

WFFLXND VMD KSTFZZFX

Diamond Alkali Company

INTER-OFFICE CORRESPONDENCE

DATE
September 12, 1960

FORM 11871A

TO

J. A. Borrer

FROM

F. R. Kennedy

SUBJECT

Boehringer Correspondence

REPLY REQUESTED BY (DATE)

SEP 15 1960

cc: R. A. Guidi

	L.P.S.	
	D.C.N.	
	M.S.W.	
	M.F.W.	
	J.A.R.	
	FILE	
	DESTROY	

Continuation of the TCP process after reaction, and methanol distillation:

The batch is cooled with jacket water and ca 100-150 gals. of H₂O added to reaction mixture. Air pressure is applied to autoclave to blow batch to an intermediate storage tank, where six batches are accumulated, then pumped to the steam stripper.

The charge to the stripper is heated with steam coils to about 90-95°C. and then steam sparged through batch.

The overheads containing methanol, anisole, TCB and water are condensed. The anisole and TCB recovered by continuous decantation. The methanol water mixture run to the industrial waste sewer.

The charge is stripped until 2 ml of the batch in 2 ml of 10% caustic and 90 ml of water gives a clear to slightly hazy mixture. This normally will take about 14 to 16 hours. We intend to hold the batch temperature below 120°C. throughout the stripping operation.

The stripper batch will then be filtered to remove the salt formed in the original reaction, and stored as a 35% solution of the sodium salt of TCP.

The recovered anisole is used as an autoclave charge when sufficient material is available.

You will note some differences with Boehringer's chloracne prevention steps. We intend to investigate these more fully when the plant is in operation.

[Handwritten Signature]
F. R. Kennedy

FRK: jp

DEPOSITION
EXHIBIT
PK-1
8/18/69 JCS

DS 00022016

Newark Beth Israel Hospital

201 LYONS AVENUE • NEWARK 12, NEW JERSEY
WAVERLY 3-8000

J. A. ROSENKRANTZ, M.D.
Executive Director

May 28 1963.

Mr. Ray Guidi
Diamond Alkali Chemical Company
80 Lister Avenue
Newark, N. J.

Dear Mr. Guidi:

Kindly refer to my preliminary report of May 21, 1963. I am submitting a more detailed report today.

On March 28, 1963 I visited your plant and made a general survey. I also held conferences with Dr. Birmingham and his Staff and with Dr. Bleiberg. We then briefly checked about 15 employees. In view of the circumstances and Dr. Bleiberg's findings, it was felt that 6 of the most severely affected cases should be hospitalized and studied thoroughly. The rest of the cases could possibly be studied on an ambulatory basis.

—, a 60 year old white male whose job was to weld leaking vats of chemicals in the factory was admitted to the Newark Beth Israel Hospital on April 17, 1963 and was discharged on April 28, 1963. He had been employed in the factory for 7 years and he noted progressively severe hyperpigmentation for the past 3 months. He recently noted that his urine became red after voiding and that his eyebrows became thicker. He had been a heavy consumer of alcohol but never ingested barbiturates. He had no bullous eruptions, no neurological complaints or abdominal symptoms. His past history and family history were essentially not significant.

Positive physical findings included multiple comedones and dermal cysts of the face, neck, chest, back and exposed parts of the hands; an enlarged liver was felt 3 fingers below the right costal margin.

Multiple laboratory tests were performed. Positive findings were glycosuria on one occasion, elevated blood sedimentation rate and elevated S G O T and S G P T. The liver profile in other respects was essentially normal. The urine was fluorescent under Wood's lamp. Tissue from a liver biopsy also fluoresced and there were change indicative of hepatic cell regeneration and hemofusion deposition. Skin biopsy reveal brown granular pigment and mild dermal chronic inflammation. Urine and stools showed increased porphyrins.

The final diagnosis was Chloracne and acquired porphyria.

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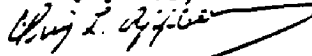
A 48 year old white male was admitted to Newark Beth Israel Hospital on April 17, 1963 and discharged on May 4, 1963. He had a history of hyperpigmentation of 2 years duration. He was a chemical operator for about 8 years. For the past 2 years he worked outside the factory as a maintenance man. The development of hypertrichosis and hyperpigmentation occurred about 2 years ago and at this time small bullae of exposed areas of skin and a dark red urine were noticed. He had been a heavy ingestor of alcohol. There were no G.I. symptoms, no neurological complaints, no known ingestion of barbiturates and both the family history and past history were not significant. Positive physical findings included hyperpigmentation of the face, neck and exposed area of hands and there was marked hypertrichosis of the eyebrows growing laterally on the forehead to meet the hair line. There were small scattered dermal cysts of the face, chest and back with multiple comedones. He also had internal and external hemorrhoids.

Multiple laboratory tests were performed. The liver profile was essentially negative but there were elevations of S.G.O.T. and S.G.P.T. The rest of the studies, including a large battery of biochemical tests and electrolyte studies, were normal. X-ray of the chest revealed small bilateral nodular lesion of the lungs, of undetermined etiology. This lesion deserves further observation and studies. The urine was not fluorescent under the Wood's lamp and liver tissue (biopsy) was faintly fluorescent. The liver biopsy showed evidence of liver cell regeneration and hemosiderin deposition. Skin biopsy showed brown granular pigmentation and chronic inflammation of the dermis. The urine porphyrins were mildly increased. The patient was discharged after hemorrhoidectomy. Apparently he had a regression of the findings of porphyria following removal from exposure during the past 2 years.

The final diagnosis was chloracne and acquired porphyria, which regressed.

This story and other studies cast serious doubt on the theory that porphyria is only a hereditary disorder of metabolism. The explosive occurrence of a large outbreak of cases of porphyria cutanea tarda in Turkey after exposure to hexachlorobenzene lends further support to accumulating evidence that porphyria may be an acquired disease. Whether there is any relationship between chloracne and acquired porphyria is unknown but in this instance it seems reasonable to suggest that 2, 4, 5 - trichlorophenol is the common denominator, responsible for both diseases.

Very sincerely yours,



IRVING L. APPLEBAUM, M.D.

ILa

(Med. bill encl)

CONFIDENTIAL

Newark Beth Israel Hospital

201 LYONS AVENUE • NEWARK 12, NEW JERSEY
WAVERLY 3-6000

J. A. ROSENKRANTZ, M.D.
Executive Director

May 21, 1963

Diamond Alkali Chemical Company
80 Lister Avenue
Newark, N. J.

Attention - Mr. Ray Guidi

Dear Sir:

On March 28, 1963, I spent the day inspecting the plant, observing a large group of employees and conferring with Mr. Guidi and Staff, Dr. Bleiberg, Dr. Birmingham and Staff. It was then decided to admit two cases into the Newark Beth Israel Hospital for special studies.

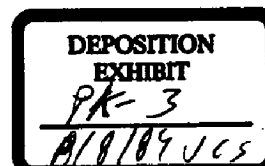
The following is a brief resume of the two cases studied in the hospital:

_____ : Male, white, age 60.
He was admitted to Newark Beth Israel Hospital April 17, 1963 and discharged April 28, 1963. He worked as a welder for leaking vats for 7 years. For several months he noticed hyperpigmentation of face and exposed areas. He also noticed a darkening urine and his eyebrows were becoming thicker. No G I symptoms, no neurological symptoms, no barbituate intake. He was a heavy consumer of alcohol but recently has abstained. Past history and family history were not significant.

He weighed 160 pounds, his blood pressure was 130/80, the pulse rate was regular at 90, the respiratory rate was 18 and the temperature was normal. There were multiple comedones and dermal cysts over the face, back and hands. No bullae. The liver was enlarged. No stigmata of cirrhosis were present. A series of many laboratory studies were made. There were elevated S G O T and S G P T. The urine fluoresced positively on the Wood's lamp and so did the liver tissue (obtained from biopsy). Urine and stools showed increased porphyrins. The diagnosis was chloracne and acquired porphyria. It is recommended that he return to work in an unexposed area.

_____ : 43 years old, white, male.
He was admitted to Newark Beth Israel Hospital April 17, 1963 and discharged May 4, 1963. He worked for 8 years as a second class operator, making up batches of chemicals, and during the past 2 years he worked outside the plant as a maintenance man. For 2 years he has noted hyperpigmentation and hypertrichosis. There was also an eruption of bullae on the hands and the urine turned dark red on standing. No barbituate intake. No G I symptoms, no neurological findings. He was a heavy drinker of alcohol. His past history and family history were not significant.

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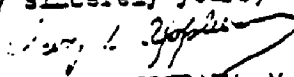
He weighed 143 pounds, his blood pressure was 150/90, the pulse rate was regular at 94. Hyperpigmentation, hypertrichosis, multiple comedones and dermal cysts were noted. The liver was not enlarged. He had internal and external hemorrhoids. Laboratory data including liver profile were negative except for elevated S G O T and S G P T. The urine, previously positive on fluorescence was now negative. Liver tissue, (biopsy) showed 1+ fluorescence. Urinary porphyrins were increased prior to admission, but were relatively normal at Newark Beth Israel Hospital. An elective hemorrhoidectomy was performed subsequent to termination of stay in hospital for studies.

This patient was not exposed for approximately 2 years and apparently finding of porphyria had regressed.

The diagnosis was chloracne and acquired porphyria, regressed.

It is interesting to note that of 26 cases tested by Ediel Laboratories, 6 urine specimens were positive for increased uroporphyrins. It is therefore incumbent upon us to study all personnel, who have contact with and exposure to the chemicals.

Very sincerely yours,


IRVING L. APPLEBACH, M.D.

ILA*2

(Med. bill encl.)

CONFIDENTIAL

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DIRECTORIAL INVESTIGATION

Conducted by

Donald J. Birmingham, M.D.
Marcus M. Key, M.D.

Occupational Health Research and Training Facility
Division of Occupational Health
Public Health Service
U. S. Department of Health, Education, and Welfare
1014 Broadway, Cincinnati 2, Ohio

Installation: Diamond Alkali Company
Electrochemicals Division
80 Lister Avenue
Newark, New Jersey

Date : March 28, 1963

Requested by: New Jersey State Department of Health
Trenton, New Jersey

Personnel Contacted:

1. Mr. Raymond A. Guidi, Plant Manager
2. Mr. William Hill, Technical Supervisor
3. Mr. Charles E. Packard, Personnel and Safety Supervisor
4. Dr. Jacob Bleiberg, dermatologic consultant
5. Dr. Roger Brodtkin, dermatologic consultant
6. Dr. I. L. Appelbaum, Director of Medical Education and
Consultant in Medicine, North Beth Israel Hospital, Newark

Nature of Operations:

The Newark Plant, Electrochemicals Division, Diamond Alkali Company, manufactures 2,4-D and 2,4,5-T. Basic materials for 2,4-D synthesis are acetic acid and phenol, which are chlorinated to monochloroacetic acid and dichlorophenol;

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respectively. These intermediates are reacted together with caustic to produce the sodium salt of 2,4-D. This is acidified to 2,4-D acid. Subsequent operations include filtering, centrifugation, esterification, amine neutralization, and formulation.

Basic materials for 2,4,5-T synthesis are tetrachlorobenzene, caustic and methanol. The tetrachlorobenzene is delivered in tank cars and must be heated to be pumped into storage and measuring tanks. The reaction between the basic materials takes place in two pressure reactors or autoclaves. Excess methanol is distilled off and recycled, and the reaction product, sodium trichlorophenol, is pumped to the steam distillation tank or steam strip via a holding tank. Here unreacted tetrachlorobenzene and a by-product, anisole, are removed. Sodium trichlorophenol from the steam strip passes through a dilution tank and intermediate storage tanks into a condensation reactor where monochloroacetic acid and caustic are also added. Here sodium 2,4,5-T is produced. This is filtered on a filter wheel to remove the mother liquor and slurried with sodium sulfate to wash off excess sodium trichlorophenol. The slurry is pumped to the acidification tank where it is treated with sulfuric acid to make 2,4,5-T acid. This product is stored in a holding tank until it is centrifuged. The centrifugate contains 85-90%

2,4,5-T acid, about 1% trichlorophenol, a fraction of a percent ash (sodium sulfate), and water. The 2,4,5-T acid is either neutralized with an amine, for example dimethylamine, or esterified with 2-ethylhexanol or butyl alcohol. The technical esters and amines thus produced may be shipped as such or the technical esters may be formulated by adding emulsifiers and kerosene.

Two buildings house the entire production operation. Initial steps in 2,4-D and 2,4,5-T production are carried out in a new building which was built three years ago after an autoclave explosion destroyed the previous building. Autoclaves and steam distillation are located just outside the new building. The remainder of the operations (condensation reaction, acidification, filtering, centrifugation, amine neutralization, esterification, and formulation) are carried out in a building approximately 50 years old. The condensation reactor is exhausted to a caustic scrubber on the roof. A third building of relatively new construction contains warehouse, maintenance shop, operations supervision, and a small dispensary. Administrative offices, laboratory, and shower and locker rooms are housed in another new building.

Problem and Investigation:

In the 12 years of operation of the Newark plant, about 46 of 48 cases of chloracne have occurred in the production of 2,4,5-T. Forty of the affected workers are cur-

rently employed at the plant. The population at risk is about 60, all males. Currently, the plant operates three shifts per day, seven days a week. The first case was observed about 12 years ago. Small outbreaks of chloracne occurred two years ago (shortly after completion of the new production building) and last summer. All of the affected workers are employed in either the new or old production buildings, but there is considerable rotation of jobs to avoid prolonged exposure in the so-called "hot spots" (areas most likely to produce chloracne) the condensation reactors and centrifuge. Although most of the production operations are enclosed, there are breaks in the process, evidenced by contamination of equipment, ceilings, floors, stairs, and hand railings, particularly in the old building. In addition to the chloracne, several workers have developed findings suggestive of porphyria, namely red urine, hyperpigmentation, and hirsutism. The company has attempted to find areas of high exposure to chloracnogens by sending various intermediates from within the production lines to Mellon Institute for reproduction of chloracne in rabbit ears. Several acnogens have been found, but it has not been possible to pinpoint sites of contamination of workmen. Also puzzling was the development of new cases after the new building was constructed, with new autoclaves, a previous "hot

port," located outside the building. Plans are being made to renovate the old building by installing a new reactor, floors, stairs, roof, ventilation system, and scrubbers. Clean uniforms are furnished by the company. Separate locker rooms for street and work clothes are provided. Clean modern shower stalls and Bradley basins are provided, along with towels and soap. Daily showers at the end of the shift are encouraged, but are not mandatory.

During the visit to the plant on March 21, Drs. Elei-berg, Brodtkin, Appelbaum, Birmingham, and Key examined 17 cases of chloracne, several of which had findings suggestive of porphyria (red urine, hyperpigmentation of exposed areas, and hirsutism, but no bullae or atrophic scars). However, a case of porphyria cutanea tarda was observed in this plant several years ago. The chloracne was manifested by comedones and cysts on exposed areas (especially the face) and at sites of friction. In one case, the chloracne was generalized.

Discussion:

The clinical picture of comedones, cysts, and hyperpigmentation of exposed areas is typical of chloracne. Additional diagnoses of porphyria and liver damage in a few cases can be made or excluded only by appropriate laboratory studies.

Outbreaks of chloracne in 2,4,5-T production have been observed in Germany,¹ France,² and the United States. In one outbreak,¹ the chloracnegenic chemical was identified as tetrachlorodibenzodioxidine.

It is commendable that the company management has undertaken the hygienic program now in effect, and is definitely planning a renovation of the old building. For control of chloracne it has usually been necessary to redesign equipment to minimize contamination and to enforce daily showering and change of clothes. Further, the work of the dermatology consultants has been most helpful. Their current plans to hospitalize and study the health status of the affected workmen are sound and necessary.

Recommendations:

1. The old production building should be renovated as soon as possible. Enclosure of the process and good house-keeping are most effective ways of preventing contamination of the workmen.
2. All workmen with severe chloracne, hyperpigmentation, hirsutism, accompanied or unaccompanied by red urine, should be hospitalized to investigate the possibility of liver damage in general or porphyria in particular.
3. In the future, when the company purchases new work clothing, it should be the one piece coverall type.

This will help prevent chloroene at the belt line.

4. Showers after work should be made mandatory.

References:

1. Kimmig, J. and Schuz, K. H.: Occupational Acne (So-Called Chloracne) Caused by Aromatic Cyclic Ethers. *Dermatologica* 115: 540-546, 1957.

So-called chloracne, previously erroneously thought to be due to free chlorine, was also seen to occur in industries where chlorinated naphthalene compounds were handled ("Ferna disease"). The authors observed the clinical manifestations of chloracne in 31 workers employed in the preparation of 2,4,5-trichlorophenol and its transformation into 2,4,5-trichlorophenoxyacetic acid or its esters. Animal experiments (brushing test substances onto a rabbit's ear) revealed that chloracne is not caused by trichlorophenol itself but by a toxic by-product formed by alkaline hydrolysis of 1,2,4,5-tetrachlorobenzol to 2,4,5-trichlorophenol. Since the materia peccans could not be isolated, various synthesized combinations were tested, of which trichloro- and tetrachlorodibenzofuran and also tetrachlorodibenzodioxidine proved very active. Since 2,3,6,7-tetrachlorodibenzodioxidine could be isolated from the above mentioned by-products it is concluded that tetrachlorodibenzodioxidine is an essential, if not the only causative factor in so-called chloracne.

2. Dugois, P. and Colomb, L.: Chloracne from 2,4,5-Trichlorophenol. *Bulletin de la Societe Francaise de Dermatologie et de Syphiligraphie* 63: 262-263, May-June 1956.

All the workmen involved in the preparation of 2,4,5-trichlorophenol used in herbicide and germicide syntheses were affected with chloracne. The skin was grayish in color, and both comedones and cysts were present. Seven of the seventeen patients had generalized involvement.

Patients with moderate and severe chloracne also complained of conjunctivitis, asthenia, anorexia, and weight loss. The digestive complaints could have been due either to gastritis or to liver insufficiency. Relapses and exacerbations were seen several months after cessation of exposure. In the chemical process, the chlorinated benzols were heated to produce polymerization, and tars and chlorinated naphthalenes were probably formed.

JACOB BLIZBERG, M. D.

22 BALL STREET

DEVENOTON 11, NEW JERSEY

ESSEX 4-3100

May 20, 1963.

Att. Mr. Guidi,
Diamond Alkali Co.,
18 Lister Avenue,
Newark, N.J.

Dear Mr. Guidi:

This is a report of some of our more important findings to date on two separate phases of investigation both of the chloracne and of the concomitant involvement of some of the functions of the liver. Originally, as you may recall, shortly after our suspicions that liver damage might be present, four men were picked for urine analysis between January 7th and January 9th, 1963. Ed Baker, your aid man, was selected to serve as a control, since his contact with the chemicals that are possibly responsible for the change has always been minimal. All of these men showed a well concentrating urine of normal color, except that the color was somewhat dark in . A trace of albumin was found in and a very marked trace in . Traces of albumin are not too abnormal and actually I paid very little attention to these findings. Interestingly enough, all the men showed traces of bile pigments in the urine, including biliverdin and bilirubin. The presence of indican in three out of the four was surprising indeed since indican usually appears in the urine only in cases of severe constipation and/or intestinal obstruction. In the absence of constipation or intestinal obstruction one must seek some abnormality of amino acid metabolism in the liver as a cause for the appearance of this chemical in the urine.

Among that first group, showed a 2+ uroporphyrin and a 1+ uroporphyrin. Each one of the urines showed at least a trace of trichloroacetic acid. This was attributed to contaminated glassware. However, it must be borne in mind that certain chlorinated hydrocarbons do tend to be metabolized in the liver and the product of metabolism is often trichloroacetic acid. A second set was checked on the same men, with glassware from the laboratory. On that date, 2/7/63, Bellamy was not available. The picture was essentially the same. A 2+ indican was found in and in . There was no trichloroacetic acid found in any of the cases.

On 4/17/63 who in the meantime had come up with an overt porphyria cutanea tarda of the acquired type and who was obviously the most

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8/8/89 JCS

5/20/63

pigmented and the worst of the chloracne, were admitted to Newark Beth Israel Hospital for medical work-up including liver biopsy. It was understood at that time that as soon as [redacted] had been worked up, his hospitalization would be changed to Blue Cross, so that he might have his bothersome hemorrhoids removed. Liver biopsy was performed on both, and there was a 4+ fluorescence of the liver fragment in [redacted] and a 1+ fluorescence in [redacted]. Both men had complete urinalysis done by the Brady Laboratories on 4/18/63 and again on 4/24/63. At this time, it was found that [redacted]'s urine was the red color characteristic of porphyria and that [redacted] did show a red urine on the first occasion but not on the second. Again traces of bile were found in the four urine specimens. Indican was found to be normal in [redacted] and above 3+ in [redacted]. On the second of [redacted]'s urine tests dated 4/24/63, the indican was 2+. This, of course, may be a simple laboratory difference or it may indicate that he was improving out of the plant environment.

In the meantime, according to the advice of Dr. Donald Birmingham of the U.S. Public Health Service, we began to run a urine profile on all the men. In the first set, which included the 25 or 26 names, apparently the laboratory was confused about [redacted] so that 26 names appear, although I feel that [redacted] is one individual and not two as indicated by [redacted]. Of this number, [redacted] Guy showed the presence of indican in the urine. There was a marked trace of bile in the urine of [redacted] a slight trace in [redacted] and [redacted], a trace in [redacted] a trace in [redacted] a marked trace in [redacted] a marked trace in [redacted] a trace in [redacted] a faint trace in [redacted] a marked trace in [redacted] and [redacted] a trace in [redacted] Indican appeared in [redacted] a trace in [redacted] the urines of [redacted] who I understand is a very recent employee. Porphyrin appeared in addition to the ones listed above in the urines of [redacted].

Certainly there is enough evidence here to indicate that there is some liver abnormality present in a considerable group of people. Those showing porphyrins alone, at one time or another, include [redacted], the two men who were hospitalized, and the others listed above. Certainly the presence of uroporphyrins in the urine is never found normally and this indicates that we do have a rather serious problem on our hands. Certainly before we can go about correcting it, it is my feeling, in which Dr. Birmingham concurs, that the entire population at risk, have the urine profile. He also feels, as I do, that some of the worst cases, particularly Dick and Trainer, be hospitalized as quickly as possible for the same procedures that were done on [redacted].

I might add that after two consultations of several hours each with Dr. Birmingham, it is his feeling that the old building is probably the source of most of our troubles and that the situation should improve greatly once that situation is corrected.

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Diamond

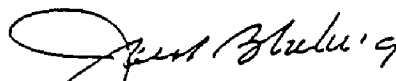
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5/20/63

I must tell you that for the good of the plant, for the good of the men, this investigation must be carried out to a sensible conclusion. If necessary I am willing to meet with Dr. McDurney and discuss this problem with him in more detail.

If there is any further information which I can give you, please feel free to call on me. I looked for you on Thursday of last week; I understand that you were tied up, but I shall be in next Thursday and hope for an opportunity to talk to you then.

Very truly yours,


JACOB BLEIER, M.D.

JB:kcc
enc 2

CONFIDENTIAL

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MAXUS1021660

June 7, 1963

Mr. R. A. Guidi - Newark
CLERK

Dr. R. W. McBurney - Fairview

I am in receipt of the complete medical reports covering
and read them with interest.

It would be my recommendation
to you, now, not to go ahead with any further hospitalization of other
employees since I can see no direct benefit to be gained by following
this procedure. There is no treatment of either of these diseases
except that of removal from the atmosphere of the contaminating sub-
stances, and, in the future, employees that are brought to our attention
with severe chloracne and a urine which fluoresces under a Wood Lamp
should be removed from exposure at the earliest possible time. Both
those diseases are, of course, self limited and reversible as the
men are removed from the atmosphere containing the trichlorophenol.

I feel quite sure that the company's decision to renovate
the old building will go far towards solving this problem permanently.
I hope that it will not be a problem to us in the future.

R. W. McBurney, M.D.

RW:CB:mme

cc: C. R. Brown
J. S. Cort, Jr.

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DS 00019519

DEPOSITION
EXHIBIT
pk-6
8/3/87 JCS

April 30, 1963

Dr. R. V. McBurney - Painesville

Mr. R. A. Giddi - Desark

MEMORANDUM

CONFIDENTIAL

C
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Y

Two of our employees, Griffin Smalley and Michael Klorer, were hospitalized last week for a series of tests as previously discussed. Mr. Smalley is now back to work, but is limited to our shop area. Mr. Klorer continues to be hospitalized for removal of piles (not job-connected). Dr. Bleiberg was most anxious to hospitalize two additional men for a complete series of tests immediately after releasing the above two men; however, I objected to same. My main reason for not going along with his request is that I can see no benefit to the Company or the men from the studies to date. No therapy or preventative has been suggested as a result of all this work; therefore, can see no advantage in sending two other men to the hospital. Secondly, our work load is particularly heavy at this time of year and for purely academic reasons, cannot justify hospitalization now. It may be that I will reconsider at some later date and send two of our more serious cases.

As quickly as the laboratory results and hospital reports are admitted to me, I will forward same for your review.

I am attaching a copy of the report entitled, "Dermatococcus Investigation", by Doctors Birmingham and Kay. I would appreciate your comments and guidance on my stand with Dr. Bleiberg and any notes you may have after reviewing the report.

Many thanks for your interest and assistance with our problem. Kindest regards.

RAG/rs

R. A. GIDDI

Attachment

cc: M. F. Wilkinson
C. E. Brown

DS 00024438

DEPOSITION
EXHIBIT
PK-7
11/8/69 JCS

June 10, 1963

Dr. E. McDermey - Cleveland

Mr. R. A. Guidi - Newark

COLORADO

COPY

I have your memo dated June 7, 1963 in which you discuss the medical reports concerning Griffin Daisley and Michael Salena. I have reviewed this subject with Mr. F. R. Kennedy who will discuss the matter with Dr. Blaiberg on his visit on Thursday, June 13, 1963. Mr. Kennedy will keep all concerned advised.

RAG/ms

R. A. GUIDI

- cc: C. R. Brown
- J. S. Cort, Jr.
- F. R. Kennedy

DS 00024423

DEPOSITION
EXHIBIT
pk-8
8/8/89 JCS

March 23, 1964

MR. J. A. FLOBECK - NEW YORK

Centerchem Incorporated

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You may recall, that while talking to Tom Cleary from your office last week, I promised to forward him any safety information we had on the handling of Trichlorophenol or its Sodium Salt.

I am attaching hereto regulations, which were derived from our files, which we feel will be helpful to Tom in appropriately safeguarding the personnel in his plant. I will appreciate your seeing that he receives a copy of these.

J. S. CORT, JR.

JSC/rvk

Attachment

cc: Mr. F. R. Kennedy - Newark
~~Mr. R. W. McDurney - P'ville.~~
Mr. E. J. Masek - Law

DS 00019474

DEPOSITION
EXHIBIT
pk-9
8/8/89 JAS

RECEIVED
MAR 24 1964
Works
Hospital

REGULATIONS FOR WORKERS HANDLING TRICHLOROPHENOL OR ITS SODIUM SALT

- 1) The chemical operator in the trichlorophenol unit must wear a clean set of work clothes daily; his face, neck, ears, hands, and all exposed skin are covered with Kerodex (a protective cream), and on termination of duty, must shower thoroughly.
- 2) Any chemical operator performing a transfer of TCP or Na-TCP is required to wear goggles and rubber gloves.
- 3) No man is permitted to enter a vessel which has contained either of the above chemicals until the vessel has been boiled out with a caustic solution, a minimum of two, and preferably three times. He then is required to wear a full face mask with an outside air supply and apply cream to all exposed parts of the skin. Immediately after completing his task, he is required to shower thoroughly and change work clothes.
- 4) In the event of an equipment failure, or accidental splash onto any portion of a man's body, we urge immediate washing with copious quantities of water for an extended period of time (15-20 minutes). This has occurred on occasion. The usual result is a mild chemical burn; however, if the prescribed remedy is not delayed, there is little, if any, damage.
- 5) Generally, all our equipment is of the closed type; where air vents are required, the line is extended to a remote location. The plant area is washed daily. However, no special detergents or procedures have been outlined at this time. In retrospect, we might say that the precautions taken in this unit are no more demanding than those of an acid plant or a caustic plant.

DS 00019475

3/23/64

October 11, 1957

R. A. Guidi - Newark

D. J. Porter - Painesville

Chloroacne - Trichlorophenol

cc: J. Burton-Newark
D. J. Lukes

Enclosed is a translation, thanks to Roland Steinkoenig, of a letter and brief report on chloroacne just received from C. H. Boehringer Sohn, Ingelheim. This confirms in essence the comments passed on to me some time back by Dr. Kudszus, of this company.

In view of John's recent comments about Monsanto's policy of limiting carefully the amount of active material present at any time in an autoclave and in view of your recent communication pointing out that the product slurry should be fairly simple to handle, it seems to me there is a great deal of incentive in our trying to run an autoclave batch at a controlled temperature.

If you run into continued difficulties with the plant scale units, perhaps we could try a run here at Painesville where the much greater surface-to-volume ratio might very effectively prevent run away temperatures.

I am attaching a sketch which resulted from some doodling the other day about ways in which a continuous autoclave unit might be set up and controlled.

D. J. Porter

DJP:sjm

Attach.

DS 00022024

DEPOSITION
EXHIBIT

PK-11
8/8/89 JCS



DS 00022025

TRANSLATION

C. H. Boehringer Sohn

A Method for the Preparation of Trichlorophenoxyacetic Acid Which Avoids Formation of Chloracne-Causing Agents

Our synthesis of 2,4,5-trichlorophenoxyacetic acid proceeds in the following steps:

1. trichlorobenzene $\xrightarrow{\text{Cl}_2}$ tetrachlorobenzene
2. tetrachlorobenzene $\xrightarrow{\text{NaOH}}$ sodium trichlorophenolate
 - a) autoclave reaction
 - b) evaporation of CH_3OH
 - c) steam distillation of anisol
 - d) isolation of trichlorophenol by acidification and subsequent distillation
3. trichlorophenol $\xrightarrow[\text{CH}_2\text{ClCOONa}]{\text{NaOH}}$ 2,4,5-trichlorophenoxy sodium acetate
4. further processing to pure, crystalline 2,4,5-T-acid

According to our experience, the chloracne causing effect is due to impurities and side reactions. These can arise in the conventional process only when sodium trichlorophenolate or other alkali salts of trichlorophenol are produced, purified, and further processed. In this case reaction conditions result which are close or tantamount to a salt force.

With this consideration in mind, the following holds with respect to the origin of chloracne agent at the various processing steps:

- At 1 and 4 - These steps are completely safe.
- At 2 - At this step the chloracne agent can originate.
- At 2a - In order to avoid this at the autoclave reaction, an overheating of the autoclave contents is to be avoided. (Maximum temperature 150° C). Further is to be observed that the work is carried on in the highest possible dilution with methanol.
- At 2b - In the methanol distillation the water formed should be retained in the distillation flask in order to avoid the dangers of heating to dryness of sodium trichlorophenolate. The temperature of the residue should not rise above 100° C.
- at 2c - The steam distillation for the separation of trichloroanisole has to be carried out in such a fashion that no change in the concentration of the sodium trichlorophenolate solution occurs. If necessary, water has to be added.

DS 00022027

- At 2d - When the crude phenol is distilled, it has to be observed that no sodium trichlorophenolate and no sodium chloride is carried over into the distilling flask and heated together with a phenol.
- At 3 - The chloracne agent can also originate at this step. In order to avoid this, the concentration of sodium trichlorophenolate with sodium chloroacetate should not be carried out in non-aqueous medium. A concentration in excess of 40% is to be avoided in any case.

The following can be said briefly about the properties of chloracne agents: As a neutral body it is volatile with steam and thus can accumulate in the trichloroanisole which is distilled off in Step 2c. It is, therefore, advisable to forego further usage of the trichloroanisole and destroy it by burning.

The chloracne agent shows distinct sublimation phenomena already at a temperature above 100° C. Therefore, the reaction product should be processed from step 2 in a completely closed apparatus. Adequate ventilation of the working area should be provided.

/s/ M. Weyland

DS 00022028

MEMORANDUM

Frankfurt, Germany
September 30, 1959

TO: J. Burton
SUBJECT: *Xauf* Boehringer - Chloracne Problem
cc: C. C. Brumbaugh
/ J. A. Borror
H. E. Everson
D. J. Porter
L. P. Seyb
H. S. Weiner

OCT 7 1959

The acne cure announced by Boehringer in Chem. Week for June 20, 1959 is confirmed as inactive for chloracne.

Boehringer has had no new cases of chloracne in 3-5 years. They did this by discovering the compound which is the bad actor and eliminating it as a by-product. After they accomplished this processwise, they then cleaned up their factory in a major fashion before re-opening - it was closed a year.

Dave Porter's memo of September 18, 1957 to you and yours to me of July 28, 1959 set forth substantially the requirements. As Dave points out, the bad actor is a tetrachlorobenzodioxime. As you pointed out, certain conditions of temperature in the process can cause the trouble.

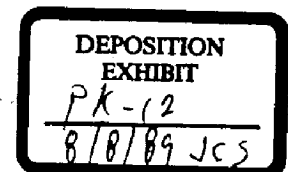
In addition, even though Boehringer is sure it has no more dioxime in its process, it ventilates its plant with great care, issues clean work clothes every day and continuously checks its trichlorophenol on rabbit ears per the test described in the Dermatologica paper (Derm. 115, 540, 1957) copy of which you sent me.

Kudszus has reneged on sending out the report he promised Dave - says the dioxime is so active as to be a chemical warfare chemical. But we have all dope orally.

Do you distill TCP? This is said to be a most dangerous step. In distillation, if any alkali or salts are present, oxime forms very rapidly. Recommend that alkali and salt be washed from crude TCP before distillation.

Referring to your points 1, 2 and 3 in your memo to me of July 28, 1957 (H. S. Weiner has a copy):

DS 00017413



J. Burton
Re: Boehringer - Chloracne Problem

-2-

September 30, 1959

1. After dilution with methanol, the reaction mass is only dangerous over 170° C.
2. Distill out major portion of methanol under 110°, then strip out remainder of methanol with steam preferably at 100° (120° C., cited by you said to be dangerous).

Boehringer offers to review your process conditions and advise of further danger points - if these ideas don't do the job.

Finally, after Boehringer did all the above, they tore out plaster walls, floors and similar parts of buildings until no remaining structure gave positive rabbit ear test. This done by carefully protected workmen. Once clean and following above process steps, they have enjoyed good experience. Better try a few rabbit ears on your joint if you are still having trouble. Oh, yes, Boehringer liver damage cases are still on compensation after more than five years!

Thornton F. Holder

TFH:sjm
10/5/59

DS 00017414

June 23, 1960

Messrs. Conrad and Doll
CELA G.M.B.H.
Ingelheim am Rhein
West Germany

Dear Sirs:

This letter is in answer to your request to our Mr. S. Honour for an exchange of information on hazards in the manufacture of 2,4,5-Trichlorophenol. We have attached an article that we think may be pertinent as well as the following discussion concerning our process.

The explosion in our 2,4,5-Trichlorophenol autoclave occurred on Feb. 20, 1960. At present, we do not know the cause. However, our laboratory is studying the chemistry of this reaction, and is also trying to develop an alternative and safe procedure for carrying out the reaction.

The batch which exploded was being reacted in our usual manner. We have found nothing abnormal in the equipment or in the raw materials, so we cannot explain why this one batch reacted violently after we had produced several thousand batches in the past ten years by the same procedure.

Our standard process is as follows. We charge 1,400 lbs. of 98% caustic soda crystals through a manhole into our 1,000 gal. autoclave. We then close the manhole and pump in 590 gal. of methyl alcohol. About $\frac{1}{2}$ of the methanol is methanol recovered from previous batches and the balance is new methanol. The agitator is then started and cooling water circulated through the autoclave jacket. The temperature rises to 70 C and then drops to 50 C or below. At this point 2,800 lbs. of molten 1,2,4,5-Tetrachlorobenzene (97-98% purity) is added, requiring approximately 20 minutes. The cooling water is drained from the jacket, and steam pressure is applied to the jacket. It usually takes about one hour for the batch temperature to reach 130-140 C. At this point the steam is shut off, and the temperature rises from the heat of the reaction to 165-175 . The batch is held at approximately 165-170 for five hours, the temperature being controlled by steam or cooling water in the autoclave jacket. The batch is then cooled to 100 C, then a vapor line valve is opened to permit the methanol to distill off. The methanol is recovered for use in subsequent batches. It contains 3-5% water, and some tetrachlorobenzene, trichloranisole, and dimethyl ether. We do not have any exact analyses of this recovered methanol.

DEPOSITION
EXHIBIT

PK-13
8/8/81 JLS

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C
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The batch which exploded behaved normally up to the point where it had been charged and heated to 130 C (pressure of 125-150 lbs./sq. in.). At this point the pressure apparently dropped about 50 lbs. suddenly, and then the pressure and temperature both rose rapidly. Cooling water was applied to the jacket but did not control the pressure rise. In 5-10 min. the pressure reached 650 lbs., and the safety rupture disk blew. However, the pressure continued to rise and in 1-5 min. the manhole weld was ruptured and the manhole blew out. The methanol fumes which were thereby released apparently ignited shortly thereafter and produced a serious explosion. The autoclave had been hydrostatically tested at 1,100 lbs./sq. in., but presumably would not actually fail until several times this pressure was reached.

During the past ten years, our process had been substantially the same. At times we varied the reaction temperature between 160 and 190 C, and the mol ratio of caustic soda to tetrachlorobenzene between 2.5 and 2.7. Until six months before the explosion, we had been charging the tetrachlorobenzene in the form of solid flakes. The rupture disk had blown several times, usually because of an inadequate supply of cooling water; however, the pressure and temperature rise were always checked by the rupture disk.

In our original laboratory work we had a batch react violently, yielding a charred mass in the one gal. autoclave. We thought this was due to a prior loss of methanol through the stuffing box.

Our laboratory is now checking the possibility of charging all of the tetrachlorobenzene to the autoclave, heating to 150-170, then slowly pumping in a caustic soda-methyl alcohol solution over a period of $\frac{1}{2}$ to 2 hours. We have also considered the possibility of charging the caustic soda and methanol, then allowing adding the molten tetrachlorobenzene but we are inclined to favor charging the tetrachlorobenzene first.

We would like to receive similar pertinent information on your reaction procedure and your ideas on whether our proposed process change will satisfactorily eliminate the hazard. If you reciprocate on this information, we will be glad to send you the results of our laboratory experiments when they are finished. Please send your information to the attention of J. A. Borror, Manager of the Technical Staff, Diamond Alkali Co., Union Commerce Bldg., Cleveland 14, Ohio.

Yours truly,

J. Burton

JBJ:js

DS 00022023



C. H. BOEHRINGER SOHN

CHEMISCHE FABRIK

	I. B. C.
	D. C. N.
	M. S. W.
	M. F. W.
<input checked="" type="checkbox"/>	J. A. S.
	FILE
	DESTROY

Postanschrift: C. H. Boehringer Sohn, ② Ingelheim am Rhein

Mr. J. A. BORROY
 c/o DIAMOND ALKALI COMPANY
 Union Commerce Building
Cleveland 14, Ohio / USA

Ingelheim 2025
 Boehringer Ingelheim
 Fernschreiber 0417 885
 Alle Codes in Gebrauch
 Landeszentralbank Mainz 46/81
 Conrad Hinrich Donner, Hamburg 1
 Deutsche Bank A.G., Filiale Mainz
 Kreisparkasse Ingelheim am Rhein Nr. 830
 Postcheckkonto: Frankfurt (Main) Nr. 1655

Ihre Zeichen Ihre Nachricht vom Unsere Nachricht vom Unsere Zeichen

Betrifft Dr. Mz/Fk
 GC/Sg

② Ingelheim am Rhein
 den
 August 10, 1960

Dear Mr. Borroy:

Recently we received a letter from Mr. J. Burton, dated June 23, 1960, addressed to Mr. Doll, Managing Director of CELA G.m.b.H. Mr. Burton requested to have the answer addressed to you. Unfortunately his letter was sent by surface mail which meant a several weeks' delay. We therefore hasten to let you have an answer and the desired information.

We thank you, also in the name of CELA, for the information regarding your process for the production of 2,4,5-Trichlorophenol from 1,2,4,5-Tetrachlorobenzene, as well as for the description of the explosion which occurred in your Factory. It was very interesting for us to read that in your laboratories you are presently working on a modified method according to which the autoclave is at first loaded with the full quantity of Tetrachlorobenzene adding slowly the solution of caustic soda. We have had good experiences over long years with a principally equal process which in our opinion offers a great operating safety if working below certain temperatures. Here below we are outlining our standard process:

We are loading the autoclave of 7400 Litres with 1400 Kg (= 6,5 Kg Mol) cold symmetrical Tetrachlorobenzene, suspended in 1000 Litres Methanol, and dilute therein with another 2500 Litres Methanol. This amount of Methanol is regenerated from former batches and has a content of 95%.

DEPOSITION
 EXHIBIT
 pk-14
 8/10/60 JCS

DS 00021951

C.H. Boehringer Sohn
Ludwigshafen am Rhein

Mr. J.A. Borroy, Diamond Alkali Co. USA

10-8-1960

The autoclave is then locked and heated to an internal temperature of 130 - 135°, the pressure thus reaching 9 atü. The steam is shut off and over a period of 5 hours 730 Kg of aqueous caustic soda solution minimum 49% are injected (= 18,24 Kg Mol 100%). The heat thus developed brings the contents of the autoclave to a temperature of 150-153° within one hour. Generally a further increase in temperature in the course of reaction of 12 hours will not take place. By the end of reaction it is necessary to add some heat in order to maintain temperature at 150°. 8 hours after having finished the injection of caustic soda solution a pressure of 20 atü is reached, which rests constant until the end of reaction.

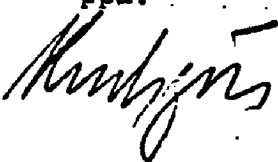
Now the contents of the autoclave is cooled down to 105° and filled in a distilling apparatus of 7000 Litres in order to distill off the Methanol. Following the evaporation of the Methanol during which the temperature must not exceed 115°, and after adding 300 Litres of water by blowing in steam (3,5 atü), the formed Trichloroanisol is distilled off. It remains a solution of about 36% 2,4,5-Trichlorophenol in surplus caustic soda solution for onward processing into Phenol.

We consider it especially important that whilst evaporating methanolic or aqueous solutions of Trichlorophenolate solutions a concentration of 40% is not exceeded because otherwise there exists the danger of a sudden exothermic formation of chloride acne-active substances which, as you know, has led to a severe damage to the staff of an important European Factory. In a letter dated September 20, 1957, addressed to your Research-Center, Painesville, Ohio, we described our own experiences in this connection.

XFL

We should be pleased if you - in supplement of your letter dated June 26, 1960 - would tell us how you elaborate the reaction product of the autoclave to Trichlorophenolate. The information regarding your process will, of course, be treated strictly confidential and we sincerely ask you to act accordingly with regard to our indications.

Yours very truly,
C.H. BOEHRINGER SOHN
ppa. ppa.



DS 00021952

October 3, 1960

Mr. Kudsus
C. H. Roehringer Sohn
Ingelheim am Rhein
West Germany

Dear Mr. Kudsus:

We thank you very much for your letter of August 13 giving information on your process for the production of 2,4,5-Trichlorophenol.

In your letter you requested additional information as to how we elaborate the reaction product of the autoclave to Trichlorophenolate. This elaboration is as follows:

Continuation of the TCP process after reaction, and methanol distillation --

The batch is cooled with jacket water and ca 100 to 150 gallons of H₂O added to reaction mixture. Air pressure is applied to autoclave to blow batch to an intermediate storage tank, where six batches are accumulated, then pumped to the steam stripper.

The charge to the stripper is heated with steam coils to about 90 to 95°C and then steam sparged through batch.

The overheads containing methanol, anisole, TCP and water are condensed. The anisole and TCP recovered by continuous decantation. The methanol water mixture run to the industrial waste sewer.

The charge is stripped until 2 ml of the batch in 2 ml of the 10% caustic and 90 ml of water gives a clear to slightly hazy mixture. This normally will take about 14 to 16 hours. We intend to hold the batch temperature below 120°C throughout the stripping operation.

The stripper batch will then be filtered to remove the salt formed in the original reaction, and stored as a 35% solution of the sodium salt of TCP.

The recovered anisole is used as an autoclave charge when sufficient material is available.

We again thank you for your informative letter and hope this information answers your question.

Very truly yours,
DIAMOND ALKALI COMPANY
Chlorinated Products Division

DS 00022015

J. A. Borer
Manager - Technical Staff

DEPOSITION
EXHIBIT

PK 15
8/11/99 JCS

March 20, 1964

Mr. S. Savage - New York Sales
COLUMBIA, SOUTH AMERICA SHIPMENTS

Mr. F. R. Kennedy - Newark

C O N F I D E N T I A L

C
O
P
Y

We have removed the retained sample of Batch H62-825 from our regular sample storage area to safekeeping in our office. Since 823 and 824 were made from the same technical material, emulsifier and solvent, within the same 24-hour period, these samples have been moved also. More on this to follow.

I spoke to Dr. J. Bleiberg about his involvement in this matter. He informed me that someone in the New York Office - I assume Larry Cecil - made arrangements for him to meet someone returning from Columbia. Dr. Bleiberg spoke with this gentleman (he doesn't recall his name) and was promised pictures of the affected personnel. He did not receive the pictures and had no further involvement in this matter.

More information will follow shortly on the number and types of containers shipped on September 24, 1962, Order #NY-75-2437. We are tracing other formulations made from the same technical stock.

F. R. Kennedy
F. R. KENNEDY

FRK/mc

cc: J. S. Cort, Jr. ✓

DEPOSITION
EXHIBIT
PK-16
8/8/89 JLS

DS 00028002

Jewel H. Perkins, Jr., Jack A. Borrer and
Raymond A. Guidi
U. S. Ser. No. 196,507
Filed May 21, 1962

STATEMENT OF INVENTION

This invention relates to a method of preparing sodium 2,4,5-trichlorophenate by the method of dechlorinating tetrachlorobenzene with heat pressure and alkali. The method of the present invention consists of dechlorinating tetrachlorobenzene in an autoclave by the method of charging tetrachlorobenzene alone into the reaction vessel, and then adding a sodium hydroxide methyl alcohol mixture at a rate determined to give the most efficient reaction. Generally, a 20% by weight solution of caustic in methanol, containing 2.2 mole of NaOH per mole of tetrachlorobenzene, is fed into molten tetrachlorobenzene at 175° C. over a period of 40 minutes to 2 hours. The reaction takes place under the autogenous pressure of the reactants, which ranges from 250 to 500 p.s.i.g. The reaction temperature is held at 175° C. until total of feed time and subsequent holding time within the reaction vessel is about 4 hours. The material produced by this method is then purified by steam distillation and recovering trichlorobenzene and methyl alcohol. The yield of sodium 2,4,5-trichlorophenate normally exceeds 96% of the tetrachlorobenzene, used as a starting material. The difference is accounted for in the amount of trichlorobenzene.

DS 00022005

DEPOSITION
EXHIBIT

PK-18

8/8/89 JCS

This invention relates to a new and improved method of preparing polyhalophenates, and more specifically refers to improvements in the preparation of sodium 2,4,5-trichlorophenate.

Polyhalophenates such as sodium 2,4,5-trichlorophenates, are used as raw materials in the production of polyhalophenoxycarboxylic acids which are widely used as herbicides, and there has been a continuing desire to produce such starting materials economically, safely, and efficiently.

Referring particularly to the preparation of sodium 2,4,5-trichlorophenate as an illustration, it is known to prepare this material by reacting molten tetrachlorobenzene with a mixture of sodium hydroxide with methanol or water, or glycol, by the method of adding all the reactants together as a charge to a reacting vessel, then heating them under pressure to 100°-250° C. to produce the required reactions. This method involves a danger due to the creation of conditions causing runaway reactions and the formation of chloracnegens, and is generally less efficient than the method of this invention. These processes require heating a large amount of a caustic-tetrachlorobenzene mixture which may result in condensation reactions, causing a reduction in efficiency.

In order to avoid the difficulties heretofore encountered, and to provide a new and improved process, the present invention has as one of its principle objects the provision of a new and improved method of producing a polyhalophenate, notably sodium 2,4,5-trichlorophenate, in high yield, in a manner which avoids the hazardous condition of reacting large amounts of hot alkali and alcohol with tetrachlorobenzene. The present invention comprises preparing polyhalophenates by the steps of reacting an alkali-alcohol mixture with molten halobenzene, whereby the halobenzene is placed in a reaction vessel and the alkali-alcohol mixture is added slowly at a controlled rate, thus avoiding the presence of an excess of alkali during the reaction. The desired reaction product is obtained in high yield and, at the same time, the undesired dangerous condition of large quantities of unreacted tetrachloro-

DS 00021889

benzene and alkali-alcohol mixture together in a pressurized high-temperature container is avoided.

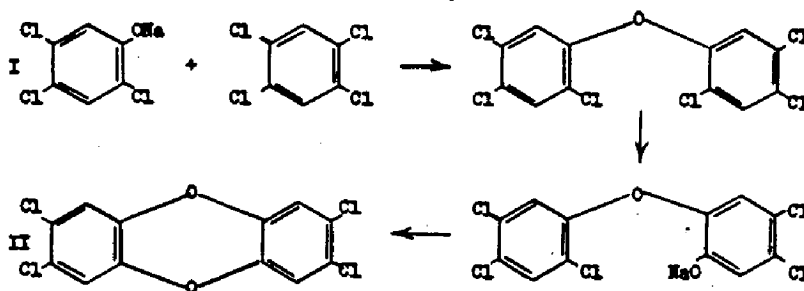
As used, "polyhalophenols" refers to various halogen derivatives of phenol, such as tetrachlorophenol. While chlorine derivatives are preferred, other halogen and halo derivatives are contemplated such as bromo, fluoro, iodo; and mixed halogen products such as bromochlorophenol.

The term "alkali", as used in the specification and claims, is intended to refer especially to an alkali metal hydroxide, preferably sodium hydroxide, although other alkali metal hydroxides, e.g., potassium hydroxide and/or lithium hydroxide can be used. It is intended to refer also to other sources of alkali, which, under the conditions of reaction, are suitable to yield the desired high conversion characterizing the practice of this invention, and otherwise to be satisfactory. An alkali metal hydroxide, notably sodium hydroxide, is especially preferred.

The term "alcohol" is intended to refer to various alkyl-oxides of all classes, primary, secondary, or tertiary. Methanol is preferred at present.

It is an essential feature of the present invention that a polyhalobenzene, preferably tetrachlorobenzene, is placed in a reaction vessel in a molten or solid state in the absence of any other reactants. The desired reaction is then carried out by the gradual addition of an alkali in alcohol mixture to the molten tetrachlorobenzene. The addition, at a controllable rate, is seen to be inherently safer than adding all the reactants at once and heating the mass to the relatively high temperatures required for the reaction. Another significant advantage of this invention is that less alkali is required. Previous methods require 3.0 mol of alkali per mol of tetrachlorobenzene. The proposed process provides nearly 100% yield at 2.4 mol of alkali per mol of tetrachlorobenzene. Formerly, large amounts of alkali present caused the following condensation reactions which resulted in a corresponding loss of the product and reduction in efficiency.

DS 00021890



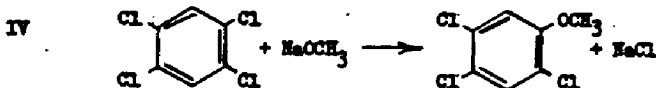
This undesirable condition is minimized by the controlled addition of small quantities of alkali-alcohol mixtures. The end product of the above reactions is termed a "chloracnegen". Condensation products of this class create the occupational hazard of skin disease known to those employed in the art as "chlor-acne". This disorder has been prevalent among operators of prior processes and the absence of the "chloracnegen" renders the method of this invention more desirable than previous processes.

10

In previous processes, large quantities of alcohol, present in the reaction vessel at the start of the reaction, are subjected to high temperatures before the reaction can be completed, resulting in losses through formation of dimethyl ether. The controlled addition of alkali-alcohol mixture to the reaction vessel, in accordance with the teachings of this invention, reduces losses in alcohol by formation of dimethyl ether by-product.

20

The sequence of reaction steps of this invention is set forth structurally in the following series of equations, it being understood that the alkali-alcohol mixture is added at a rate pre-determined to produce the most efficient reaction possible. It will then be appreciated that the reaction proceeds only as the reactants become available in the reaction vessel.



DS 00021891



With the practice of the invention, as outlined in the foregoing equations, conversion of greater than 90% of 1,2,4,5-tetrachlorobenzene to sodium 2,4,5-trichlorophenolate is obtained. The reaction temperature typically varies from 140° C. to 250° C., preferably maintained at 175° C. The reaction time typically is 3 to 6 hours, although in commercial operations a longer reaction time of up to 8 hours is not disadvantageous with respect to high yields obtained.

The proportions of the reactants generally can be varied. Thus, 10 molar ratios in the alkali-alcohol mix can be from 1:2 to 1:20 mols of alkali to alcohol, respectively. The overall molar ratios of alkali to tetrachlorobenzene can be from 2:1 to 4:1, respectively. The overall molar ratios of alcohol to tetrachlorobenzene can be in the range of 4:1 to 80:1, respectively. It is the preferred method to add 2.04 pounds of alkali-alcohol solution per pound of 1,2,4,5-tetrachlorobenzene into the reactor at a uniform rate over a period of 2 hours, maintaining the temperature at approximately 175° C. Steel equipment is employed in the examples of this invention, and steel is the preferred material of construction.

In order that those skilled in the art may more completely understand the present invention and the preferred method by which the same may be 20 carried into effect, the following specific examples are offered.

Tetrachlorobenzene is weighed into a pressure reactor, such as an autoclave, melted and brought up to the reaction temperature. An alkali methanol solution is heated to 55°-65° C. and added to the reactor over a period which may vary from 40 minutes to 5 hours. When all of the alkali methanol solution has been charged, the reactor temperature is held constant for a period which may vary from 40 minutes to 3 hours. During the reaction,

DS 00021892

the pressure within the reactor will be in the range of 250 p.s.i.g. to 700 p.s.i.g., due to the autogenous pressure of the alcohol, and will vary according to the amount of alcohol added. When the reaction is complete, the charge is cooled to reduce pressure. Steam is applied to the reaction vessel to distill off all the unreacted methanol which is collected through a condenser system and recovered. When all the methanol has been removed, water is added to the reaction mass which is now a crude sodium trichlorophenate. The crude sodium trichlorophenate is transferred to a distillation vessel, where by steam distillation the intermediate reaction product, trichloroanisole, is removed and recovered. The steam-stripped sodium trichlorophenate is then pumped through an enclosed filter, which removes the salts, and is then diluted and stored for later use in the 2,4,5-trichlorophenoxyacetic acid production.

In the following examples, carried out in the manner indicated, the results are indexed comparatively:

DS 00021893

TABLE I

	1	2	3	4	5	6	7	8	9	10	11	12	13
<u>Mole Ratio</u>													
$\frac{NaOH}{CH_3OH}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$
$\frac{NaOH}{TCB^*}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.5}{1}$	$\frac{2.5}{1}$	$\frac{2.5}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$
$\frac{CH_3OH}{TCB^*}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{12.5}{1}$	$\frac{12.5}{1}$	$\frac{12.5}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$
10 <u>Conditions</u>													
% Excess $NaOH$	10	10	10	10	- 25	25	25	10	10	10	10	10	10
Total charge ga.	3280	3280	3280	3280	3580	3580	3580	3280	3280	3280	3280	3280	3280
Feed Time (hrs.)	2	5	2	3	5	3	4	2	2	2	2	1	3/4
Hold Time (hrs.)	2	4	1	1	1	1	1	2	3	1	2	2	3
	1	2	3	4	5	6	7	8	9	10	11	12	13

* 1,2,4,5-tetrachlorobenzene

DS 00021894

TABLE I continued

	1	2	3	4	5	6	7	8	9	10	11	12	13
Reaction Temp., °C.	140-72	165-68	164-65	165	164-66	163-64	163-64	157-62	163-64	174-75	170-88	164-67	173-79
% Conversion to Sodium Trichlorophenate	72.2	73.9	89.3	74.5	90.0	85.7	83.3	82.7	92.7	90.2	96.0	89.9	96.8
Maximum Pressure PSIO	340	225	305	360	565	400	280	265	320	420	330	370	385
	1	2	3	4	5	6	7	8	9	10	11	12	13

DS 00021895

EXAMPLE 14

To the reaction vessel is added 1,080 g. (5 mol) of 1,2,4,5-tetrachlorobenzene. A 20% by weight NaOH in methanol solution is prepared by adding 440 g. (11 mol) NaOH pellets to 1,920 g. (60 mol) of commercial grade methanol and heated to 63° C. The reaction vessel is heated to 170° C., at which time the alkali methanol mixture is added to the reaction vessel over a period of 1 hour at a uniform rate, which will ultimately provide a 2.2:1 mol ratio of alkali to tetrachlorobenzene, respectively. At the end of 1 hour, when all the alkali methanol mixture has been added, the closed reaction vessel is maintained at 175° C. for a period of 3 hours. The pressure within the container reaches a maximum of 492 p.s.i.g. approximately one hour after the end of the alkali methanol addition. After cooling, pressure is reduced, and steam is applied to the reaction vessel to distill off the unreacted methanol. When all the methanol has been removed, water is added, and the crude sodium trichlorophenate may be purified if desired.

It is to be understood that, although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the full intended scope of this invention, as defined by the appended claims.

DS 00021896

WHAT IS CLAIMED IS:

1. A process of preparing alkali metal polyhalophenates which comprises heating polyhalobenzene in a closed vessel to a temperature in the range of about 140° to 250° C., adding at a controlled rate mixture of alcohol and alkali metal hydroxide wherein the mol ratio of alcohol to alkali metal hydroxide is about 2:1 to 20:1 and maintaining the reaction temperature in the range of about 140° to 250° C. under superatmospheric pressure which is at least equal to the autogenous pressure of the reaction mixture, the amount of alcohol-alkali mixture being such as to provide a mol ratio of alkali to polyhalobenzene of about 2:1 to 4:1.

2. A process, as claimed in Claim 1, wherein the polyhalobenzene is tetrachlorobenzene.

3. A process, as claimed in Claim 1, wherein the alkali metal hydroxide is sodium hydroxide.

4. A process, as claimed in Claim 1, wherein the alcohol is methanol.

5. A process, as claimed in Claim 1, wherein the reaction vessel pressure is maintained in the range of about 250 p.s.i.g. to 700 p.s.i.g.

6. In a process for preparing alkali metal polyhalophenates, the steps which comprise heating polyhalobenzene in a closed vessel to a temperature in the range of about 140° to 250° C., adding at a controlled rate in the range of about 0.4 to 11 mol alkali metal hydroxide per hour contained in a mixture with alcohol wherein the mol ratio of alcohol to alkali metal hydroxide is about 2:1 to 20:1 and maintaining the reaction temperature in the range of 140° to 250° C. under superatmospheric pressure which is at least equal to the autogenous pressure of the reaction mixture,

DS 00021897

the amount of alcohol-alkali being such as to provide a mol ratio of alkali to polyhalobenzene of about 2:1 to 4:1.

7. In a process for preparing sodium trichlorophenate, the steps which comprise heating tetrachlorobenzene in a closed vessel to a temperature of about 175° C., adding at a controlled rate about 11 mol per hour of sodium hydroxide contained in a mixture with methanol wherein the mol ratio of alcohol to sodium hydroxide is 5.4:1 and maintaining the reaction temperature at about 175° C. for a period of 3 hours, under a pressure of from 270 p.s.i.g. to 490 p.s.i.g., the amount of methanol-sodium-hydroxide mixture being such as to provide a mol ratio of sodium hydroxide to tetrachlorobenzene of about 2.2:1.

8. In a process of preparing alkali metal polyhalophenate by the method of alkaline hydrolysis of a polyhalobenzene, the improvement which comprises adding an alkali metal hydroxide alcohol mixture having an alcohol to alkali mol ratio in the range of 2:1 to 20:1, into a molten bath of polyhalobenzene at a rate in the range of 0.4 to 11 mol alkali metal hydroxide per hour, the amount of alkali-alcohol mixture such as to provide a mol ratio of alkali to polyhalobenzene of about 2:1 to 4:1.

9. In a process for preparing sodium trichlorophenate, the improvement which comprises adding a sodium hydroxide methanol mixture having a methanol to sodium hydroxide mol ratio in the range of 2:1 to 20:1 into a molten bath of tetrachlorobenzene at a rate in the range of 0.4 to 11 mol per hour, the amount of sodium hydroxide methanol mixture being such as to provide a mol ratio of sodium hydroxide to tetrachlorobenzene of about 2:1 to 4:1.

10. Each and every novel element, combination of elements, step in a method and combination of steps or methods herein disclosed and claims.

DS 00021898

July 30, 1964

Mr. J. S. Cort, Jr. - Cleveland

FROM

Mr. F. R. Kennedy - Newark

SUBJECT:

CHLORACNE

C O N F I D E N T I A L

I have enclosed an article written by Dr. Bleiberg, et al, on "Industrially Acquired Porphyria". This was published in the June 1964 "Archives of Dermatology". He has been receiving letters of interest from colleagues throughout the country, one of which is attached. I have asked him to supply Dr. McBurney with a copy of the article and any correspondence that might be relevant to our problem.

My interpretation of the article is that there are two distinct diseases involved, related only in that they both may have the same irritant as a cause.

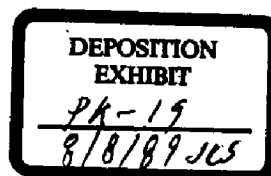
We are running urinalysis checks on the entire Plant in an attempt to gather information which may be of some value.

FRK/nc

F. R. KENNEDY

Enclosures

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Industrially Acquired Porphyria

JACOB BLEIBERG, MD
 MARVEN WALLEN, MD
 ROGER BRODKIN, MD
 AND
 IRVIN L. APPLEBAUM, MD
 NEWARK, NJ

Twenty-nine patients working in a chemical factory engaged in the manufacture of 2,4-dichlorophenol (2,4-D) and 2,4,5-trichlorophenol (2,4,5-T) exhibiting features of chloracne were studied for the presence of porphyria cutanea tarda. In 11 cases urinary uroporphyrins were elevated.

Two of these patients who showed evidence of acquired porphyria with chloracne were hospitalized. The features of chloracne as well as the clinical and laboratory features of acquired porphyria have been discussed. There appeared to be an etiologic but not quantitative relationship between the chloracne in workers engaged in the manufacture of 2,4-D and 2,4,5-T and porphyria cutanea tarda of the acquired type. It is our feeling that either the finished chemicals or some intermediate are responsible for both diseases.

Since Waldenström first implied that porphyria cutanea tarda might be acquired, a growing number of chemicals have been implicated in the pathogenesis of this disease. These chemicals have included alcohol, sedatives, fungicides, etc.¹⁻¹³ While treating a severe outbreak of chloracne in a factory which manufactures 2,4-D and 2,4,5-T, a number of workers were noted to have hyper-

pigmentation, hirsutism, fragility of the skin and vesiculobullous eruptions on exposed areas of skin, together with cutaneous findings of chloracne. Investigation revealed evidence of porphyria cutanea tarda of varying degrees of severity in 11 out of 29 workers investigated. Porphyria cutanea tarda has never before been described as related to chloracne, nor has it been ascribed to industrial exposure in the United States. This outbreak is therefore of interest in adding more evidence to the growing concept that porphyria cutanea tarda may be an acquired disease occurring after various insults to the liver. Three cases were studied in detail.

Report of Cases

CASE 1.—A 48-year-old white male who was employed at the factory for three years as a chemical operator. His work brought him into intimate contact with the suspected chemicals. His past history included two attacks of biliary colic prior to 1953. He was never a heavy user of alcohol. A diagnosis of cholecystitis had been made and a cholecystectomy was performed early in 1953. After this he came to work at the factory in question. In 1956 he began to notice some darkening of his skin and suffered right upper quadrant pain. A diagnosis of common duct obstruction was made, and this patient was operated on again in January of 1956. An unsuccessful attempt was made to probe the common duct, and no further operative procedure was done. During the postoperative course, this man received 2 gm of barbiturates. The patient stated that his urine had turned "the color of Coca-Cola" at least one year prior to the second operation. That spring, an eruption of bullae appeared on the face, ears, and hands. These lesions could be produced either by exposure to the sun or

From the Departments of Dermatology and Medicine, Newark Beth Israel Hospital.

Chief of Dermatology, Newark Beth Israel Hospital (Dr. Bleiberg); Senior Resident Physician in Medicine, Newark Beth Israel Hospital (Dr. Wallen); Assistant in Dermatology, Newark Beth Israel Hospital (Dr. Brodtkin); Director of Medical Education and Consultant in Medicine, Newark Beth Israel Hospital (Dr. Applebaum).

Appendix B

DEPOSITION
 EXHIBIT
 Ph-20
 8/8/89 JCS

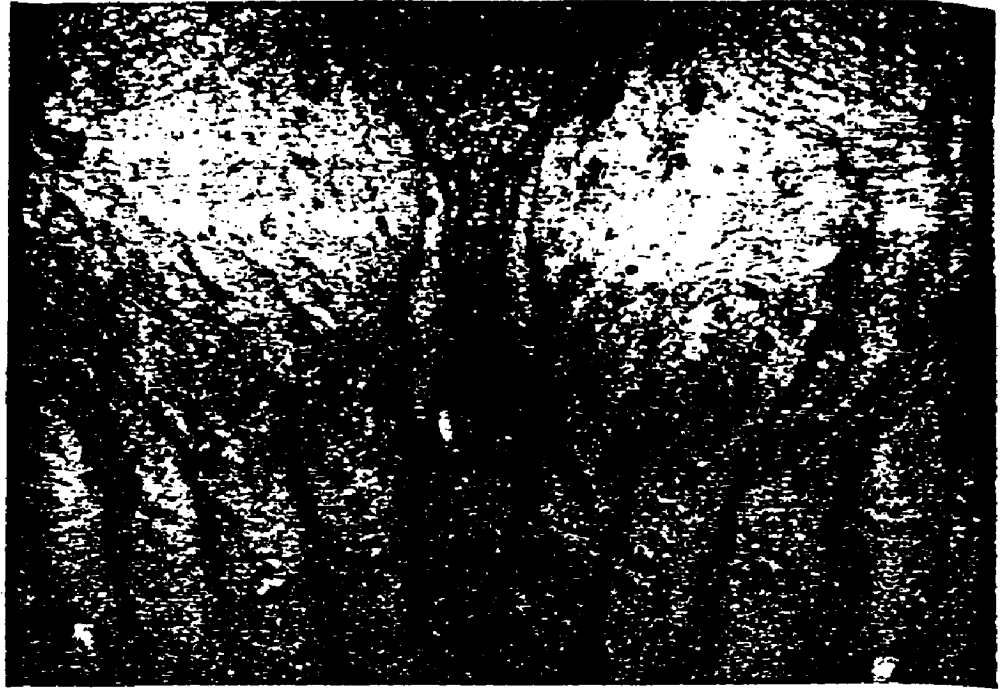


Fig 1.—Crusted bullae and atrophic scars on the dorsal surface of the hands.

Fig 2 (Case 3).—Illustrates hirsutism of the eyelids and lateral surface of the forehead.



by pressure. In addition to the vesicular eruption, the patient noted progressive darkening of his skin and marked hirsutism, especially over the temples. Inspection of the urine revealed a Coca-Cola coloration and, under the Wood's light, a brilliant red fluorescence. The exact laboratory data on this patient are no longer available except for the presence of quantitatively markedly increased excretion of urinary porphyrins including uroporphyrins, coproporphyrins, and porphobilinogen.

This man is now alive and well and apparently is suffering minimal if any symptoms of porphyria cutanea tarda. His present job does not entail the use of any chemicals. He has failed to present himself for further testing.

CASE 2.—This is a 60-year-old white male who has been employed in the factory for seven years as a welder. In the course of his work, which consisted of welding tanks and pipes, he was brought into frequent and prolonged contact with chemicals. He was admitted to the Newark Beth Israel Hospital for investigation. He stated that three months prior to admission, he had noted an increased darkening of the skin, thickening of the eyebrows, and a darkening and reddening of his urine. His family history and his past medical history were unrevealing, except for moderately heavy alcohol intake for some years.

Physical examination revealed numerous comedones and small epidermoid cysts and furuncles of

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of the hands.

to the vesicular eruption, excessive darkening of his skin especially over the temples revealed a Coca-Cola coloration under Wood's light, a brilliant red color under ordinary light. Laboratory data on this patient, except for the presence of increased excretion of uroporphyrins, coproporphyrins, and urobilinogen.

He is well and apparently has no symptoms of porphyria. His present job does not entail the use of chemicals and he has failed to present himself for treatment.

A 30-year-old white male who has been in the factory for seven years. Because of his work, which consists of cleaning and pipes, he was brought to the attention of the Newark Beth Israel Hospital. He stated that three months ago he noted an increased darkening of the eyebrows and the color of his urine. His family and social history were unremarkable. He had a history of heavy alcohol intake for

years and revealed numerous comedones, epidermoid cysts and furuncles on his face, chest, and shoulders. There was intense grayish-brown hyperpigmentation with a purplish tint on the exposed surfaces of the face, neck, chest, and hands and moderate hypertrichosis of the temples. The scalp hair showed a lusterless, dull silver color change. The liver edge was palpable about 3 cm below the right costal margin and was smooth and nontender. The remainder of the physical examination was within normal limits. A casual urine specimen revealed a strong tea color with a deep fluorescence, reddish, under the Wood's light.

Laboratory studies revealed increased urinary uroporphyrin, coproporphyrin, and urobilinogen excretion. There was no demonstrable porphobilinogen. The feces showed increased uroporphyrins and coproporphyrins. All porphyrin determinations were qualitative and done by the Watson-Schwartz method. Other significant findings included an elevated serum glutamic oxaloacetic transaminase ranging between 41 and 51 units on five different days. Serum glutamic pyruvic transaminase on corresponding days ranged between 33 and 64 units. The sulfobromophthalein retention was 6% in 30 minutes. The erythrocyte sedimentation rate (Westergren) was 94 mm in the first hour. All other studies, which included complete blood count, bleeding and clotting time, urinalysis, glucose tolerance test, serum bilirubin, blood urea nitrogen, total proteins, albumin-globulin ratio,

serum cholesterol, alkaline phosphatase, cephalin flocculation, and thymol turbidity, serum electrolytes and CO₂ combining power, as well as serological tests for syphilis were all within normal limits. Electrocardiograms and chest x-rays were normal. A liver biopsy was performed and the specimen immersed in isotonic saline. It fluoresced intensely under the Wood's light. The red pigment diffused out into the saline, so that the entire tube fluoresced. The microscopic examination of the liver specimen revealed parenchymal cell regeneration and hemofuscin deposition. A skin biopsy from clinically hyperpigmented postauricular skin showed a normal epidermis except for the dermoepidermal border, where there was a striking deposition of brown granular pigment. In addition, there was mild infiltrate of small round cells in the dermis. No sebaceous glands were visible in the sections. Shortly after discharge from the hospital in June, 1963, the patient was treated for a chronic trichophytosis of the feet with griseofulvin 0.5 gm twice daily. About four days after the onset of this treatment, a severe vesiculobullous eruption on the dorsal surface of the hands appeared. The griseofulvin was stopped, but the eruption progressed for another two weeks. Healing time was very prolonged, and at present, residual atrophic scarring is visible on both hands (Fig 1). In the scars occasional milia are seen.

Summary of Data for 26 Workers Whose Urine Was Tested for Porphyrins

Patient	Chloracne *	Hyperpigmentation	Hirsutism	Urine Uroporphyrins	Chemical † Contact	Skin Fragility
1	Severe	Mild	Moderate	Pos.	Moderate	Pos.
2	Mild	None	None	None	Severe	Neg.
3	"	Mild	"	"	"	"
4	Severe	"	Mild	"	"	Pos.
5	Mild	None	"	Pos.	"	"
6	"	"	None	None	Moderate	Neg.
7	"	Mild	"	Pos.	Moderate	"
8	Severe	Moderate	Severe	None	"	"
9	Mild	Mild	Mild	"	"	"
10	Moderate	Moderate	Moderate	"	Severe	"
11	Severe	"	"	"	Moderate	"
12	None	None	None	"	Severe	"
13	"	"	"	"	"	"
14	"	"	"	Pos.	Moderate	"
15	Moderate	Mild	Moderate	None	"	Pos.
16	"	Moderate	Marked	"	Severe	"
17	Mild	Mild	None	"	Mild	Neg.
18	Moderate	Moderate	Marked	"	"	"
19	Severe	Marked	None	Pos.	"	"
20	Mild	Mild	Moderate	Pos.	"	"
21	None	None	None	None	"	"
22	"	"	"	"	"	"
23	Mild	"	"	"	"	"
24	None	"	"	"	"	"
25	"	"	"	Pos.	"	"
26	"	"	"	Pos.	"	"

* Severity of chloracne is judged on the presence of comedones, epidermoid cysts, and furuncles and pustules.
† The extent of exposure is difficult to truly judge because of such variables as personal hygiene and work habits.
‡ Brief period of employment.

Bisberg et al

Vol 86, Jun, 1964

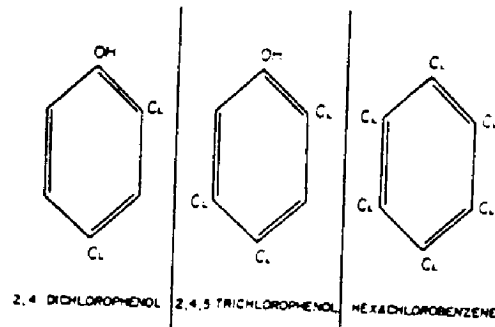


FIG 3.—Comparison of structural formulae of weed killer manufactured and fungicide responsible for acquired porphyria cutanea tarda. Note the similarities.

CASE 3.—This is a 48-year-old white male employed at the factory for eight years mixing batches of chemicals. During the past two years, he had developed hyperpigmentation of the exposed skin of the face and hands. There was marked hirsutism which involved the temples. The dull silvery tint of the hair was visible. He stated that in the past he had had episodes of blistering of the exposed skin. He also had noticed that his urine was dark on voiding. His family history was noncontributory. The physical examination revealed an intense hyperpigmentation of the face, neck, and hands. There was severe hirsutism involving the eyelids, eyebrows, and lateral aspects of the forehead (Fig 2). Comedones and small epidermoid cysts were very prominent, and there were numerous furuncles scattered over the entire body. The remainder of the physical examination was within normal limits except for prolapsed hemorrhoids. The following laboratory studies were within normal limits: complete blood cell count, urinalysis, bleeding and clotting time, prothrombin time, blood glucose tolerance test, urea nitrogen, cholesterol, bilirubin, alkaline phosphatase, total protein and albumin-globulin ratio, cephalin flocculation, thymol turbidity, serum electrolytes including sodium, potassium, chlorides, CO₂ combining power, calcium, and phosphorus. The serum glutamic oxaloacetic transaminase on five successive days ranged between 39 and 56 units while the serum glutamic pyruvic transaminase on corresponding days ranged between 47 and 72 units. The sulfobromophthalein retention was 85% in 30 minutes. The electrocardiogram was normal. The chest x-ray revealed a diffuse nodular infiltration of both lungs due to pneumoconiosis. This was consistent with the patient's history of having worked a number of years as a coal miner. The plain film of the abdomen was negative. The urine revealed a negative Watson-Schwartz test. The urine failed to fluoresce under the Wood's light. The erythro-

cyte sedimentation rate (Westergren) was 24 mm in the first hour.

A liver biopsy was performed and the specimen immersed in saline. Under the Wood's light the specimen and saline in which it was immersed fluoresced faintly. On microscopic examination, the liver biopsy showed evidence of liver cell regeneration and hemosiderin deposition. A skin biopsy showed brown granular pigmentation at the basal margin of the epidermis. There was a mild chronic inflammatory infiltrate scattered through the dermis. No sebaceous glands were visible in the sections.

Since this man's chloracne has been so severe, he had been removed from contact with chemicals two years prior to his admission to the hospital. This probably was responsible for the failure to prove qualitative chemical evidence of porphyrins in the urine. It also may indicate that acquired porphyria cutanea tarda is reversible.

Screening Tests

Twenty-six additional men working at this chemical factory were studied on an ambulatory basis. In addition to routine urinalysis, each urine specimen was tested for uroporphyrin by the Watson-Schwartz method. Eight out of the 26 manifested significantly increased excretion of urinary uroporphyrins by the Watson-Schwartz method. If the three cases described in the case reports above are added, this is a total of 11 cases of porphyria cutanea tarda of varying degrees of severity out of 29 patients tested, or 37.5% (Table).

Comment

Hyperpigmentation in these workers was limited to the sun-exposed areas of the head, neck, and hands. It was more frequently observed in the Negro patients involved. The degree of hyperpigmentation was roughly proportional to the severity of the chloracne. The hyperpigmentation varies from mild redness in extremely fair individuals to dark gray intense dusky bronzing of the skin. The degree of hirsutism was also proportional to the severity of the chloracne. This too was quite variable in degree but always involved the temples between the lateral half of the eyebrow and the temporal hair of the scalp. The hirsutism in a few cases, notably case 3, extended beyond this and involved both the upper and lower eyelids. The hair was of approximately the same texture and density as that of the eyebrows.

esterol) was 24 mm. and the specimen - the Wood's light fluorescence examination, the liver cell regeneration. A skin biopsy at the basal there was a mild chronic through the dermis were visible in the

has been so severe, he contact with chemicals two to the hospital. This or the failure to prove of porphyrins in the that acquired porphyria

Tests

working at this chem- an ambulatory basis. analysis, each urine speci- phyrin by the Watson- of the 26 manifested tion of urinary uru- -Schwartz method. If the case reports above of porphyria leg. of severity out % (Table).

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these workers was ed areas of the head, more frequently ob- tients involved. The tation was roughly ity of the chloracne. varies from mild red- individuals to dark ing of the skin. The also proportional to acne. This too was but always involved lateral half of the al hair of the scalp nes, notably case 3. d involved both the . The hair was of texture and density

The occupational environment of these men consists of a group of basic chemicals including acetic acid, phenol, monochloroacetic acid and sodium hydroxide, plus the finished products 2,4-D and 2,4,5-T as well as many unknown intermediary products. It is known that one of the intermediaries is a highly volatile chlorinated phenolic ether which contains six chlorine atoms. This particular compound, because of its volatility, is strongly suspected of being a possible causal agent. Porphyria has been described in many cases as a result of ingestion of hexachlorobenzene^{2,3} chemically a closely related compound (Fig 3). This would lend support to the concept that porphyria cutanea tarda is not necessarily genetically produced, unless the genetic defect is an extremely common one.

An analysis of the table of the 26 surveyed workers (Table 4) reveals: the severity of chloracne does not usually correspond to the degree of exposure to chemicals (patients 1, 8, 11, 19 or patients 2, 3, 5, 10, 12, 13, 16). The severity of prophyria does not usually correspond to the degree of chemical exposure (patients 7, 20, 25, 26 or patients 2, 3, 4, 10, 12, 13, 16). The severity of chloracne does not usually correspond to the presence of porphyria (patients 1, 4, 8, 11, or patients 5, 20, 25, 26). Therefore it would appear that there is some individual susceptibility to these diseases. It has been observed in general that: (1) Patients with adolescent acne tend to get worse chloracne; (2) Possibly previous liver damage (alcoholism, etc) predisposes to porphyria. Also there must be in these cases some etiologic relationship between chloracne and porphyria since a relatively large number of both diseases began to appear and have persisted at the same time.

On the basis of the elevated transaminase levels and the histological signs of liver cell regeneration in the liver biopsies, it may be assumed that the basis of the disturbed

porphyrin metabolism is a hepatotoxic effect of one or more of the chemicals in this factory environment. The synergistic roles of other known liver toxins such as alcohol and barbiturates, or griseofulvin (1 case), cannot be overlooked.

We would like to express appreciation for the help offered by Dr. Donald J. Birmingham of the division of Industrial Dermatology of the US Public Health Service, to Dr. Marcus Key, and to Dr. Norman Olivier.

Jacob Bleiberg, MD, 40 Union Ave, Irvington, NJ.

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CONFIDENTIAL

TO: Mr. H. S. Weiner (3)

FROM: Mr. R. A. Guidi

SUBJECT: Safety & Health Hazards
in 2,4-D Building

DATE: March 25, 1960

cc: Messrs. J. Burton
F. Kennedy
P. J. Koskey
H. A. Smith

Paul Koskey, Homer Smith, and I have discussed the 2,4-D building with regard to safety, health hazards, and operational difficulties. The tabulation below lists those items which should be considered for improvement for a safer and more efficient unit.

FUME SCRUBBER

The basic unit does not adequately remove fumes from the building which is obvious from the intensity of the odors, particularly in the 2,4-D building at any time of day or night. The scrubber itself is in need of rebuilding because of attack on the metal. The duct system in the operating area has seriously deteriorated and is damaged, even more as a result of the recent explosion.

VENTILATION

Because of the low ceiling heights over the D & T acid platforms, the summer temperatures in this area often rise to 110°F. The situation is even more difficult during the manufacture of the amine salts. The high humidity plus amine fumes make for an impossible situation. There are five blowers in the esters and acid building. However, because of the size and particularly the height of this building, it is impossible to properly ventilate. Additional blowers will only expel more fumes into neighboring facilities.

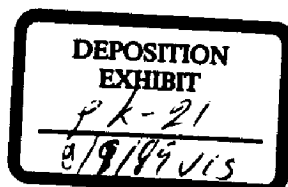
FLOORS AND SEWERS

The floors in these two working areas (esters and D & T) are at different levels. These floors are rough and make it particularly difficult to move acid dollies, which makes for a potential safety hazard. The pitch of the floor is quite inadequate. The sewer system through which we dispose of D & T acid wash liquors is small and does not have sufficient pitch. This system of disposing of wash liquors further complicates the fume problem. A disposal system for efficient elimination of phenols should be considered. It is suspected that the authorities will make this mandatory at some future time.

SOLVENT HAZARDS

DS00018265

Presently, we have sizable quantities of solvents in the ester room and smaller amounts in the 2,4-D area. This condition is aggravated



by the fact that adjacent to both of these are electrical rooms in which are located non-explosion proof disconnects and magnetic starters.

BOILERS

The large E & W boiler is separated from the ester room where sizable quantities of solvents are used by a common brick wall. However, through this wall is a personnel door which might very well be hazardous in the event of an alcohol spill or alcohol fumes from the process area. The smaller fire tube boiler, also adjacent to this building, has a door connecting to the 2,4-D room. Opposite this doorway, approximately 20 ft. away at the other end of the room, the various alcohol and acid mixes are prepared for the ester unit. Although remote, it is conceivable that alcohol vapors (since the make-up batches are steam heated) could penetrate into the boiler areas and be ignited.

MATERIALS HANDLING

For some time, we have discussed the economics of improved facilities for handling wet 2,4-D and 2,4,5-T. Consideration has been given to installing a fully automatic centrifuge to process 2,4-D. However, this too, has not been justified economically. The present system for handling wet acids in dollies is a hand operation. The intermediate storage is accomplished by means of some 30 odd dollies placed at random points on the main floor which is unsightly and further complicates the housekeeping. This condition also constitutes a safety hazard. We have considered bulk storage to improve the drumming of wet acid, but have not been able to solve this problem principally for lack of space.

ROOF HAZARD

Several of the roof slabs are damaged as a result of corrosion of the reenforcing steel, and some failure as a result of the explosion. This problem is aggravated further by the installation of several tanks on the roof, and the accompanying piping through the roof. As an example, temporary protection has been set up to keep falling pieces of concrete from entering the product at the 2,4-D 6 x 6 filter. The roof over the small boiler must be replaced in the near future, since the wood is dry-rotted.

FORMULATION AND PACKAGING

This area is congested and does not permit a good flow of materials; empty cans and drums in, and full units out. The floors in this area are hazardous, making it dangerous when moving material by hand truck. The complete operation could be improved and expanded, whereby we would fill units now packaged under contract. The savings involved should be calculated; I feel this is sizable. There are times when the limited dock facilities create scheduling problems, since we can accommodate only one truck at any one time.

D.S.00018266

LOCKER ROOM

The main locker room is located near the "T" ester process area where the large volumes of alcohols are stored as mentioned previously. Certainly, a fire at an inopportune moment could endanger the lives of many men. This location for the locker room is also bad since it is near the 2,4-D area which generates the fumes causing our "odor" problem. These change room facilities are exceedingly hot during the summer. The ventilation is inadequate, and because of the proximity to the process areas, is difficult to correct.

WATER SUPPLY

The primary process water is dependant on a deep well which is not completely reliable since the present pump unit is expected to perform only for an additional six months. This results from a corrosion problem which has not been resolved. The secondary supply comes from river water. However, with extreme tide conditions, this water is unavailable for several hours each day. Both of these systems are dependant on plant power which might not be available in the event of a fire. As for city water, this is totally inadequate.

GENERAL LAYOUT

As for the equipment layout, as a visitor once commented, it is "shoe-horned in". Because the various reactors are so "tight" to one another or to the walls of the building, this has complicated the maintenance to where, in some cases, unaffected units must be removed to reach the damaged equipment. Furthermore, it is nearly impossible to install additional equipment which might well be necessary for expansion purposes. Much of the old piping is poorly installed, completely lacking in supports, and so tight that it is not possible to insulate or apply coatings to protect against further corrosion. There has been occasion where idle pipe has not been removed since other piping has been supported from the idle pipe.

Each of the above items can be considered as a problem in itself, and I feel certain we can correct these. Surely, this work will be costly and time-consuming. This improvement program would require the attention of a competent design engineer for fully two years, and require extensive planning and organizing so as not to hamper seriously the operations of the production department during the renovation.

R. A. Guidi

RAG: jp

D.S00018267

NEWARK REHABILITATION

DISCUSSIONS OF FLOW DIAGRAMS

Present at Discussion: P. Koskey
M. Kennedy
J. R. Siemoneit

Date of Discussion: March 25, 1960

2,4,5-T Acid Unit

If revision of rebuilding of this unit was considered, the following changes should be incorporated:

1. Design a new conveyor system to get away from carts.
2. Install a new, totally enclosed automatic batch type centrifuge to help relieve the chloracne problem.
3. Install a new 2400 gallon Monel acidification tank with pump for handling TCP recovery from rotary filter mother liquor.

This tank would do away with the need for a mother liquor holding tank (8400 gallon) and would not hold up the normal process by joint use of 2,4,5 T acid acidification tank.

2,4 D Acid

The desired changes in this unit also include a totally enclosed batch centrifuge and redesign of the material handling system to get away from carts. A closed screw conveyor should replace the present system of hoisting carts to the second floor for dumping. The above changes would improve the odor, eye irritation and chloracne problem.

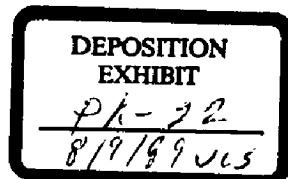
Esters and Amines

No major changes in principle are required but rehabilitation would include resizing of a few tanks and a better look at the handling of alcohol inside of a building.

J. R. Siemoneit
J. R. Siemoneit

JRS:ejk
4-6-60

DS 00028375



Diamond Alkali Company

INTER-OFFICE CORRESPONDENCE

DATE

October 7, 1963

TO

J. S. Cort, Jr.

FROM

F. R. Kennedy

SUBJECT:

CHLORACNE

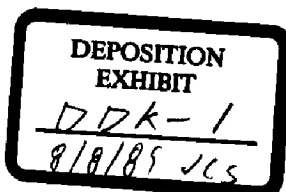
The test furnished by Dr. McBurney is the one familiar to Dr. Bleiberg, and one used previously for some of our people here.

Plans are being made to sample the entire plant to develop records of porphorin levels every 6 months. Some saddle of degree of flourescence will have to be developed in order to note changes in levels over the 6 month periods.

With the plant now on stream, and operators on regular shifts, testing can start next week. The lab can probably handle 4 or 5 analysis/day, so that a complete test can be accomplished in 10 days to 2 weeks.


F. R. KENNEDY

FRK/jw



CONFIDENTIAL

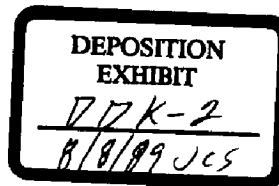
REGULATIONS FOR WORKERS HANDLING TRICHLOROPHENOL OR ITS SODIUM SALT

C
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P
Y

- 1) The chemical operator in the trichlorophenol unit must wear a clean set of work clothes daily; his face, neck, ears, hands, and all exposed skin are covered with Kerodex (a protective cream), and on termination of duty, must shower thoroughly.
- 2) Any chemical operator performing a transfer of TCP or Na-TCP is required to wear goggles and rubber gloves.
- 3) No man is permitted to enter a vessel which has contained either of the above chemicals until the vessel has been boiled out with a caustic solution, a minimum of two, and preferably three times. He then is required to wear a full face mask with an outside air supply and apply cream to all exposed parts of the skin. Immediately after completing his task, he is required to shower thoroughly and change work clothes.
- 4) In the event of an equipment failure, or accidental splash onto any portion of a man's body, we urge immediate washing with copious quantities of water for an extended period of time (15-20 minutes). This has occurred on occasion. The usual result is a mild chemical burn; however, if the prescribed remedy is not delayed, there is little, if any, damage.
- 5) Generally, all our equipment is of the closed type; where air vents are required, the line is extended to a remote location. The plant area is washed daily. However, no special detergents or procedures have been outlined at this time. In retrospect, we might say that the precautions taken in this unit are no more demanding than those of an acid plant or a caustic plant.

DS 00019475

3/23/64



July 25, 1963

Mr. J. S. Cort, Jr. - Cleveland

Mr. F. R. Kennedy - Newark

PLANT INSPECTION ON TUESDAY, JULY 23, 1963

Our skin specialist, Dr. Jacob Eleiberg, visited the Plant on the above date for treatment of our men. Accompanying him were Dr. D. J. Birmingham, Medical Director-Chief, Dermatology Section, U. S. Public Health Service, Cincinnati, Ohio; Dr. E. Burtado of the State of New Jersey Department of Health in Trenton, New Jersey; Mr. Preston C. Shiner of the State of New Jersey Department of Health and Dr. O'Quinn from the Louisiana State University.

The 2,4-D and 2,4,5-T Acid Building was inspected and the group also observed the medical care given to the men. Dr. Birmingham was very pleased with conditions in the building since the roof has been partially removed and feels that the renovation work will go a long way in clearing up our problem. This was the first visit for the State doctors who were quite impressed with our locker and shower facilities. Our new program of supplying clean towels each day was considered excellent.

Due to the close friendship of Dr. Birmingham with Dr. Eleiberg, and his interest in our problem, we can expect that Dr. Birmingham will again visit us when our new facilities are completed.

FRE/nc

F. R. KENNEDY

cc: Dr. R. W. McBurney

CONFIDENTIAL

DEPOSITION
EXHIBIT

DDK-3
8/8/85 JCS

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Y

Diamond Alkali Company

OFFICE CORRESPONDENCE

DATE
March 30, 1965

TO: Mr. J. S. Cort, Jr. - Cleveland ✓

FROM

Mr. F. R. Kennedy - Newark

SUBJECT: CELOPACNE - DOW TESTING

FILED BY DATE

I am including a rough draft of notes taken at Midland last Wednesday. I made no attempt to develop these, as Ed's report has covered all phases thoroughly and accurately. As mentioned in my notes, the color slides of their patients are not similar to our local condition. Our cases usually start with a number of blackheads around the outer area of the eyes. We have not had any complaints of fatigue or listlessness.

As Ed has pointed out, this material seems to have strange properties. A high vapor pressure would account for bi-lateral infection; however, this does not agree with lab procedures of concentrating in benzene or chloroform solutions by removal of the solvent by distillation. Dow's attempts at air sampling were inconclusive due to problems in collecting representative samples. I believe they said they were trying again. They are setting up tests in their Bio Lab for exposure of rabbits to air samples.

I have suggested to Dr. Bleiberg to contact Dr. Holder of Dow for the exchange of medical information. Dr. Bleiberg feels he might obtain more helpful clues on a medical level.

The program is being developed at the Plant to establish curves for this material on our chromatograph for different concentration levels. Once this has been accomplished, we will check every product and waste stream throughout the entire "T" production areas. Wipe samples of equipment, valve handles, tools, etc., will be taken in these areas also. Due to the nature of the high pressure reaction, it might be necessary to call on Research's high pressure lab to investigate the suppression of the dioxin formation in the caustic fusion step. If this is the solution and a removal process is necessary, some of this work might possibly be accomplished at Newark.

Work has not started in the Lab as yet, as I feel an exhaust system should be installed to handle the effluent gases from the chromatograph to minimize exposure of the technicians. This will be accomplished by a temporary exhaust blower borrowed from the Maintenance Department. We should be able to start toward the latter part of this week.

FRK/nc

F. R. KENNEDY

Enclosure

cc: Dr. E. L. Chandler

0500012609

DEPOSITION
EXHIBIT

172K-4
8/10/89 JCS

MEETING HELD ON WEDNESDAY MORNING, MARCH 24, 1965
AT DOW'S BIO-CHEMICAL RESEARCH LABORATORIES, MIDLAND, MICHIGAN

Other visitors to the meeting included Mr. Dodds, who accompanied Dr. Frawley from Hercules Powder. Dr. Kelly from Monsanto did not attend, but had visited with Dow the previous week. The Dow people at the meeting were as follows: V. K. Rowe, Assistant Director - Bio-Chemical Research Lab; Dr. Holder, M.D., Physician responsible for treatment of patients; Dr. Sadek, Pathologist; K. Silverstein, Chemist; J. Peterson, Chemical Engineer handling statistics, and Howard (?), Chemist responsible for the development of the gas chromatograph method of analysis.

Dr. Holder opened the meeting with colored slides of Dow patients being treated as a result of exposure in 1963. The pictures showed a typical blackhead formation around the eyes and forehead. The eruptions pictured were much more intense than anything I personally have seen at our Plant.

V. K. Rowe had said they had 5 to 10 cases, but this statement was quickly corrected by Dr. Holder, to 70 to 75 cases. During a question and answer period, Dr. Holder described the presence of comedones and carbuncles across the shoulder blades, back and buttocks areas. Up until this point, I wondered if there were two separate types of chloracne we were discussing. He claims that 2-1/2 years out of the contact area is sufficient to clear a patient of symptoms. This does not seem possible, since 2-1/2 years have not elapsed. He claims to have noted fatigue as a symptom also.

Five of their more severe cases were submitted to extensive testing, which included open (?) liver biopsy; porphyrins; standard metabolic tests; kidney, thyroid, lung and heart functions. In all cases, all of these tests showed normal functioning of the organs involved. Skin biopsies taken did not show any abnormalities other than the characteristic increase in kerotins. They

have not as yet ascertained whether exposure is through fumes or is systemic. They are reasonably positive that it is not caused by direct contact, as every case is bi-lateral.

Contrary to some of our feelings, they put little stock in natural immunity and experience no difference in skin types. Dr. Holder seems to be paralleling the treatment work done by Dr. Bleiberg, that of treating the symptoms by blackhead and comedone removal and the administration of vitamins, particularly Vitamin A.

The entire Dow group are completely convinced that the chloracne is 2,3,6,8-dichloro-dibenzo-p-dioxin. This is the compound suggested by Cy Perkins in a report to Jack Berror on June 27, 1960. There is an unsymmetrical isomer - 1,3,7,8 - this has some activity, but does not approach that of the symmetrical. In their studies, they looked for the dibenzene-furan, a known acneogen in naphthalene production. They did not find this compound, but had not eliminated its possibility. The dioxin solubility is less than 10 ppm in ethanol and about 400 ppm in benzene. Benzene was used to extract wipe samples in the Plant and as a carrier for their rabbit tests. One interesting note - the significantly short time of contact necessary that will cause chloracne. In one case, they washed off with dioxin 15 minutes after application. The rabbit's ear became affected in spite of continuous washings every one-half, up to 4 hours.

Dr. Sadak showed slides of cell structure which is in the skin of rabbit ears, with mild and severe cases of chloracne. Most of his presentation was beyond my comprehension. The rabbit sustained liver damage in almost all cases. This damage (necrosis?) occurred very close to the bile duct. Dr. Sadak stated that in cattle, hyper-keratinosis correlated very closely with

Vitamin A deficiency. The build-up of Vitamin A in the blood stream is a very slow process. The amount of work done by the Bio-Chemical Section was thorough and extensive. Tests of a small dose of 20 ppm showed no response. 40 ppm developed a slight folliculitis in 11 days. A single dose of 100 ppm caused a severe reaction in 8 days. Dow uses a word scale of 5 terms, varying from "No Response" to "Very Severe", so that interpretation of results is confusing. On a multiple application of 1 ppm, a moderate response was detected after 9 applications, and a severe response after 11 applications. 25 applications each of 10, 20 and 100 ppb showed no effect.

As part of their program, they tested samples from all competitors and were kind enough to send the results of their findings personally to me at the Plant. Three of our T-acid samples produced in September of 1961 showed slight response after 13 days on the rabbits, and 2 of the samples showed 5 and 16 ppm analytically. Of two samples of trichlorophenate, one showed a slight to moderate response in 14 days, while the other showed no response in 26 days. Neither of these samples were analyzed by chromatograph. At this time, the origin of the phenate samples has not been determined.

White rats are not used for this type of skin test because they do not respond properly (?); do not develop chloracne (?).

H. H. Rowe stated that phenates as high as 20 ppm were found and T-acid as high as 1/2 ppm. This latter figure does not agree with the analytical results of 16 sent to me. When Dow was experiencing their problems in the Plant, they detected 20 ppm in their phenate. K. Silverstein spoke of cleaning up their plant area, tools, etc., with various solvents. Although benzene and acetone were good solvents for the material, they were impractical for plant use. He further stated that 1,1,1-trichloro-ethane worked

as well. Strong detergents are not effective without intense scrubbing and hard work. From his comments, I imagine a decontamination process was performed in their unit. From their tests, it was determined that the dioxin decomposes at 600°C. Even though Dow has a very large industrial waste burner with furnace temperatures of over 1200°C, they continue to bury their wastes. They were hesitant to continue discussions along these lines.

Laboratory wastes, including gloves required in handling this material, are incinerated. Howard (?) stated that the chromatographic method of analysis can detect 10 ppm in an anisole sample and 1 ppm in TCP and T-acid. As of yet, they have no method for esters or formulations. TCP sample preparation for analysis is as follows: 20 grams of TCP were converted to the sodium salt and extracted with 20 cc of chloroform. The chloroform extract is concentrated 10 to 1 and injected into the machine. Phenate solutions are reduced to a 10% phenate concentration extracted with chloroform and handled as above. T-acid samples are prepared by extracting 20 grams of the T-acid with 40 cc of chloroform. The chloroform is filtered and caustic-washed with one-tenth normal caustic and the chloroform concentrated as above.

Plant wipe samples were extracted with 2 cc of chloroform and used as such. We will have to develop our own method of determining chromatograph response in terms of ppm. Throughout the entire meeting, one theme seemed to be presented. For everyone's protection, everyone should clean up his final product and certainly on the local level, this is very necessary. Mr. Rowe stated many times that each organization could handle the problem in their own way.

200012613

From his presentation, I gathered that detection was the primary problem and that steps to eliminate its carry-over into the final product was well within the capabilities of all people involved. A small sample of the dioxin was given to each company attending the meeting.

DS00012614

DBK-2
8-8-89

N O T I C E

As part of our continuing effort to control and eliminate the chlorine problem within the Plant, a urine check has been proposed.

We intend to perform a standard urinalysis in our own Laboratory, for every member of the Plant. A schedule will be issued shortly to facilitate the taking of samples. This procedure will be repeated in three months' time.

It must be emphasized that this test is of an exploratory nature, and that no results can be expected until a series of runs for each person has been made. The information gathered may or may not give us further insight into the problem.

Your full cooperation and patience with this program will be most appreciated.

FRL/DC

F. R. KENNEDY

11/25/63

ROOM: LOCKER ROOM

DS 00024347

ATTENTION

EMPLOYEES OF DIAMOND ALKALI COMPANY
60 LISTER AVENUE
NEWARK, N. J.

DISTRICT 50, UNITED MINE WORKERS OF AMERICA received a letter signed by several of your fellow workers. This stated many of your working conditions and job in-security.

Although it will make our letter to you long, we strongly feel each of you should read a copy of the letter we received, it is an exact copy, we have only withheld the signatures. "The following is an exact copy received by District 50, U. M. W. A."

Mr. J. Tavaglione,

Enclosed find a mailing list of employees of the Newark Plant of Diamond Alkali Chemical Co. All marked "okay" are possible men who will go in favor of a union.

At lease 60% of these men are now doctoring for a skin rash and chemical disease known as chloro acne, which attacks the liver and gives lumps to the skin filled with pus. It wears down the system. Yet a lot of these men have bought homes, and are forced to take the gaff. In 2,4, D department, there are no vents for fresh air. The smell of alcohol will knock you down (so what) say the plant personel. In 2, 4, 5, T the chemical that turns the skin black in time, no protection either (so what). And on Saturday when some of the boys can get some overtime, they let them stay home and bring in Man Power men at \$1.15 an hour (so what). What happened to all the men who got the rash and liver disease? They just let them go (so what) sue me.

Sir these are the points I want you, as a union man, to write each employer. We have a three man committee who takes in our beefs (so what). We have a working agreement, not a contract, with the company. It isn't worth the papers it's printed on.

We manufacture weed and brush killers. This is made up of a base called (D.C.P.) Di Chloro Phenol, it is this product that causes chloro acne. It has been proven by German chemical plants that this disease can be prevented, but not cured. Last year the plant records show that over \$18,000 was spent on doctors for the men with the rash but very little was spent to improve working conditions.

An example is Mike Kalena of 68 Joseph St., Newark, N. J. Mike doesn't know it yet, but the company is about to discharge him. His face is black, his body covered with sores. Mike worked in 2, 4, 5, T for about 9 years, now Dr. Blieburg of 22 Ball Ave., Irvington,; a skin doctor, advised the company to let him out in the yard where he can get fresh air and sunshine. (What a joke.) Stop in and see Mike, he gets home about 4 o'clock. You have to see some of those men to believe it. Dr. Blieburg, the phony, is stupid himself. He treats.

DS 0002800

DEPOSITION
EXHIBIT

D175-1

8/19/89 JES

every man different. Some he gives shots to, others he burns the skin with the electric needle, others he gives pills; he is just making a fast buck. What we suggest is a mimeographed copies of this letter with the ighlights and a union card for each man to sign, stressing that all this is kept in the strictest of confidence.

You start the ball rolling, we will work from within the plant.

Hoping your letters will be sent out soon.

Sincerely,

NAMES WITHHELD FOR OBVIOUS REASONS

P.S. Another highlight, what happened to all the men who were discharged for having chloro acne?

EACH of you are aware of each of the points brought forward in this letter.

The time-tested way to correct these conditions is to organize as one.

District 50, U. M. W. A., represents the largest membership in the Chemical Industry; including several plants of Diamond Alkali Company. With the vast experience gained in negotiating thousands of contracts covering wages; hours of work and working conditions for employees of the Chemical Industry; we of District 50, U. M. W. A., know that we can correct many of the adverse conditions now existing at your plant.

However, the first step must be made by YOU.

SIGN THE ATTACHED CARD, this gives District 50, U.M.W.A. the right to petition the National Labor Relations Board to conduct an election at your plant so that you and all of your fellow workers will have a union of your choosing, and that union is DISTRICT 50, UNITED MINE WORKERS OF AMERICA!

SIGN THE ATTACHED CARD

PLACE IT IN THE ENVELOPE

DROP IT IN THE MAIL BOX

NO STAMP NEEDED

District 50, U. M. W. A.
Organizing Committee on
behalf of employees of
Diamond Alkali Company

4/30/62

DS 00028009