear that Dioxin is a very active chemical physiologically. 1 ppm corresponds to one microgram per ml.

J 4061

[illegible] Dow (Midland) carries out its own toxicity [illegible]. We were shown their laboratory where inhalation [illegible] done. They had many cages and larger compartments where literally all possible types of atmospheric pollution throughout the Dow plant are tested. For chlorinated hydrocarbons, Dow (Midland) has designed much of its own equipment, including such automatic recording devices as ionization - conductivity analyzers.

[illegible], Manager of Plant Life Division at Dow (Midland) joined us for lunch. He and Ross were somewhat surprised that Silverstein had discussed with Johnston and me almost entirely results with Dioxin solutions, rather than Dioxin in 2,4,5-TCP or in 2,4,5-T acid. With TCP, burning of the skin would result and perhaps greater damage, from any Dioxin present, whereas if 2,4,5-T acid spilt on the skin were washed off promptly, any Dioxin present might penetrate the skin less and cause less damage. The hope was expressed that Naugatuck would not wish to sell 2,4,5-T products containing Dioxin. It was said that following the shutdown of the 2,4,5-TCP process, Dow's improved process no longer produced TCP containing Dioxin. All TCP and 2,4,5-T products are analyzed for Dioxin content at Dow (Midland). I asked whether the improved TCP process increased the assay of 2,4,5-TCP in addition to reducing Dioxin content, but the biochemists could not answer this question. It was said that Dow (Midland) has a warehouse full of 2,4,5-T products containing Dioxin. Presumably, the Dioxin can be removed by treatment of the 2,4,5-T acid with benzene, for example, but this was not discussed. It appeared from the conversation

2065

that Dow (Midland) was not receiving too much cooperative response from other USA producers of TCP re the Dioxin problem.

Analyses

Samples of Dioxin will be sent from Midland to THE. It was suggested that HAT use these samples and try the GLC methods sent to us previously via Ross Mulholland. I would have visited the Midland Analytical Department, but thought it better for HAT to do so later. Dow (Midland) offered to analyze some samples of ours for Dioxin, in order to test HAT's analyses, and would be willing to have HAT visit their Analytical Department at Midland, to discuss these analytical methods.

To repeat, Dow (Midland) would like Naugatuck not to sell 2,4,5-T products containing Dioxin. It was said that if one used the Dow (Midland) process for 2,4,5-T products and Dow 2,4,5-TCP which does not now contain Dioxin, the resulting 2,4,5-T product would not contain Dioxin. Presumably, this would also be true using the Naugatuck process. However, if Monsanto TCP contains Dioxin, this introduces a number of problems for AMC. It is also interesting to speculate where Dow's Tordon herbicide fits into the brushkiller picture. I believe it was stated that the Tordon price was $12 a lb now and that this is approaching the competitive price stage.

Ronnel insecticide, O,O'-dimethyl-O'-(2,4,5-trichlorophenyl)-phosphorothioate, used for animal treatment is also made from 2,4,5-TCP and was an additional reason for Dow's concern about Dioxin.

Agricultural Products Division, Midland

This is a new building, two or three miles from the main complex, and outside Midland. The laboratory area is of conventional construction, but the office areas have corridors arranged somewhat like the rim and spokes of a wheel.

There are, perhaps, five acres of orchards, mainly apples, and a few acres of air-conditioned greenhouses, etc. The cement floors in the laboratory corridors appeared to have a urethane coating.

Our main contact here was Eugene E. Kenaga, who is principally concerned with insecticides, and who is a chemist and an ornithologist. He is the editor of a periodical listing insecticides, etc., published by the American Entomological Association. He was interested to add Naugatuck's name to the list of DDT producers.

In the greenhouse and laboratory areas they have aluminum table tops which when inverted are trays, that will hold many plant specimens. The legs supporting the trays are arranged so that the tray plus the plant samples can be removed with battery-powered trucks. In the laboratory the whole plant may be dipped in a herbicide solution or an insecticide solution. This is considered to give more uniform and complete wetting than would a spray.

Dow (Midland) carries on considerable work with various types of insects at different metamorphic stages. They operate nurseries for flies, various beetles, roaches, army worms, also Daphne, snails, grey(gold)fish.

... (Midland) may use as many as eleven plant varieties ...ultaneously for routine checking. These will include ...s, beans, several grasses, several cereal grains, etc.

...sidue analyses and effects of insecticides, and the effect of substrate on insecticide residue are important considerations.

... (Midland) maintains a small, stainless steel simulated ...oom in which furniture prototypes, fabrics, rugs, etc ... tested together with insecticides which show promise ...

It may or may not be a coincidence that we did not get ... near Dow's fungicide work or corridors labelled 'Residue Analyses', 'Fungicides', etc.

CONCLUSION

The overall atmosphere at Dow (Midland) was very cordial and friendly. The door is definitely open for further contacts, and these should be maintained.

T. H. Evans

mhl T. H. Evans

...3 3065