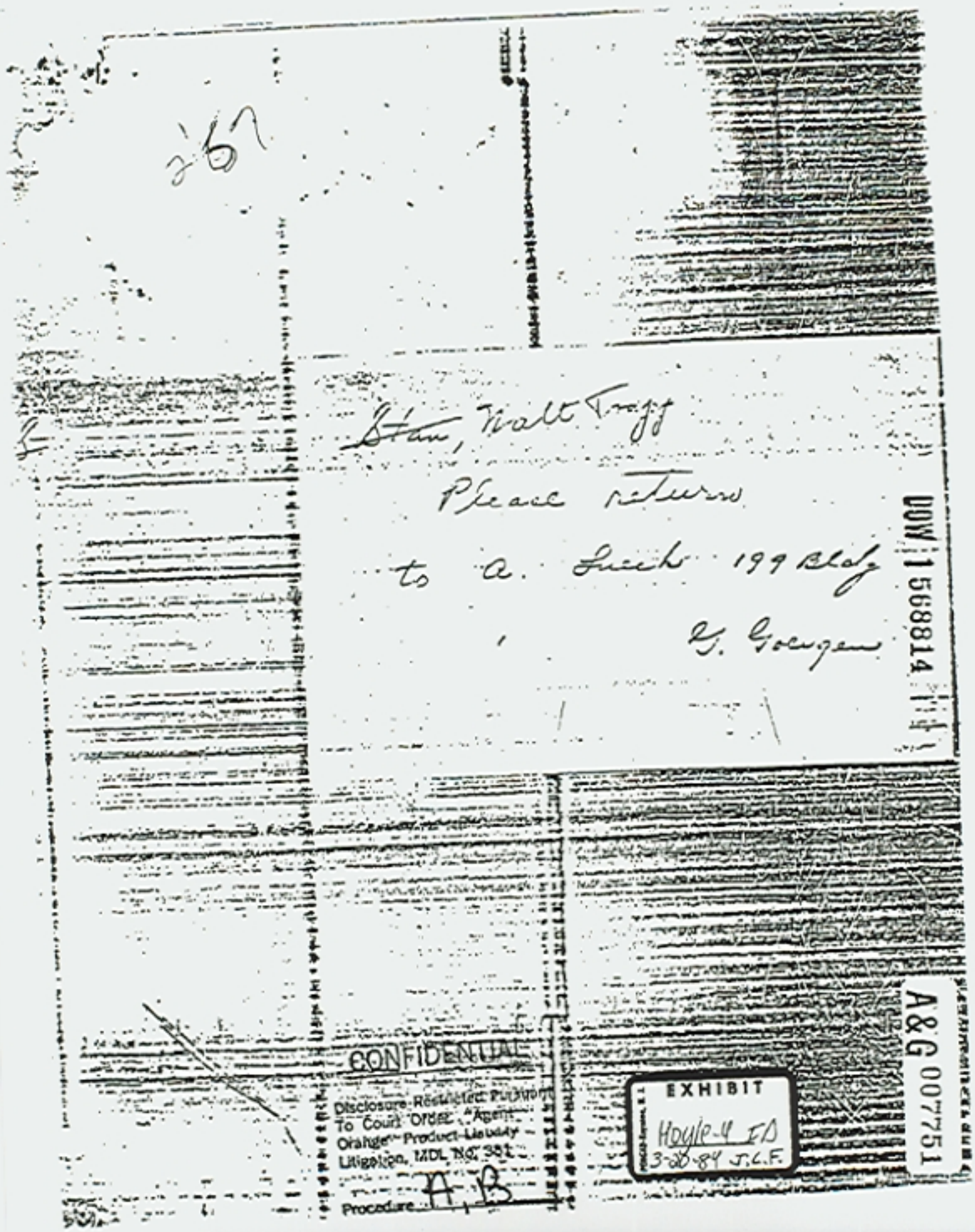
Stan, Walt Trogg
Please return
to a. Lueck 199 Bldg
G. Goergen
DOW 01568814
CONFIDENTIAL
Disclosure Restricted Pursuant
To Court Order And Agreement
Orange Product Liability
Litigation, MDL No. 381
Procedure
EXHIBIT
Hoyle-4 ID
3-28-84 J.C.F.
A&G 007751

cc: A. M. Griswold, Executive Res.
J. C. VanderWeele, Penta Office
Rowe/Hoyle, Biochem. Res. Lab.
W. A. Melching, Dowicides
Knapp/Kleine, Zurich
J. R. Myers
FBS File

FEB 25 1957

DOW CHEMICAL INTERNATIONAL LIMITED

DOW

CABLE: DOWINTAL

1574 EASTMAN ROAD
MIDLAND, MICHIGAN U.S.A.

DOW 1568815

February 22, 1957

C. H. Boehringer Sohn
22b Ingelheim am Rhein
Germany

Reference: Dr. Wey/B

Gentlemen:

Subject: Preparation of Trichlorophenol to Avoid Chloracne

Thanks very much for your letter of February 11 and the attached description of the work you have done on the preparation of Trichlorophenoxyacetic Acid to avoid the formation of Chloracne exciters and consequent dermatitis to your workmen. This work is of very great interest to us and we appreciate your thoughtfulness in remembering our earlier correspondence on this matter.

Yours very truly,

O.K.
F.B.S.

Frank B. Smith
Technical Director

FBS/mmc

cc: Otto Krahn

NOTE: Early in 1955 subject company communicated with L. Givaudan & Cie. S. A. in Geneva concerning skin irritation from 2,4,5-Trichlorophenol which was referred to us by the Givaudan Corp., Delawanna, New Jersey. On January 27, 1955 we wrote to Boehringer enclosing a data sheet describing the hazards due to toxicity and precautions for safe handling and use of 2,4,5-Trichlorophenol and answered seven specific questions regarding experience in our own plant.

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F.B.S.

161

C. H. Boehringer Sohn
223 Ingelheim am Rhein
Germany

Dow Chemical Company
1714 Eastman Rd.
Midland, Michigan
USA

February 11, 1957

Our ref: Dr. Wey/B

Re: The chloracne. Preparation of Trichlorophenol

Gentlemen!

We hereby refer to our 1955 correspondence on the above subject. At that time you were kind enough to share your experience with us.

Since our own work on avoiding chloracne exciters has come to a type of conclusion, we should like to make the results available to you and are accomplishing that by attaching a short description.

We hope that we have been able to give you, by means of this explanation, a contribution to the assurance of the synthesis of trichlorophenoxy acetic acid and assume that the contribution will also be of interest to you.

Sincerely

attch.

DOW 1568816

A&G 002753

The Preparation of Trichlorophenoxy acetic Acid
Avoiding the Formation of Chlorakne Exciters

Our synthesis of 2,4,5 trichlorophenoxy acetic acid runs in the following stages:

1. Trichlorobenzene $\xrightarrow{Cl_2}$ tetrachlorobenzene
2. Tetrachlorobenzene $\xrightarrow{NaOH}$ trichlorophenol sodium
   a. Autoclave reaction
   b. Evaporation of CH_3OH
   c. Water vapor distillation of anisole
   d. Isolation of trichlorophenol by acidification and subsequent distillation
3. Trichlorophenol $\xrightarrow{NaOH,\ CH_2ClCOONa}$ 2,4,5-trichlorophenoxy-acetic acid sodium
4. Additional working up to pure crystalline 2,4,5 T-acid

In our experience the chlorakne exciting effect on impurities may be traced back to by-products that can be formed by the usual conventional process only if trichlorophenol sodium or other alkali salts is prepared from trichlorophenol, purified, and worked up further, and if there are thereby reaction conditions that are similar to or exactly the same as those of a salt melt.

From this point of view with regard to the formation of chlorakne exciter for the individual steps in the method, the following are valid:

For 1 and 4. These steps are not at all dangerous.

For 2. The chlorakne exciter may be formed at this step.

For 2a. In order to prevent this in the autoclave reaction it is necessary to avoid the superheating of the autoclave contents (highest temperature C) and in addition care must be taken to assure that the work is done at the greatest possible dilution with methanol.

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For 2b. In the methanol distillation the water that is formed should be kept back in the distillation vessel so that the dangerous dry heating of trichlorophenol sodium will be avoided. The sump temperature should not exceed

For 2c. The water vapor distillation for driving off the trichloroanisole must be done in such a way that there will be the smallest possible (or no) change in the concentration of the sodium trichlorophenol solution. If necessary water must be added.

For 2d. In the distillation of the crude phenol it is necessary to see that no sodium trichlorophenol and no table salt enter the distillation vessel and are heated with the phenol.

For 3. In this step it is also possible for the chlorakne exciter to be formed. In order to prevent this the condensation of sodium trichlorophenol with chloroacetic acid sodium should never be conducted in an anhydrous medium. A concentration above should be avoided in all cases.

In short, the following may be said about the properties of the chlorakne exciter: as a neutral substance it is volatile with water vapor so that it may become enriched in sept 2c in the trichloroanisole that is distilling off. Therefore it is best to avoid the addition of more trichloroanisole and to destroy it by burning.

Since the chlorakne exciter shows clear evidence of sublimation even at a temperature of over in spite of its high melting point, the reaction product from steps 2 and 3 should be worked up in completely closed apparatuses and care must be taken that the working area be sufficiently ventilated.

Signed: Weyland