Diamond Alkali Company

INTER-OFFICE CORRESPONDENCE

DATE 3/25/65

TO JOHN CORT, JR. ✓

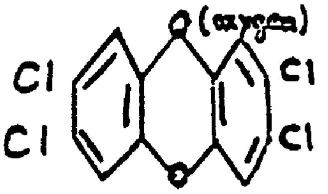
FROM E. L. CHANDLER

SUBJECT CHLOROACNE - DOW MEETING

cc: F. R. Kennedy - Mgr., Newark plant
J. O. King
M. F. Wilkerson

On March 24, Mike Kennedy and I met with two people from Hooker Chemical Co., two from Hercules, and with the Dow group to discuss the toxicological impurities associated with 2,4,5 trichlorophenol and related materials.

Dr. Rowe of Dow Chemical opened the meeting by stating that they had operated for 25 years without trouble; but, in the last year, they had 60 to 70 cases of chloroacne. Ten of these were moderate, and five to ten were extremely severe. Their approach was a qualitative one at first. They wanted to find the causative material, learn how to identify it, and try to avoid continual trouble with the unknown. They tested various materials from tar fractions and from, as they put it, "gunk", etc. They found that there are a number of suspect materials, probably 26 or 27; but the major "bad actor" that they identified and which seemed to consistently cause the problem was 2,3,7,8-Tetrachlorodibenzo p-Dioxin (symmetrical).



→ 2,3,7,8-TETRACHLORODIBEN
p-Dioxin
(Symmetrical)

This incidentally was previously listed as a suspect material by Cy Perkins of our company. A similar material is the unsymmetrical 1,3,7,8-TCDBD, also sometimes listed as 2,3,7,9-TCDBD.

The Dow people used the white glove approach and found this contaminant on tool handles, benches, instruments, and other fomites. In test animals, they could consistently cause the symptoms to appear. Dr. Holder of Dow, one of their medical doctors, had excellent color slides of the various patients. The difficulty starts with multiple blackheads resulting in closed cystic structures which make the patient look like he needs to wash his face. The disease develops slowly, not appearing until six weeks to two months after mild exposure but appearing in five to seven days with very heavy exposure.

One bench chemist has been under treatment for two years and his face is starting to show signs of clearing. Dr. Holder says that he believes this man's problems will be solved in another six months. Dr. Sadek, who does their microscopic work in connection with their animal laboratory, showed photo micrographs of the cysts as they formed in the ears of rabbits. The cysts correlated with those found on the faces of the men.

CONFIDENTIAL

Guidi Exhibit
#12 I.D.
2/19/87 KOD

Basically, there is a carotinoid deposit in the hair follicles and oil ducts in the face. These eventually go from the blackhead stage to form a closed, heavy core deposit. The chemical cannot be found in the facial tissues or in the cores, but the problem still persists after exposure. The best description of the acute stage is that the facial tissues resemble the exaggerated surface texture of an orange, rather glazed and marbly with the enclosed hard core deposits.

A secondary symptom, which does not correlate directly with the amount of facial dermatitis, is a fatigue reaction where the employee is completely listless, tired out, and nearly incapacitated. A complete biopsy of liver, kidney, etc., shows no degeneration of major organs. A complete clinical examination of the patients showed no measurable affect on heart, blood pressure, respiration rate, blood sugar, etc. The fatigued patients seemed to be helped by heavy doses of vitamins, perhaps related in some way to the carotene metabolism of the body (involving vitamin A, etc.)

An oral dose of 17 micrograms immediately killed the test animals. The Dow people did not lower this dosage to obtain an LD_{50} but decided that, when they can detect this compound, it should not be in the product. They found that, after exposure to the material, washing within 15 minutes did not help a great deal, but did slow down the speed at which the symptoms appeared. Washing after one hour was of absolutely no help whatsoever in reducing total dermatitis or speed of appearance of the reaction. Moderate scrubbing with detergent does not remove this material. Extremely hard scrubbing can accomplish the task or the use of solvents, such as 1,1,1-trichloroethene.

Dow has developed a new analytical method in which they have confidence in their sensitivity to 1 ppm. They can only state in levels below this that some may be present below the 1 ppm. They stated that they have not used micro-colorimetric methods, and the electron capture tests that they ran made only a very slight improvement in sensitivity with this compound. Their analytical chemist stated that the electron cell saturates because of the presence of other materials in high concentration compared to the dioxin.

This material has some strange properties. It has a fairly high vapor pressure but nevertheless is quite persistent as a contaminant. It can be separated from benzene by boiling if it is not carried down to dryness. The Dow people are extremely careful in all of their work with this compound. They use PVC throw-away gloves, and all samples are burned in a special furnace which operates at 800°F. These samples are sealed before going to the burner. They use bioassay methods on rabbits for qualitative checking only.

CONFIDENTIAL

The Dow people state that they intend to set a limit of zero with sensitivity of plus or minus 1 ppm on this material. They have analyzed materials from other companies. including our company, and have found amounts as high as 10 ppm in 2,4,5-T acid and 20 to 30 ppm in phenates.

They have made a single application to the ears of test rabbits and found that 20 ppm will not give folliculitis. Forty ppm does give a slight effect, and 100 ppm is severe. They have made repeat applications of from 10 to 100 ppb, and 25 of these treatments do not cause a response; however, 1000 ppb (1 ppm) gives a slight response with nine applications and a severe reaction with 11 applications.

They conclude, therefore, that 1 ppm with repeat exposure can create a real problem.

Dow's people outlined a method for extracting and running samples on 2,4,5-T; 2,4,5-TP; and phenols. It involves a chloroform extraction, followed by a caustic wash, and a reduction by boiling to one-tenth the volume before putting it in the chromatograph. They have given the gas-liquid chromatography method to us, along with analytical-grade dioxin material. Mike Kennedy has these materials and intends to pursue the laboratory work necessary to ascertain where and how much, if any, of this dioxin appears in our 2,4,5-T process.

The purpose of this meeting was obviously designed to help us solve this problem before outsiders confuse the issue and cause us no end of grief. Dow is sending the test results on our material to us, incidentally; and this will further check our technique, etc.

Sincerely,

E. L. Chandler

ELC:een

CONFID

June-Aug. 1962

Eighth Report on Evaluation of Chloracne-Producing Potential of Various Chlorinated Organic Compounds

Guidi
Exhibit
#1
I.D.
2-19-87
KO'D

CONFIDENTIAL

DISTRIBUTION

4 - Dr. Guidi 8/28/62

1 - Tox Lab

1 - Survey Correspondence

1 - Survey Reports

6 - extras

CONFIDENTIAL

INDUSTRIAL HYGIENE FOUNDATION OF AMERICA, INC.
MELLON INSTITUTE, 4400 FIFTH AVENUE
PITTSBURGH 13, PA.

Eighth Report on

EVALUATION OF CHLORACNE-PRODUCING POTENTIAL OF VARIOUS CHLORINATED ORGANIC COMPOUNDS

for

DIAMOND ALKALI COMPANY

June-August, 1962

by

James M. McNerney, M.P.H.
Research Toxicologist

Mary Ann Babyak
Research Assistant

Marianne Kaschak
Research Assistant

Paul Gross, M.D.
Research Pathologist

H. H. Schrenk, Ph.D.
Managing Director

CONFIDENTIAL

INTRODUCTION

This report presents the results of the evaluation of the chloracne-producing potential of 14 samples collected at various points from a Trichlorophenol process and is a continuation of a series of reports on similar compounds. The test materials were evaluated on the response of rabbit ears to repeated applications. Conclusions were based entirely upon gross ovservations which included measurement of the thickness of the exposed ears.

MATERIALS AND METHODS

The materials tested were:

Sample No.	Description
C-1	Sample from autoclave batch 708-W. Autoclave digestion temperature range 160-175°C. Maximum temperature during MeOH addition - 180°C. Methanol distilled in the laboratory, residue diluted with water to approximately 23% and pH adjusted to 9.
C-2	Recovered Methanol from laboratory distillation of batch 708-W for sample C-1.
C-3	Sample from autoclave batch 718-W, Autoclave digestion temperature range = 145-175, maximum temperature during Methanol addition - 200°C. Methanol distilled in the laboratory residue diluted with water to approximately 23% and pH adjusted to 9.
C-4	Recovered Methanol from laboratory distillation of batch 718-W for sample C-3.
C-5	Laboratory distilled plant recovered Methanol. Fraction distilled between 55-85°C.

CONFIDENTIAL

Sample No.	Description
C-6	Residue from laboratory distillation in C-5. Brown with yellow solids. pH adjusted to 9.
C-7	Sample from plant still after Methanol distillation and water dilution - 5/7/62 date sampled. Sample diluted with water to approximately 23% and pH adjusted to 9.
C-8	Same sample as C-7, but steam stripped in laboratory until caustic solubility test on residue was satisfied. Residue diluted with water to approximately 23% and pH adjusted to 9.
C-9	Same sample as C-7, but purified in laboratory by dilution method. The Na salt was made from the recovered TCP and diluted with water to approximately 23% and pH adjusted to 9.
C-10	Sample from plant still batch used in C-7, but after plant steam stripping until caustic solubility test satisfied. Diluted with water to approximately 23% and pH adjusted to 9.
C-11	Filtrate from sulfate wash of Na 2,4,5,-T salt on 3 x 3 filter. Filtrate acidified. Na salt prepared from recovered TCP and diluted with water to approximately 23%; pH adjusted to 9. Amber color with considerable amount of solids.
C-12	T-Acid Sulfate wash water. pH adjusted to 9.
C-13	Plant T-Acid (dustless) dissolved in IPA. 23% solution.
C-14	Recovered Methanol from plant recovered Methanol storage tank - 5/4/62 date sampled.

The materials were incorporated into a vehicle that consisted of 30 grams of "Carbowax" 4000 and 20 milliliters of propylene glycol heated to 95°C. The amount of samples C-1, C-3, C-6, C-7, C-8, C-9, C-10, C-11, and C-13 added to their respective vehicles was adjusted to equal 2.5% by weight of a 25% solution of Trichlorophenol so that all of the

CONFIDENTIAL

emulsions were of comparable strength. The maximum amount of the remaining samples that could be incorporated into the vehicle, 6.25 grams, was added to their respective vehicles.

A series of 15 applications was made onto the inner surface of one ear of six albino rabbits during a three-week period. Two compounds were tested on each group of six rabbits. The ears were examined closely to detect early changes in appearance and observations were recorded following the 5th, 10th, and 15th applications. The thickness of the ears was measured at a point equidistant from the tip of the ear and the outer margins and was located and marked with dye on the back of the ear. Measurements were made prior to the first application and again on the day of the 15th application with a dial-type micrometer having a range of 0.001 to 0.250 inch.

The grade of response was established according to the following characteristics:

1. Mild: This response is characterized by an increased prominence of the hair follicles on the inner surface of the ear. The follicles appear as fine dots which may be slightly raised as the response progresses. There may be a mild erythema and slight loss of hair. Although an increase in thickness may not be detectable grossly, micrometer measurements reveal a slight thickening.

CONFIDENTIAL

2. **Marked:** In this stage, the follicles appear to be raised and hard, thus giving the ear a definite "sandy" feeling. The follicles are also enlarged and tend to merge. Usually marked erythema is observed, accompanied by a marked loss of hair. Moderate epithelial hyperplasia resulted in a thickening which is evident grossly and is confirmed by micrometer measurements.

3. **Severe:** This degree of response is manifest as a gross thickening of the ear to many times normal. The increased thickness causes the ear to be heavy, very stiff, and drooped. The marked erythema present at first is gradually obscured by the epithelial hyperplasia. The follicles are raised, hard, and merged, thereby giving the ears an encrusted appearance. As the condition progresses, there is extensive exfoliation of the epithelium leaving the ear deeply pitted.

Plus signs were included with the grades of response to indicate the trend of the reaction within a particular group.

RESULTS

The response of each of the rabbit ears to fifteen applications of the test materials during a three-week, overall period is presented, respectively, in Tables 1 through 14. The effects that the vehicle, alone, produced are shown in Table 15. A summary of the observations of the responses produced by each sample is presented in Table 16.

SUMMARY AND CONCLUSIONS

Samples C-1, C-3, C-6, and C-7 produced marked responses in rabbits and samples C-8 and C-14 produced effects tending towards a marked response. These materials, therefore, should be regarded as having definite human chloracne-producing potential.

Samples C-9, C-10, and C-13 produced mild responses in rabbits and, therefore, could possibly produce chloracne in humans.

Samples C-2, C-4, C-5, and C-12 produced either no response or a minimal one in rabbits and, therefore, the probability of these materials producing human chloracne could be considered slight. The mild response that was noted could have been due to simple irritation.

Sample C-11 produced no appreciable response in rabbits and, therefore, there is no basis in this testing procedure to expect this material to produce human chloracne.

CONFIDENTIAL

Table 1 -- Response of Rabbit Ears to Application of Sample C-1

Rabbit No.	Ear	Response at End of Each Week			Thickness (inch)	
		1	2	3	Initial	Final
1	Left	Mild	Mild	Mild	0.038	0.045
2	"	"	Mild+	Marked	0.038	0.053
3	"	"	"	"	0.039	0.058
4	"	"	"	Mild+	0.038	0.052
5	"	"	"	Marked	0.036	0.053
6	"	"	"	Mild+	0.037	0.052
				Mean	0.038	0.052

Table 2 -- Response of Rabbit Ears to Application of Sample C-2

Rabbit No.	Ear	Response at End of Each Week			Thickness (inch)	
		1	2	3	Initial	Final
1	Right	None	Mild	Mild	0.038	0.044
2	"	"	"	"	0.040	0.043
3	"	"	"	"	0.040	0.045
4	"	"	None	"	0.039	0.045
5	"	"	Mild	"	0.037	0.045
6	"	"	"	"	0.039	0.047
				Mean	0.039	0.045

Table 3 -- Response of Rabbit Ears to Application of Sample C-3

Rabbit No.	Ear	Response at End of Each Week			Thickness (inch)	
		1	2	3	Initial	Final
1	Left	Mild	Mild+	Marked	0.039	0.051
2	"	"	"	"	0.038	0.060
3	"	"	"	"	0.038	0.071
4	"	"	"	"	0.040	0.060
5	"	"	"	Marked+	0.039	0.074
6	"	"	"	Marked	0.039	0.059
				Mean	0.039	0.063

CONFIDENTIAL

Table 4 -- Response of Rabbit Ears to Application of Sample C-4

Rabbit No.	Ear	Response at End of Each Week 1	2	3	Thickness (inch) Initial	Final
1	Right	None	Mild	Mild	0.040	0.043
2	"	"	None	"	0.039	0.042
3	"	"	"	"	0.040	0.044
4	"	"	"	"	0.039	0.042
5	"	"	"	"	0.039	0.043
6	"	"	Mild	"	0.039	0.045
				Mean	0.039	0.043

Table 5 -- Response of Rabbit Ears to Application of Sample C-5

Rabbit No.	Ear	Response at End of Each Week 1	2	3	Thickness (inch) Initial	Final
1	Left	None	None	None	0.039	0.051
2	"	"	"	Mild	0.037	0.047
3	"	"	"	"	0.038	0.043
4	"	"	"	"	0.039	0.045
5	"	"	"	None	0.039	0.041
6	"	"	"	"	0.041	0.051
				Mean	0.039	0.046

Table 6 -- Response of Rabbit Ears to Application of Sample C-6

Rabbit No.	Ear	Response at End of Each Week 1	2	3	Thickness (inch) Initial	Final
1	Left	Mild+	Mild+	Marked	0.034	0.042
2	"	"	"	"	0.040	0.063
3	"	"	"	Mild+	0.037	0.047
4	"	Mild	Mild	Mild	0.045	0.050
5	"	Mild+	Mild+	Marked	0.041	0.068
6	"	"	"	Mild+	0.036	0.051
				Mean	0.039	0.054

CONFIDENTIAL

Table 7 -- Response of Rabbit Ears to Application of Sample C-7

Rabbit No.	Ear	Response at End of Each Week			Thickness (inch)	
		1	2	3	Initial	Final
1	Right	Mild+	Mild+	Mild+	0.031	0.047
2	"	"	"	Marked	0.038	0.063
3	"	Mild	"	Mild+	0.035	0.045
4	"	"	"	"	0.044	0.048
5	"	Mild+	"	Marked	0.039	0.054
6	"	"	"	Mild+	0.035	0.042
				Mean	0.037	0.050

Table 8 -- Response of Rabbit Ears to Application of Sample C-8

Rabbit No.	Ear	Response at End of Each Week			Thickness (inch)	
		1	2	3	Initial	Final
1	Left	Mild+	Mild+	Mild+	0.040	0.054
2	"	Mild	Mild	Mild	0.039	0.050
3	"	Mild+	Mild+	Marked	0.037	0.050
4	"	Mild	"	Mild	0.034	0.043
5	"	Mild+	"	Mild+	0.034	0.053
6	"	Mild	Mild	Mild	0.040	0.050
				Mean	0.037	0.050

Table 9 -- Response of Rabbit Ears to Application of Sample C-9

Rabbit No.	Ear	Response at End of Each Week			Thickness (inch)	
		1	2	3	Initial	Final
1	Right	Mild	Mild	Mild	0.038	0.042
2	"	"	"	"	0.040	0.044
3	"	"	"	"	0.035	0.039
4	"	"	"	"	0.034	0.037
5	"	"	"	"	0.035	0.041
6	"	"	"	"	0.040	0.045
				Mean	0.037	0.041

CONFIDENTIAL

Table 10 -- Response of Rabbit Ears to Application of Sample C-10

Rabbit No.	Ear	Response at End of Each Week			Thickness (inch)	
		1	2	3	Initial	Final
1	Left	Mild	Mild	Mild	0.041	0.053
2	"	"	"	"	0.041	0.059
3	"	"	"	"	0.040	0.049
4	"	None	None	"	0.035	0.040
5	"	Mild	Mild	"	0.033	0.042
6	"	"	"	"	0.037	0.044
				Mean	0.038	0.048

Table 11 -- Response of Rabbit Ears to Application of Sample C-11

Rabbit No.	Ear	Response at End of Each Week			Thickness (inch)	
		1	2	3	Initial	Final
1	Right	None	None	None	0.040	0.043
2	"	"	"	"	0.039	0.043
3	"	"	"	"	0.044	0.047
4	"	"	"	"	0.033	0.034
5	"	"	"	"	0.035	0.037
6	"	"	"	"	0.039	0.042
				Mean	0.038	0.041

Table 12 -- Response of Rabbit Ears to Application of Sample C-12

Rabbit No.	Ear	Response at End of Each Week			Thickness (inch)	
		1	2	3	Initial	Final
1	Left	None	None	Mild	0.039	0.041
2	"	"	"	"	0.037	0.042
3	"	"	"	"	0.039	0.044
4	"	"	"	"	0.037	0.044
5	"	"	"	None	0.038	0.042
6	"	"	"	"	0.041	0.045
				Mean	0.039	0.043

CONFIDENTIAL

Table 13 -- Response of Rabbit Ears to Application of Sample C-13

Rabbit No.	Ear	Response at End of Each Week 1	2	3	Thickness (inch) Initial	Final
1	Right	None	None	Mild	0.040	0.048
2	"	"	"	"	0.040	0.048
3	"	Mild	Mild	"	0.039	0.056
4	"	"	"	"	0.039	0.042
5	"	None	None	"	0.039	0.048
6	"	"	"	"	0.041	0.047
				Mean	0.040	0.048

Table 14 -- Response of Rabbit Ears to Application of Sample C-14

Rabbit No.	Ear	Response at End of Each Week 1	2	3	Thickness (inch) Initial	Final
1	Left	Mild	Mild	Mild	0.040	0.049
2	"	None	None	"	0.035	0.038
3	"	Mild	Mild	"	0.036	0.042
4	"	"	"	Mild+	0.037	0.056
5	"	"	"	"	0.037	0.051
6	"	"	"	Mild	0.038	0.044
				Mean	0.037	0.047

Table 15 -- Response of Rabbit Ears to Application of the Vehicle Alone

Rabbit No.	Ear	Response at End of Each Week 1	2	3	Thickness (inch) Initial	Final
1	Right	None	None	None	0.040	0.048
2	"	"	"	"	0.039	0.044
3	"	"	"	"	0.042	0.045
4	"	"	"	"	0.043	0.046
5	"	"	"	"	0.039	0.044
6	"	"	"	"	0.042	0.047
				Mean	0.041	0.046

CONFIDENTIAL

Table 16 -- Summary of Observations

Sample No.	Response	Ear Thickness (inch) Initial	Ear Thickness (inch) Final	Ear Thickness (inch) Increase
C-1	Marked	0.038	0.052	0.014
C-2	Mild	0.039	0.045	0.006
C-3	Marked	0.039	0.063	0.024
C-4	Mild	0.039	0.043	0.004
C-5	Mild	0.039	0.046	0.007
C-6	Marked	0.039	0.054	0.015
C-7	Marked	0.037	0.050	0.013
C-8	Mild+	0.037	0.050	0.013
C-9	Mild	0.037	0.041	0.004
C-10	Mild	0.038	0.048	0.010
C-11	None	0.038	0.041	0.003
C-12	Mild	0.039	0.043	0.004
C-13	Mild	0.040	0.048	0.008
C-14	Mild+	0.037	0.047	0.010
Vehicle alone	None	0.041	0.046	0.005

CONFIDENTIAL

I.D.
Guidi
Exhibit
#2
2-19-87
KO'D

State of New Jersey
DEPARTMENT OF HEALTH
[illegible]

February 27, 1963

Mr. R. A. Guidi, Plant Manager
Diamond Alkali Company
80 Lister Avenue
Newark, New Jersey

Dear Mr. Guidi:

At your request, personnel of this Program visited your plant on January 9, 1963. The purpose of this visit was to study the plant operation and examine several employees with a skin condition diagnosed as chloracne.

As the reports from the Mellon Institute indicate, you are handling several compounds which are potentially causative agents of the chloracne condition in evidence. The sanitary facilities available for chemical workers were deemed excellent. However, their effectiveness can only be measured by their use. It is suggested that the employees be required to shower in the plant. Persons suffering from chloracne should be supplied with a daily change of clothing treated to be impervious to chemical agents. The same is true for undergarments.

Dr. Donald J. Birmingham, Medical Director-Chief, Dermatology Section, U. S. Public Health Service, Cincinnati, Ohio, has been notified of the situation and is expected to contact you in the future.

The recommendations listed below are offered for possible alleviation of the condition. To identify the specific cause is difficult since a part of the problem is certainly personal hygiene.

RECOMMENDATIONS

Engineering

1. Clothing changes should be offered daily.
2. Treated clothing to increase impermeability to chemical agents may be substituted for the type now used.

CONFIDENTIAL

3. Repair leaks and leaking valves in pipe system especially of sublimable compounds.

Medical

4. Thorough daily washing should be enforced after each shift.

5. Soft brushes or clean wash cloths should be supplied to each worker to facilitate good personal hygiene. Warm water should be readily available.

6. Towels, changed daily, should be furnished by the Company.

Should you desire further elaboration of this report or other assistance, please feel free to call us.

Very truly yours,

Lynn Schall

E. Lynn Schall
Chief
Occupational Health Program

MEL:hfh

CONFIDENTIAL

[illegible] COMMISSIONER OF HEALTH

[illegible]

State of New Jersey
DEPARTMENT OF HEALTH
BOX 1540, TRENTON 25

Guidi I.D.
Exhibit
3
2/19/87
KO

April 18, 1963

Mr. Raymond A. Guidi, Plant Manager
Diamond Alkali Company
Electrochemicals Division
80 Lister Avenue
Newark, New Jersey

Dear Mr. Guidi:

Attached is the report of the dermatosis investigation conducted in your plant by representatives from the U. S. Public Health Service. The report is self explanatory.

If we can be of additional assistance, please feel free to contact us.

Very truly yours,

Lynn Schall

E. Lynn Schall
Chief
Occupational Health Program

ELS:hfh
encl.

CONFIDENTIAL

APR 11 1963
RECEIVED

DERMATOSIS 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 Brodkin, 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 monochloracetic acid and dichlorophenol,

CONFIDENTIAL

1

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 stream 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 monochloracetic 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 55-90%

CONFIDENTIAL

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-

CONFIDENTIAL

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 chloracnegens by sending various intermediates from within the production lines to Mellon Institute for reproduction of chloracne in rabbit ears. Several acnegens 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 spot," 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 28, Drs. Bleiberg, Brodkin, 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.

<u>Discussion</u>:

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 housekeeping 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.

CONFIDENTIAL

This will help prevent chloracne at the belt line.

4. Showers after work should be made mandatory.

CONFIDENTIAL

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 ("Perna 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.

CONFIDENTIAL

Guidi
Exhibit #4
- 2/19/87
KO

Newark Beth Israel Hospital
201 LYONS AVENUE • NEWARK 12, NEW JERSEY
WAVERLY 3-6000

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 by 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.

CONFIDENTIAL

______ . 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 fluorscent. The liver biopsy showed evidence of liver cell regeneration and hemofusion deposition. Skin biopsy showed brown granular pigmentation and chronic inflammation of the dermis. The urine prophyrins 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 <u>chloracne</u> 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 hexachlorbenzene 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 - trichlorphenol is the common denominator, responsible for both diseases.

Very sincerely yours,

IRVING L. APPLEBAUM, M.D.

ILA*m

(Med.bill encl)

CONFIDENTIAL

Guidi Exhibit
#5
I.D.
2/19/87
KD

Diamond Shamrock

June 10, 1983

Michael Catania
Office of Regulatory Services
Department of Environmental Protection CN402
John Fitch Plaza
Labor and Industry Building - 8th Floor
Trenton, New Jersey 08625

Re: Former Diamond Shamrock Premises
80 Lister Avenue, Newark, New Jersey

Dear Mr. Catania:

Enclosed is the information Diamond Shamrock Corporation agreed on June 3 to provide on the Lister Avenue facility. On June 6, we provided the legal and technical contacts you requested. On June 7 we sent the list of employees and a NIOSH report on the facility derived from information we had previously submitted to NIOSH.

We have prepared an overview of the history and operations at the site. Our submittal represents our best effort in the time available to us and represents a reconstruction of the operations to the best of our knowledge. The corrections to the NIOSH report were deferred in order to answer the issues raised in Mr. Hughey's letter. We will provide further information on the NIOSH report as soon as practical. As indicated we ceased production in August 1969 and sold the property in March 1971. We are not knowledgeable as to changes that have occurred on site since we sold the property.

After your review of this information, we are ready to meet at your earliest convenience to discuss site remediations. We wish to express again our commitment to work with the State of New Jersey on the expeditious and proper containment of the site.

Very truly yours,

James B. Worthington

James B. Worthington
Director, Environmental Affairs

Hutton-3 ID
1/14/87

/lkh

Diamond Shamrock Corporation
World Headquarters, 717 North Harwood Street, Dallas, Texas 75201 Phone 214 745 2000

REPORT ON LISTER AVENUE FACILITY

JUNE 10, 1983

PLANT LOCATION AND HISTORY

Diamond Alkali purchased from Kolker Chemical a 1.8 acre tract of land located at 80 Lister Avenue, Newark, New Jersey in March of 1951. The plant (as shown in Table 1) was operated as an agricultural chemicals manufacturing facility by Diamond Shamrock until August 1969 when the plant was shut down. Records reflect that all of the manufacturing took place on the 1.8 acre site. In January of 1956, an easement was acquired for the construction of a 10" sewer line under the railroad tracks on the east side of the property. Additional 1.6 acres of property were leased from Triplex Oil and Refining Company (subsequently Walter Ray Holding Company and eventually William Leckie) in April 1960 and this property accommodated storage facilities and warehouses (outlined by dashed areas in Figure 1). The only other major property associated with the plant appeared to be a parking lot leased in 1963 from Sergeant Chemical Company (Figure 2, dashed line, Site D.A.C.O. L2).

In March 1971, the 1.8 acre site was sold and the 1.6 acre site lease was assigned to Chemicaland Corporation. Principals of Chemicaland were George W. Mitchell and Raymond A. Guidi (a former plant manager of the facility). It appears the plant was involved in the production of benzoic acid, with a small amount of 2,4-D being manufactured for Diamond Shamrock for a limited time. In 1980, the 1.8 acre site was purchased in a tax sale by Mr. William Leckie (Ray Holding Company) and was subsequently sold to Marisol Company in early 1981.

GENERAL PROCESS DESCRIPTION

The production of 2,4,5-trichlorophenoxyacetic acid esters involves several process steps. The initial step is the production of sodium trichlorophenate followed by reaction with sodium monochloroacetate to yield the sodium salt of trichlorophenoxyacetic acid. This salt was, in turn, reacted with sulfuric acid to yield the 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) with a suitable alcohol at the proper reaction conditions to give the corresponding ester or with a suitable amine to give the corresponding amine salt.

CONFIDENTIAL

Over the period 1951-1969 when the Newark facility was operated, the process was altered several times to improve operability and to increase capacity. These changes and the dates made are outlined in Table 2. The total 2,4,5-T production capacity of the Lister Avenue facility accounted for less than 10% of the total U. S. manufacturing capacity in 1969.

Production capacity changes are summarized in Table 3.

PROCESS LOCATION - SITE PLAN AND WASTES GENERATED

Dioxin formation has been identified as inherent in the process for manufacturing sodium 2,4,5-trichlorophenate by the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene. Consequently, the following discussion relates specifically to this process. The primary chemical reaction in this process is shown in Figure 3.

Period 1951 - 1960

Manufacture of starting and intermediate chemicals was conducted in a five story, 50 year old building which occupied 29,000 square feet of a 1.8 acre plant site. The building was located adjacent to the Passaic River and is shown in outline form on Figure 4 dated February 14, 1959. This building also housed the offices, laboratory maintenance facilities and first aid dispensary for the plant.

The phenoxy acids, esters, amine salts and formulations thereof were prepared in a separate smaller building located to the east of the main manufacturing building.

All processing equipment for the manufacture of sodium 2,4,5-trichlorophenate (NaTCP) and other primary chemicals were located within the main building. Little information is available as to the exact location of the NaTCP equipment within the building because the records were destroyed in the explosion which occurred in 1960. A block flow diagram of the process used from 1951 to 1954 is included as Figure 5.

Wastes produced in this process included a filter cake which contained water insoluble materials, such as 1,2,4,5 tetrachlorobenzene (T_4CB), 2,4,5-trichloroanisole (TCA), and would likely trap any dioxin present in the reaction product. This process was replaced in 1954 (see Figure 6) with a steam distillation to remove T_4CB and TCA. Any dioxin present, because of its volatility, would also be removed either partially or totally. The distillate (organics) from this process step were stored for

CONFIDENTIAL

recycle in the future, subject to development of a process for their use. The first recycle of recovered organics from the steam distillation was made in December 1956 and was henceforth made a routine operation.

Liquid wastes from the process consisted of aqueous solutions of sodium chloride and sodium sulfate. Prior to October 1954, the aqueous solutions of sodium chloride and sodium sulfate were separate. After this date, the process was modified such that the sodium chloride and sodium sulfate were discharged as a single solution from the 2,4,5-T acid process.

Condensate (aqueous layer) from the steam distillation was the other liquid waste from the process.

Muriatic acid was also produced as a by-product in the main process building from the hydrogen chloride produced in the chlorination of acetic acid/anhydride to monochloroacetic acid and the chlorization of phenol to 2,4-dichlorophenol. This acid was produced in processes not related to the production of 2,4,5-trichlorophenol. The acid was generally sold to reclaimers.

Period 1961 - 1969

After the explosion in February 1960, the main process building was completely replaced with a new three story structure devoted exclusively to manufacture of NaTCP, 2,4-dichlorophenol (2,4-DCP), monochloroacetic acid (MCA) and by-product muriatic acid.

Two additional buildings separate from the process building were also provided. The largest of these housed the maintenance shop, production and shipping offices, and an area for materials storage. The smaller building housed the general plant offices, the quality control laboratory, and the dressing room. The site plan (Figure 7) shows the location of each of these new buildings.

Other improvements related to bulk materials storage were also made at this time.

The new process building was designed to have all drainage trenches discharge through a sump into the industrial sewer.

The plant was expanded in 1967 by the addition of a new 2,4-D acid unit and conversion of the old 2,4-D acid unit to 2,4,5-T acid manufacture. The warehouse was expanded and an extension added to the Process Building to house the NaTCP purification process. These changes are outlined on site plan (Figure 8).

CONFIDENTIAL

The basic process for preparation of NaTCP was not changed but provision was made for the removal of sodium chloride by filtration from the stream stripped solution of NaTCP and the removal of dioxin (2,3,7,8-TCDD) by adsorption on activated carbon (Figure 9). The sodium chloride recovered in the filter was dissolved in water for disposal by the industrial sewer.

The activated carbon in the adsorption column was treated with muriatic acid and hot water washes to remove iron hydroxide. These treatment solutions were then disposed of to the industrial sewer. Spent carbon was removed from the unit and handled by a disposal firm.

The basic processes for manufacturing the 2,4,5-T acid, esters or amine salts were not changed.

Production operations were terminated in August 1969.

OTHER MANUFACTURING ACTIVITIES

Several other products as listed in the following table were manufactured during the period 1951-1960, but were discontinued for economic reasons and not produced after the explosion in February 1960. It is believed that the records of these products were also in the explosion.

Product	Chemical Name
HCB	Hexachlorobenzene
DDT	dichlorodiphenyl trichloroethane
	Ovex, Multicide
K101	p-chlorophenyl-p-chlorobenzene sulfonate
Compound 923	2,5-dichlorophenyl-p-chlorobenzene sulfonate
Chloral	1,1,1-trichloroacetaldehyde
BSC	benzenesulfonyl chloride
BCBSC	p-chlorobenzenesulfonyl chloride
BCBSA	p-chlorobenzene sulfonamide
44-DDS	4,4-dichlorodiphenylsulfone
PAABSC	p-acetylaminobenzene sulfonyl chloride
PMBSC	p-methoxy benzenesulfonyl chloride

CONFIDENTIAL

ENVIRONMENTAL MANAGEMENT

Information about environmental activities at the Lister Avenue plant is limited, particularly in the pre-1960 period. The relationship of the levels of dioxin in the water, air, and solid waste by-products is based upon process evaluations and projections.

Information about wastewater practices indicate that in 1956, process wastewaters were discharged through a 10" industrial sewer to the Passaic Valley Severage Commission. In the fifties and sixties, there are indications of acid discharges to the Passaic River, but these releases were likely muriatic acid and sulfuric acid. The only acid discharges appeared to be amounts that were not sent to acid reclaimers. Both the muriatic acid and sulfuric acid should not have been contaminated with dioxins since they were not directly associated with the TCP processes. It is believed that the TCP acid waste streams were routed to a sump before the over-flow was discharged to the industrial sewer. Since the dioxins are relatively insoluble in water and adsorb readily to suspended particles, it is believed that the sump could have eliminated some of the waste before discharge to the sewer. The sump was in operation in 1965 and perhaps earlier. Process wastewaters including acid wastes were estimated to be 30,000 gallons per day in 1960, and approximately one-third could have contained some dioxins. Since the process areas were under a roof, storm run-off exposure to process wastes were limited. All run-off from tank storage areas after 1961 was discharged to the industrial sewer system.

Information on air emissions indicated that all vents were inside the process buildings until the late 1960's. Emissions of dioxins would likely be in the form of a particulate and not a gas. This likely reduced the level of emissions going off-site. A 20,000 SCFM, 7' diameter Peabody caustic scrubber was in operation in 1963. This scrubber emitted through a 20 foot high stack and cleaned the process vent emissions from the plant. In 1966, a construction permit was filed with the State for a plant modification. The application cited the controlled emissions to be:

	lb/hr	ppm
Sodium salt of 2,4-D	0.18	2
Sodium salt of DCP	0.12	1.4
Sodium salt of MCA	0.12	1.3
Sodium salt of 2,4,5-T	0.06	0.8
Sodium salt of TCP	0.06	0.8

CONFIDENTIAL

All process vent emissions were controlled by the scrubber from 1967 to the plant shut-down in 1969. In 1969, emissions were controlled by the scrubber to a level of 10 pounds per day of organic particulates.

Solid wastes generated at the site consisted of non-combustible process wastes, miscellaneous combustible and non-combustible containers and trash. All wastes were hauled off-site by a contractor, Mr. Nick Toscano.

The process wastes were filter cake from product filtration, spent carbon from the carbon column and sludge removed from the process area waste sump. In 1967, these wastes totaled eight (8) tons per year. In 1969, the wastes totaled three and a half (3.5) tons per year.

A carbon column was installed to remove dioxin from the TCP production in September 1967. The first column was a "pilot" unit 12" diameter. This unit was used from September 8, 1967, until the installation of a full-scale column in July of 1968 during the plant's annual shut-down. In January, 1969, the carbon in the "new" column was replaced. This carbon was in use when production of 2,4,5-T was discontinued in July, 1969.

The carbon bed was washed with acid when the dioxin level of the TCP could not be maintained at an acceptable level, or the column plugged. The dioxin was bonded firmly to the carbon. Although the spent acid was severed, it is unlikely that the dioxin desorbed from the carbon. The spent carbon was drummed and disposed of off-site by waste disposal contractor. This appeared to be done in January, 1969. After the process was shut down, the column was reportedly included in the sale to Chemicaland Corporation. The management of Chemicaland was informed of the contents of column.

The water-related upsets are limited to acid releases to the Passaic River largely during the fifties and early sixties. In 1964, an acid release was corrected by the relocation of a process over-flow. A citation in 1968 resulted from a sulfuric and hydrochloric acid discharge.

An explosion occurred in the trichlorophenol unit in February 1960. The vessel which ruptured was the 1,000 gallon reactor used to hydrolyze 1,2,4,5-tetrachlorobenzene to sodium 2,4,5-trichlorophenate. Although the reason for the failure was unknown, it was postulated that a runaway reaction which produced a large volume of gaseous products was responsible for the failure. The dispersal of this material discharge was partially contained by the building structure and directed away from the adjacent property.

Table 1

Ownership History

Date	Event
3/51	1.8 acres purchased from Kolker Chemical Works, Inc. by Diamond Alkali (as shown by Figure 2).
1/56	Acquisition of easement and construction of 10" clay sewer pipe in 36" reinforced concrete casing 355' East of Brown Street under tracks (See Figure 1).
4/60	DSC lease of 1.6 acres of adjacent property owned by Triplex Oil Company.
11/63	Lease of parking lot from Sergeant Chemical Company.
8/69	DSC production ceased.
3/70	Production of 2,4-D by former employee.
3/71	Sale of 1.8 acres tract and manufacturing facilities to Chemicaland Corporation; assignment of Triplex 1.6 acre lease to Chemicaland Corporation.
1980	Property purchased in tax sale by William Leckie (Ray Holding; formerly Triplex Oil Company).
1981	Property sold to Marisol Company.

CONFIDENTIAL

Table 2

Process and Plant Changes

Date	Change
Early 1951	Initiated production of 2,4,5-TCP and 1,2,4,5 tetrachlorobenzene in a 500 gallon reactor. Used a dilution process with filtration to remove water insoluble organics from reaction mix.
January 1952	Initiated the use of purchased 1,2,4,5 tetrachlorobenzene because time was not available to make our own.
May 1952	Decision to increase capacity from 40,000 lb/mo to 120,000 lb/mo by installation of an additional 1,000 gallon reactor.
Feb/March 1953	Probable time for start-up of the new 1,000 gallon reactor.
September 1954	Steam stripping substituted for dilution process for the removal of organics on a routine basis.
December 1954	Do not remove salt (sodium chloride) from the NaTCP reaction mass but carry it through to the 2,4,5-T process and then separate all the salts at one time.
January 1955 to November 1956	No major process changes were made during this time frame.
December 1956	Initiated recycle of recovered organics.
January 1956 to February 1960	No major process changes during this period.
February 20, 1960	Explosion in NaTCP autoclave. Process building destroyed. Production of all materials ceased.
June 1960	Approval to reconstruct the plant. Reconstruction included complete replacement of the old process building.
February 1961	Rebuilt plant start-up. NaTCP now involved two 1,000 gallon reactors. Salt to be removed from NaTCP after steam stripper.
August 1967	2,4,5-T acid facility (old 2,4-D unit) was completed to produce a capacity of 3 MM lbs/yr of 2,4,5-T.

CONFIDENTIAL

September 1967	2,4,5-TCP purification facility completed for removal of p-dioxin (2,3,7,8-TCDD).
November 1967	New 2,4-D acid facility completed with a capacity of 12 MM lb/yr.
August 1969	All production terminated.

CONFIDENTIAL

Table 3

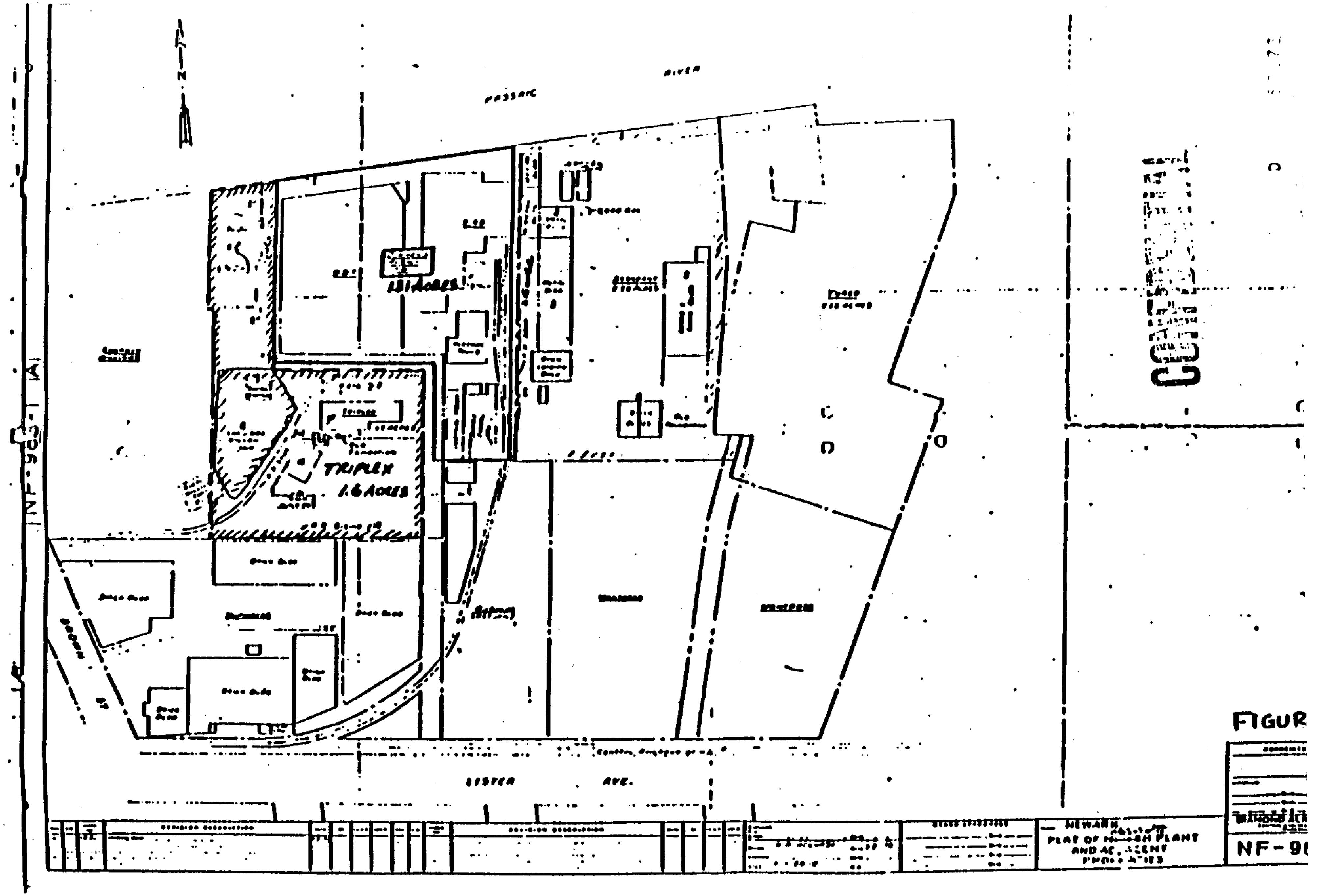
Production Capacity Changes

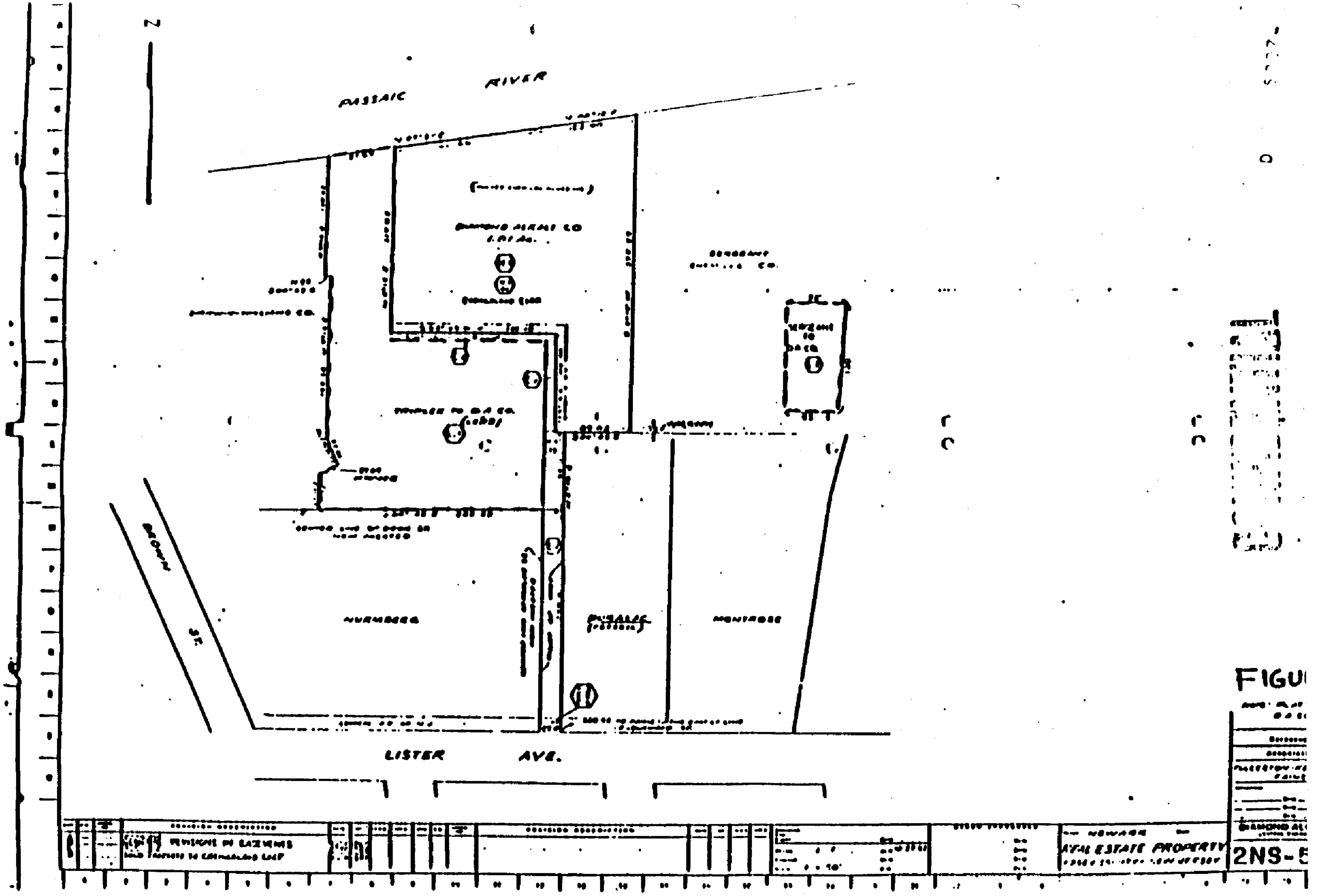
	TCP	2,4,5-T Acid
January 1951	*0.5 MM lb/yr	*0.65 MM lb/yr
February to March 1953	*1.5 MM lb/yr	*2.0 MM lb/yr
February 1961	*1.9 MM lb/yr	*2.5 MM lb/yr
November 1967	*2.3 MM lb/yr	*3.0 MM lb/yr

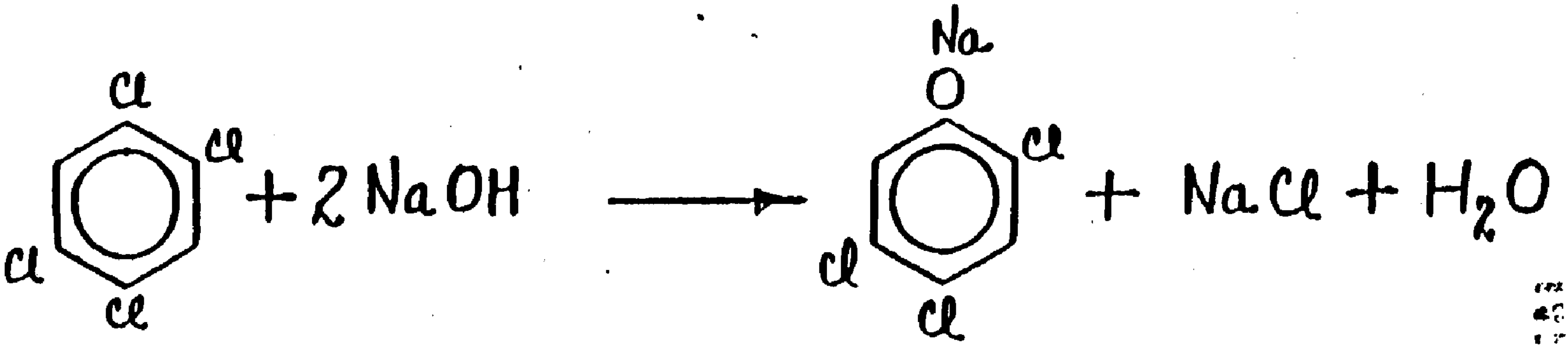
---

* Production by the capacity of the 2,4,5-T acid unit.

CONFIDENTIAL


N
PASSAIC
RIVER
1.1 ACRES
TRIPLEX
1.6 ACRES
LISTER
AVE.
FIGUR
NEWARK
PLAT OF [illegible] PLANT
AND AC.ACENT
PROP.RTIES
NF-9


N
PASSAIC RIVER
DIAMOND ALKALI CO
BROWN ST.
NURNBERG
PASSAIC
MONTROSE
LISTER AVE.
FIGU
NEWARK
REAL ESTATE PROPERTY
DIAMOND AL
2NS-5



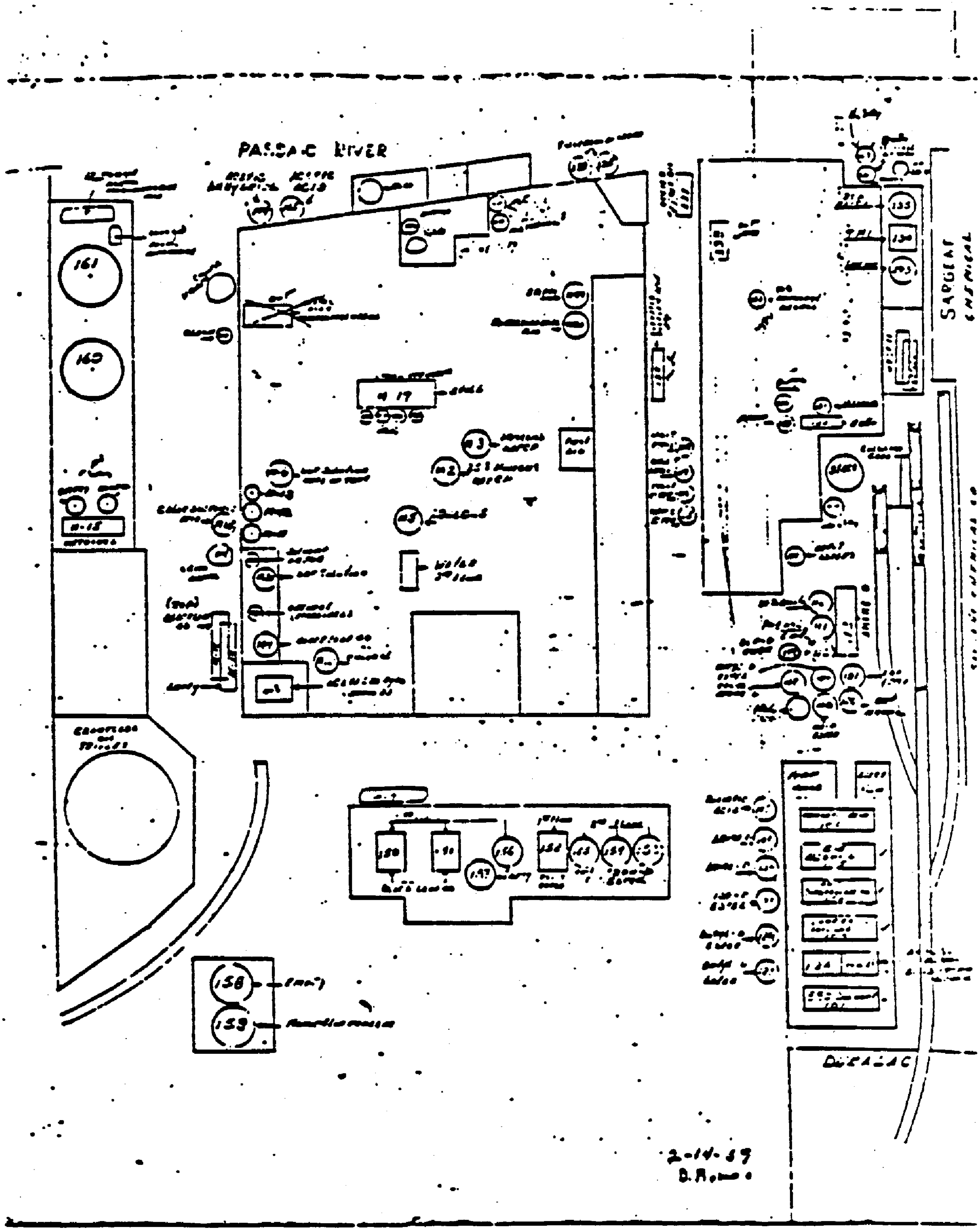
1,2,45-Tetrachlorobenzene
(T4CB)

Sodium 2,4,5-trichlorophenate
(NaTCP)

Diamond Shamrock
Gulf Coast Area
Environmental Control

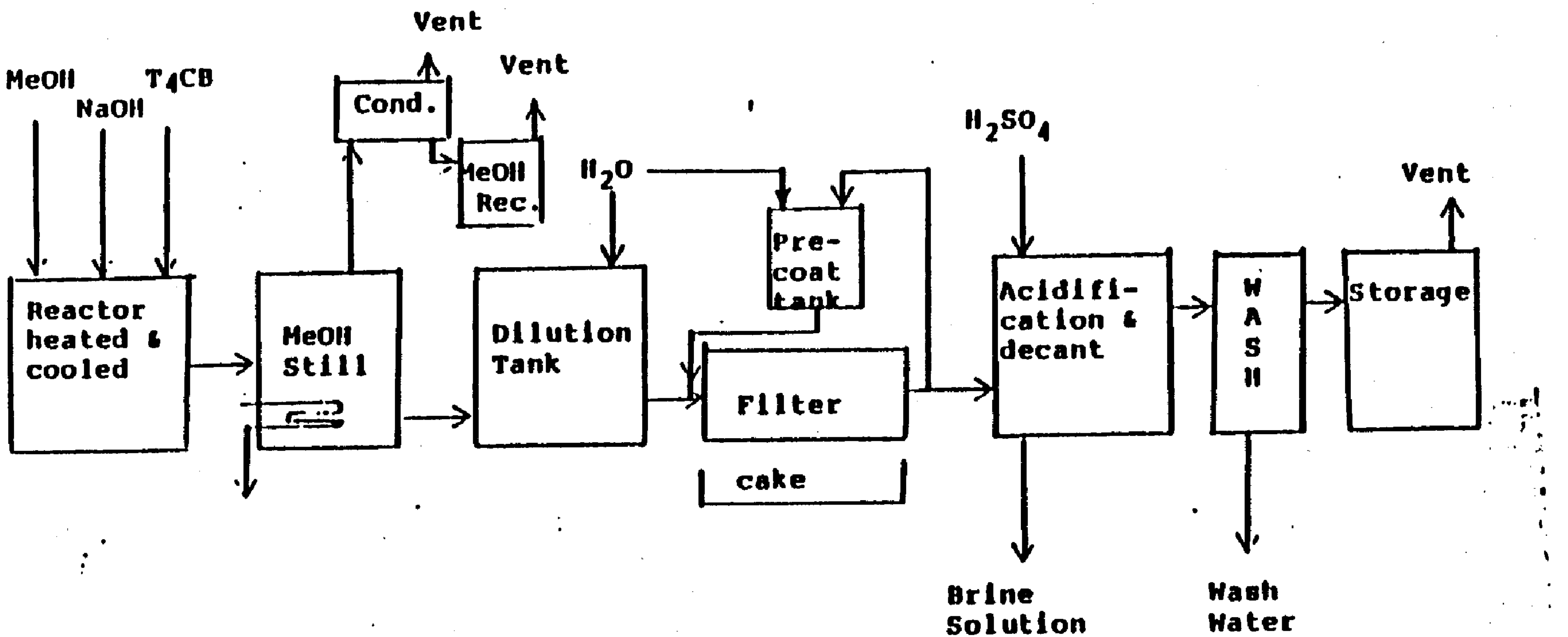
PRIMARY CHEMICAL REAC

Dr. By	Date	Scale	Drawing
Appr. By	Date		FIGURE



CONFIDENTIAL

FIGURE 4

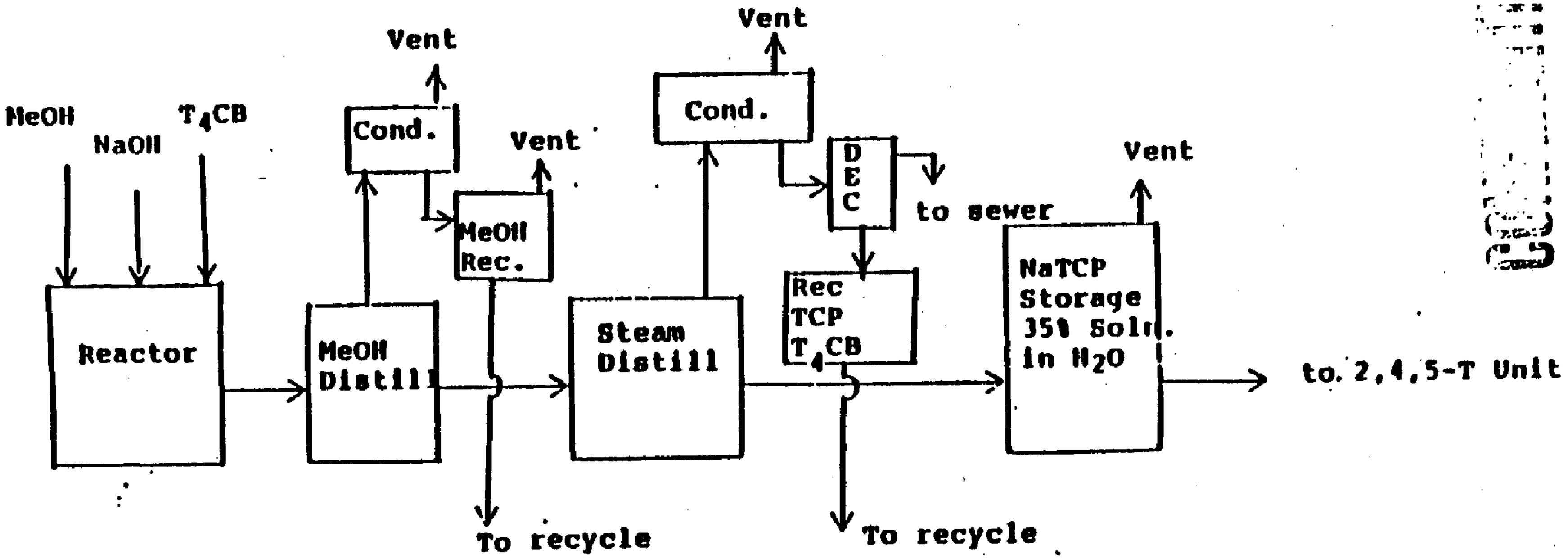


Diamond Shamrock

Environmental Control

Na 2,4,5- TCP
Flowsheet 1951 - 1954
Dilution Process

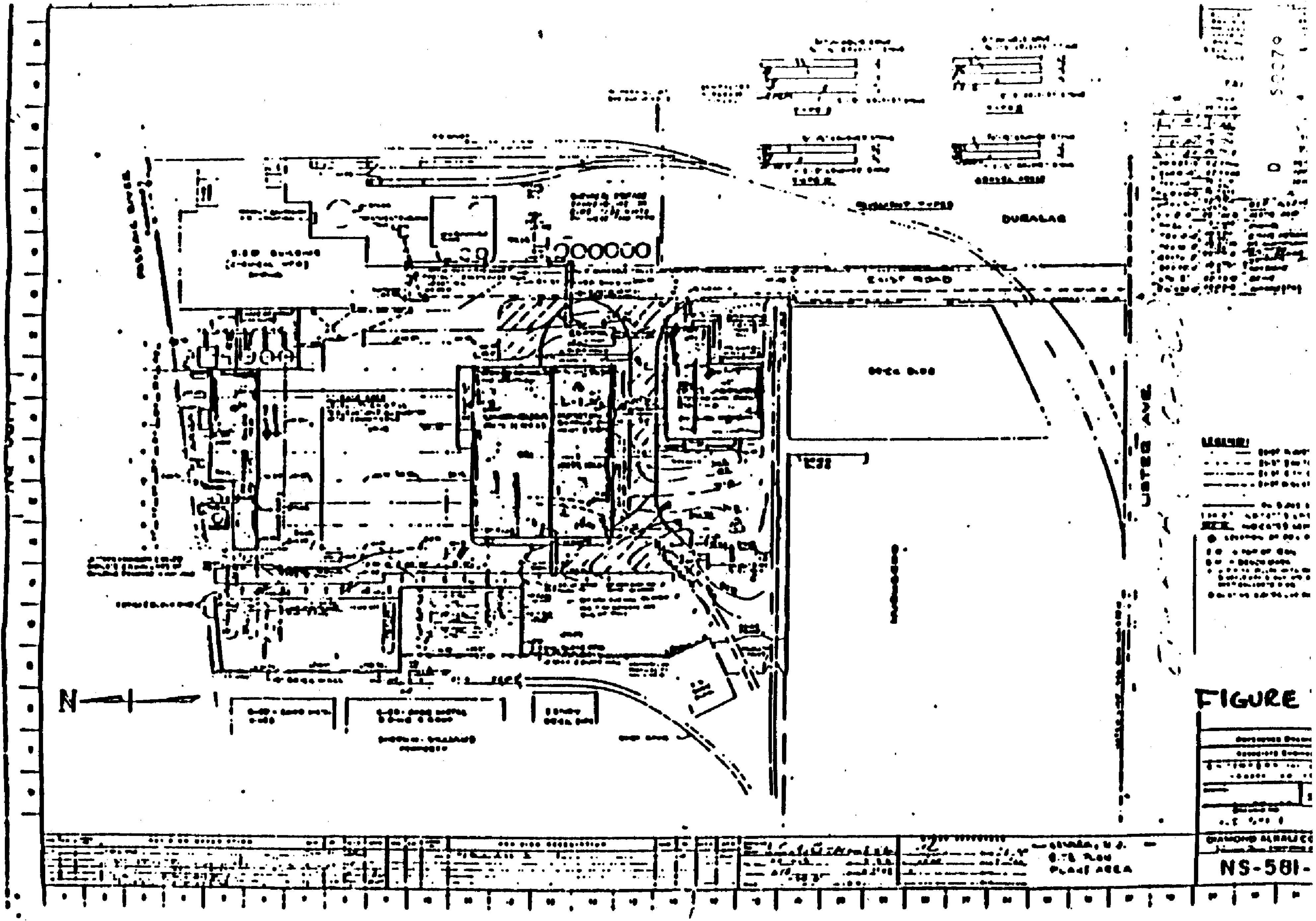
Dr. By	Date 4/11/83	Scale	Drawing
Appr. By	Date		



Diamond Shamrock
Environmental Control

Na 2,4,5-TCP
Flowsheet 1954 - 196
Steam Distillation Process

Dr. By
Date [illegible]
Appr. By
Date
Scale
Drawing N
[illegible]

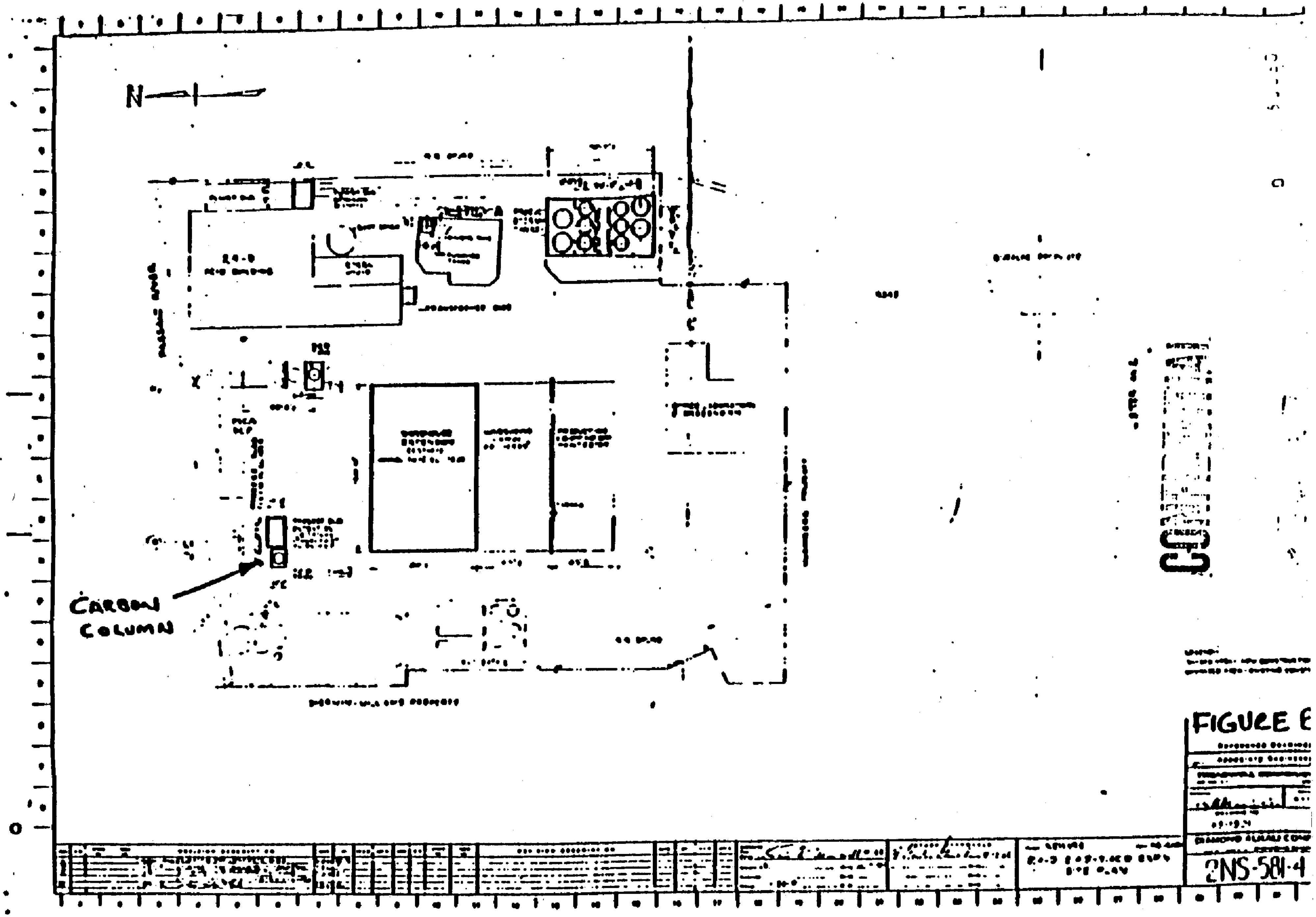


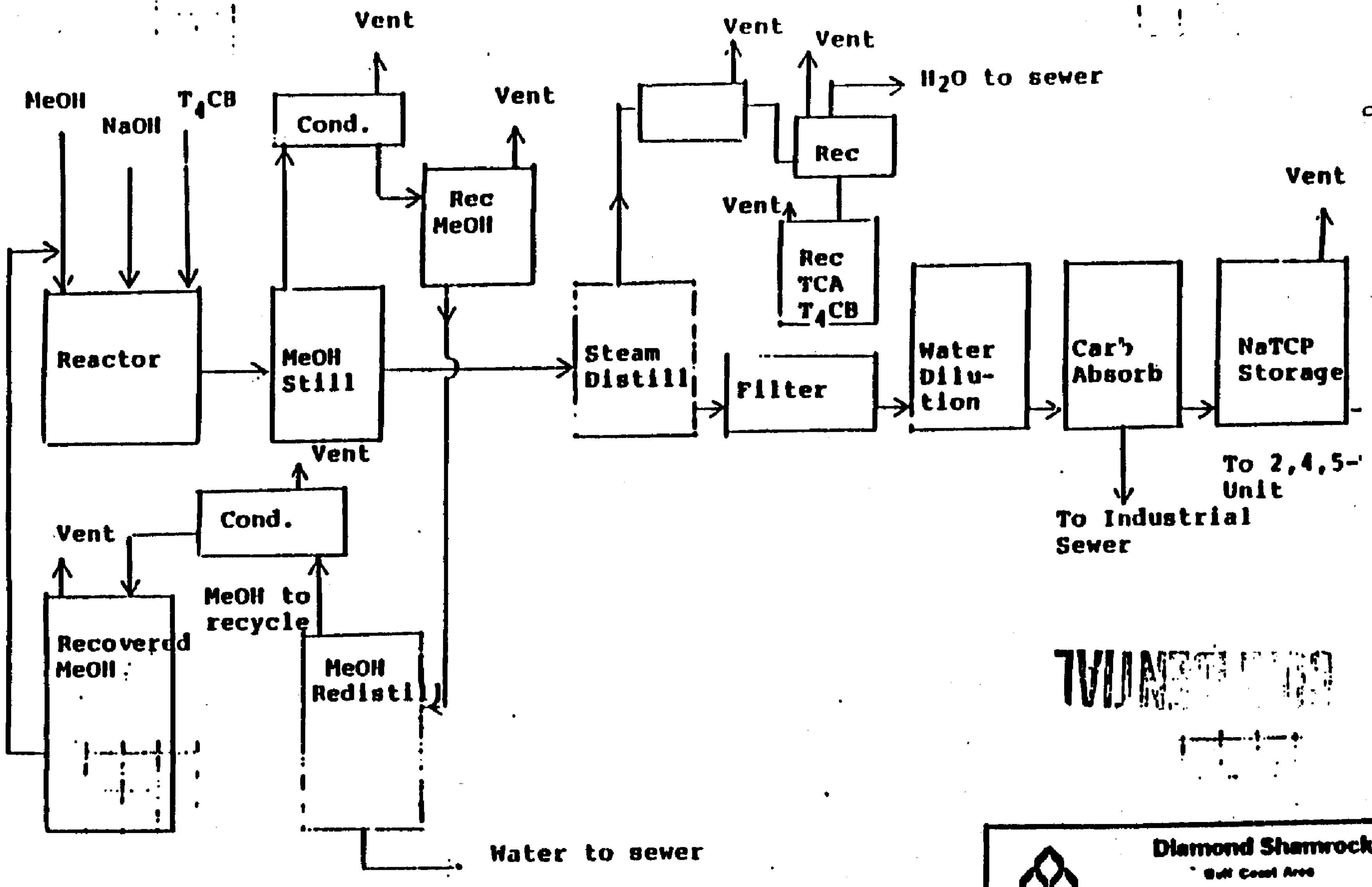
FIGURE

NEWARK, N.J.
SITE PLAN
PLANT AREA

DIAMOND ALKALI CO

NS-581-


N
CARBON COLUMN
FIGURE E
DIAMOND ALKALI CO
2NS-581-4



Diamond Shamrock
Gulf Coast Area
Environmental Control

Na 2,4,5- TCP
Flowsheet 1960 - 1969
Steam Distillation Process

Dr. By	Date	Scale	Drawing N
Appr. By	Date		

Guidi Exh.
#6
I.D.
2/19/87
KOD

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 to75 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.

CONFIDENTIAL

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 chloracnegen 2,3,6,8-dichloro-dibenzo-p-dioxin. This is the compound suggested by Cy Perkins in a report to Jack Borror 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 acnegen in napthalene 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 continous washings every one-half, up to 4 hours.

CONFIDENTIAL

Dr. Sadek 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. Sadek stated that in cattle, hyper-kertosis 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 8 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 develope chloracne (?).

CONFIDENTIAL

V. K. Rowe stated that phenates as high as 20 ppm were found and T-acid as high as 10 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 800°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.

mr. R

Laboratory wastes, including gloves required in handling this material, are incinerated. R 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.

CONFIDENTIAL

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.

X

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.

CONFIDENTIAL

Guidi Exh.
#7 I.D
2-19-87 KD

F

July 9, 1962

Mr. R. A. Guidi - Newark Plant

Dr. E. L. Chandler

The question of chloro-acne has not been resolved in the consideration of two sizeable customers. Bill Champion of Riverdale Chemical says that he gets better formulations using other suppliers' herbicides, and he insists that he has a chloro-acne problem when he uses Diamond esters.

As you will recall, the Quaker City Tree personnel were rather severely affected by this dermitological problem, and we have definitely lost them as a customer.

Jim King would like a reply from you, giving your personal convictions as to the possible reoccurrence of this problem in the future.

E. L. CHANDLER

ELC:jl
cc: H. S. Weiner

COPY

CONFIDENTIAL

D 2537-5

Guidi Exhibit
No. 8 I.D.
2-19-87 Ko'D

7-9

COPY

March 15, 1963

Dr. A. Buinno
1180 Raymond Boulevard
Newark, New Jersey

Dear Dr. Buinno:

I am attaching a copy of a letter recently received from our dermatologist, Dr. Jacob Bleiberg. This letter contains comments concerning the selection of employees with severe acne in adolescence or excessively oily skins, as these are extremely poor risks as regards chloracne at our Plant. Although Dr. Bleiberg suggests that such individuals might be used elsewhere in our Plant, we must urge that in your pre-employment physicals, you do not consider such applicants at all, as all our employees are exposed to the same conditions.

If you should like to discuss this matter further with me, please do not hesitate to call.

Very truly yours,

R. A. Guidi
Plant Manager

RAG/nc

Attachment

cc: Dr. J. Bleiberg

CONFIDENTIAL

Guidi Exhibit
#9 I.D.
2-19-87
KO'D

August 14, 1963

COPY

Mr. Raymond A. A. Guidi
Diamond Alkali Company
80 Lister Avenue
Newark 5, New Jersey

Dear Mr. Guidi:

This is in reply to a letter from Dr. Bleiberg that we do routine testing on the chloracne division in our laboratory there in New Jersey. I am sending for your inspection a rather simple type of routine test for porphyrins in the urine and should like you to institute the testing as Dr. Bleiberg suggests. We will further approve of laboratory tests of those individuals contacting porphyrin in the urine and those who have chloracne, on an outpatient basis, subject to recommendations of Dr. Bleiberg. If the laboratory should have any further questions about running these test which I included, would you kindly have them contact me at the Painesville Plant.

Sincerely,

DIAMOND ALKALI COMPANY

Richard W. McBurney, M.D.
Plant Physician

RWMCB:rme

Enclosures

cc: Mr. C. Richard Brown
~~Mr. Frank Jarvis~~

CONFIDENTIAL

CONFIDENTIAL

March 25, 1963

Mr. R. A. Guidi - Newark

Mr. H. S. Weiner

Chloracne

I appreciated your memo of March 20 keeping me up to date on this subject.

In the third paragraph of Dr. Bleiberg's letter, he mentions the willingness of the U. S. Public Health Service to enter your plant with a team of engineers to do various samplings and spectroscopic examinations of atmosphere. I strongly recommend that you do not permit a team from any government agency to enter your plant unless a very specific and detailed program is established. This program should be cleared not only with Diamond's medical adviser but also with Marty Wilkerson.

Furthermore, in preparing such a program, you should establish what the consequences might be and the course of action you might take under the various circumstances.

In other words, we want a consistent, organized and planned approach to solving this problem, but do not want a disorganized group from any government agency entering the plant. This might well result in very wide and unfair newspaper publicity as is usually done to sensationalize.

H. S. Weiner

HSW:mk

cc: Mr. M. F. Wilkerson

COPY

CONFIDENTIAL

Guidi
Exh. #10
I.D.
2-19-87
KO'I

253733

June 7, 1963

Mr. R. A. Guidi - Newark

CHLORACNE

Dr. R. W. McBurney - Painesville

COPY

I am in receipt of the complete medical reports covering [redacted] and [redacted] and read them with interest. There appears to be little doubt, of course, that both were suffering from chloracne and acquired porphyria. 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 substances, 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 these diseases are, of course, self limited and reversible as the men are removed from the atmosphere containing the trichlorphenol.

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.

RWMcB:mme

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

CONFIDENTIAL

Guidi
Exhibit
#11 I.1
2-19-87
KO