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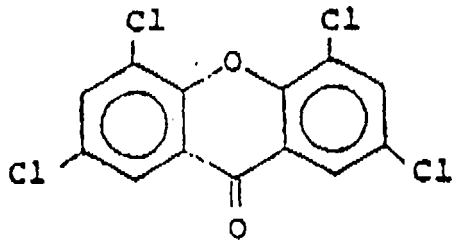
INTRODUCTION

A process for preparing high purity 2,4-D was started in May 1977 at 948 Building. The high purity molten acid is transferred by pipeline from 948 Building to 489 Building where it is formulated into esters and water soluble amine salts. Starting in late October 1977, precipitates were observed regularly in diluted amines formulations that were found to be made up of a number of impurities associated with the process but that were never detected during laboratory or pilot plant development work. In addition, these impurities were not found in the old 489 Building 2,4-D process. R. McLachlan[1] analyzed the precipitates and found 1,3,6,8-tetrachloroxanthone (I: TCX), 1,1'3,3'6,6'8,8'-octachloro-9,9'-spirobixanthene (II: OCSX), and marginally soluble salts of 2,4-D.



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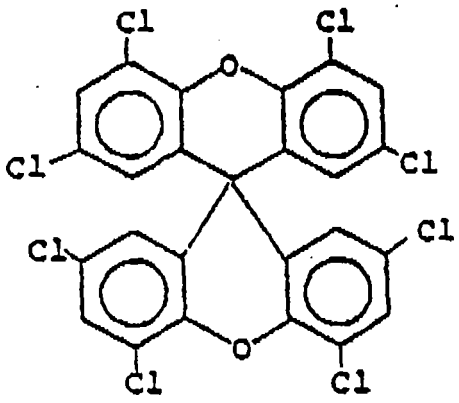


(II)

A screening program in the plant showed TCX at levels of 200-500 ppm in the crude reaction mass, the recycle solution, and in the final product. Levels of 1000-2000 ppm were found in the solvent and as much as 10% in the still tars.

McLachlan[1] analyzed a sample of still tars and his results are summarized in Table 1.

D-9

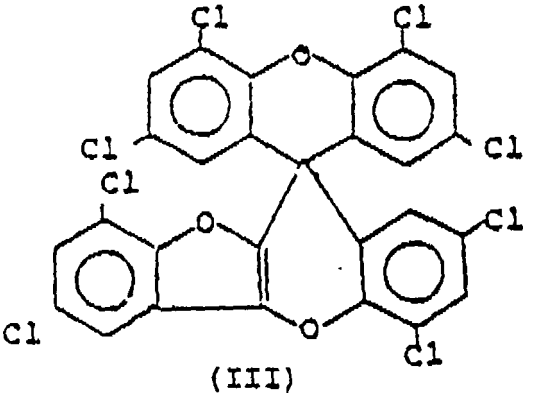
Table 1: An Analysis of One Tar Sample

Structure	Approximate Percentage	Comment
	60%	Main Component
	25%	From a heat exchanger leak (Dowtherm J)
DCP	0.5%	raw material
2,4-D	0.01%	Product
TCX (I)	1.5%	
OCSX (II)	1.1%	
Dichlorophenyl-dichlorovinyl ether	1.2%	Rxn product
Dichlorophenyl-trichlorovinyl ether	0.8%	

Plus:

at least eleven other minor components structurally similar to the above. See Ref. 1 for details.

A project was started to study the formation of TCX and OCSX in some detail to learn more about their formation and fate in the process because it is not obvious how they are made. Several months after starting this study, another significant impurity was found in the product and, to a lesser extent, in the tars. It was identified as (III: "8-5") 2,2',4,4',5',7,7',9-octachlorospiro-(benzofuro(3,2-b)-benzopyran-11,9'-xanthene).



(III)

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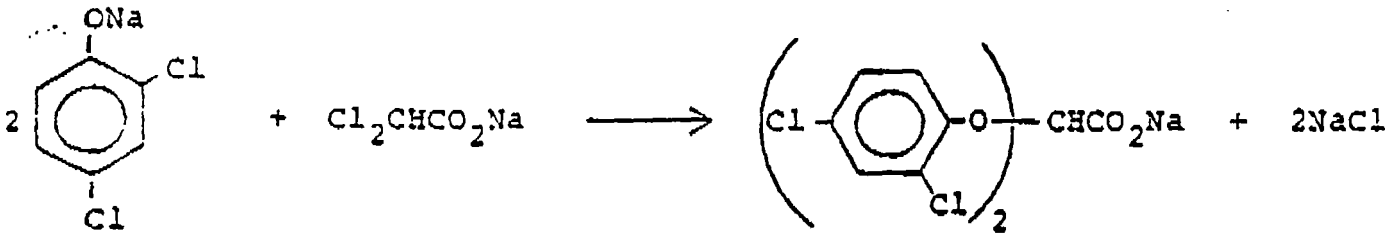
DOW CHEMICAL

Important Side Reactions

$$ClCH_2CO_2Na + NaOH \longrightarrow HOCH_2CO_2Na + NaCl$$

Glycolic Acid



"Bis 2,4-D"

The reaction is performed in two stages by first reacting 2.2 moles of DCP with 1.2 moles of caustic (added as 50% NaOH) to form a solution of NaDCP in DCP.

High purity 2,4-dichlorophenol (2,4-DCP) made by the chlorination of phenol with sulfuryl chloride in the presence of $FeCl_3$/Diphenyl sulfide catalyst is used with chloroacetic acid (MCAA) made by the oxidation of vinylidine chloride to make 2,4-D as shown above. The typical raw materials analyses for each is shown in Table 2.

Table 2: Typical Raw Material Analyses for the 2,4-D Process

	DCP		MCAA
2,4-DCP	98.5%	MCAA	99.0%
2,6-DCP	~0.8%	Dichloroacetic acid	0.3%
Other Chloro-phenols	~0.5%	Chloromaleic acid	~0.05%
		H_2O	<1.0%

DOW 267740

A rapid initial screening of the toxicity of purified TCX and tars gave the following results.

	Oral LD_{50} (single dose)	Skin/Eye
Tar (contains 3-5% TCX + OCSX)	>5g/Kg	slight transient initiation. Chloracne response after 10 applications of neat tars.
Purified TCX	>4g/Kg	not irritating. Chloracne response after 10 applications of 1% solution in $CHCl_3$.

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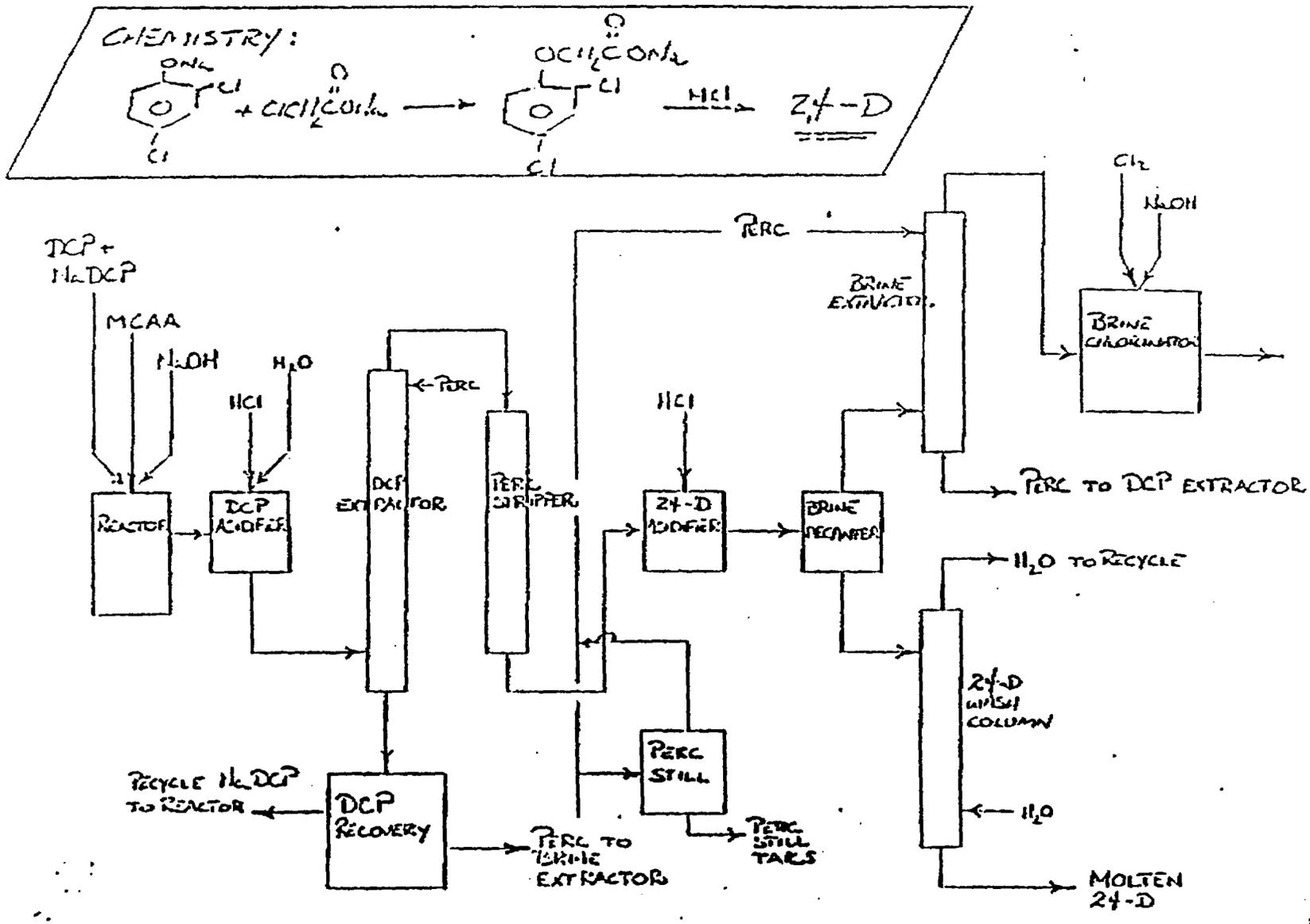


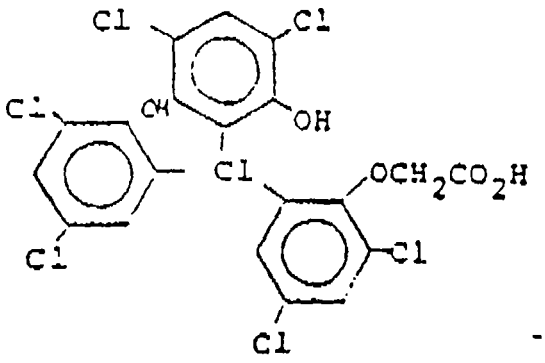
2,4-D PROCESS

OC/78-05

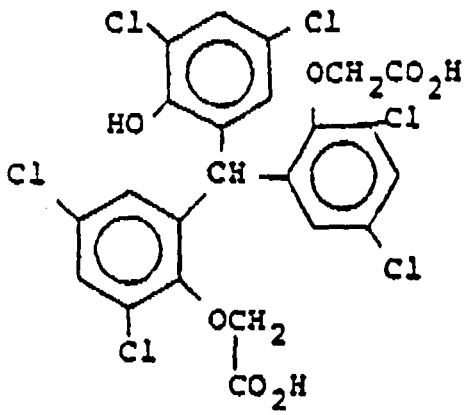
These results are encouraging from a plant hygiene standpoint, but more data is necessary regarding long term effects. When the impurities were first discovered in the plant, the still was used very occasionally

The still was originally added to the process as a way of purging contaminants out of the stream to maintain high quality recycle solvent. At this point, tar impurities made up 60-75% of the precipitates formed in diluted amines formulations.

About February 1978, the capacity of the still was increased and the average levels of TCX levels dropped to ~50 ppm in the crude reaction mass and product and to 200-500 ppm in the recycled From the period of March-May 1978, the ability to produce quality 2,4-D continued to improve and the amount of tar impurities found in the dilution test precipitates dropped . The balance were sparingly soluble metal salts of 2,4-D and some new impurities called Complex 1 and Complex 2, two of which are shown below (IV & V).



IV



V

In July 1978, the still capacity was increased and efforts gained at understanding the parameters affecting formulation quality by S. Siegel (OCR), S. Schell (Production 489), and J. King (Formulation - 9001 Bldg) and their co-workers have greatly improved

the consistency with which 948 Bldg. 2,4-D can be formulated. Based upon partition coefficients and data on the rate of formation of TCX to be discussed later in this report, K. E. First[4] (Process Engineering) generated a computer program which predicted that by distilling of recycle the steady state level of TCX in the product would be ~10 ppm and in the recycled perc the TCX level would be ~40 ppm.

The purpose of this report is to present data on the formation and fate of the impurities in the 2,4-D process. In addition, the results of experiments aimed at reducing or eliminating the impurities by chemical and physical methods will be presented.

RESULTS AND DISCUSSION

This study was divided into the following sections and the results of each are discussed separately.

(A) The mechanism of TCX formation.
(B) The distribution of TCX in the process.
(C) Reduction of TCX by chemical means.
(D) Reduction of TCX by physical means.

Although there are many impurities formed in this process, it was decided to focus the research on TCX for several reasons: (1) The rate and mode of formation of TCX was the most predicable of the major multicyclic impurities; (2) it was a major impurity; (3) a pure sample was readily obtained (by D. Humbert, Anal. Lab); (4) the analysis is not complicated; and; (5) structurally, it is the simplest of the multicyclic impurities.

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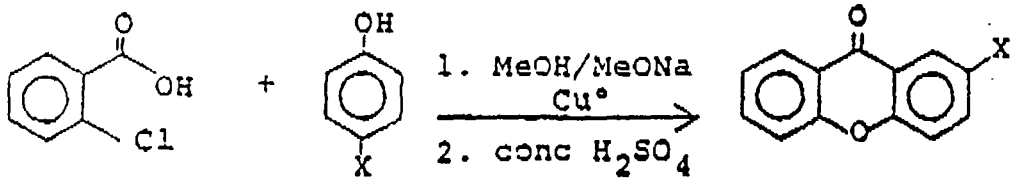
(A) The Mechanism of TCX Formation

A brief search of the literature including Chemical Abstracts showed that the xanthone ring system is formed from a number of reactions.[5] A common synthetic reaction is shown below in which the -X is included



to show the orientation of reaction. Xanthone is formed along with other products from the pyrolysis of o-chlorobenzoic acid, salicylic acid, aspirin, o-phenoxybenzoic acid, and salts of the carboxylic acids. Most of these cyclizations take place in the presence of acidic catalysts such as P_2O_5, $AlCl_3$, Acetic anhydride, or sulfuric acid. Xanthone is prepared in reasonable yield[6] by the pyrolysis of nenol salicylate with or without a catalyst.

The ease of formation of ring systems that are structurally similar to xanthones is most clearly shown by the formation of fluorescein and flucrescein dyes. Fluorescein[7] is made by reaction of phthalic anhydride and resorcinol as shown on the following page.

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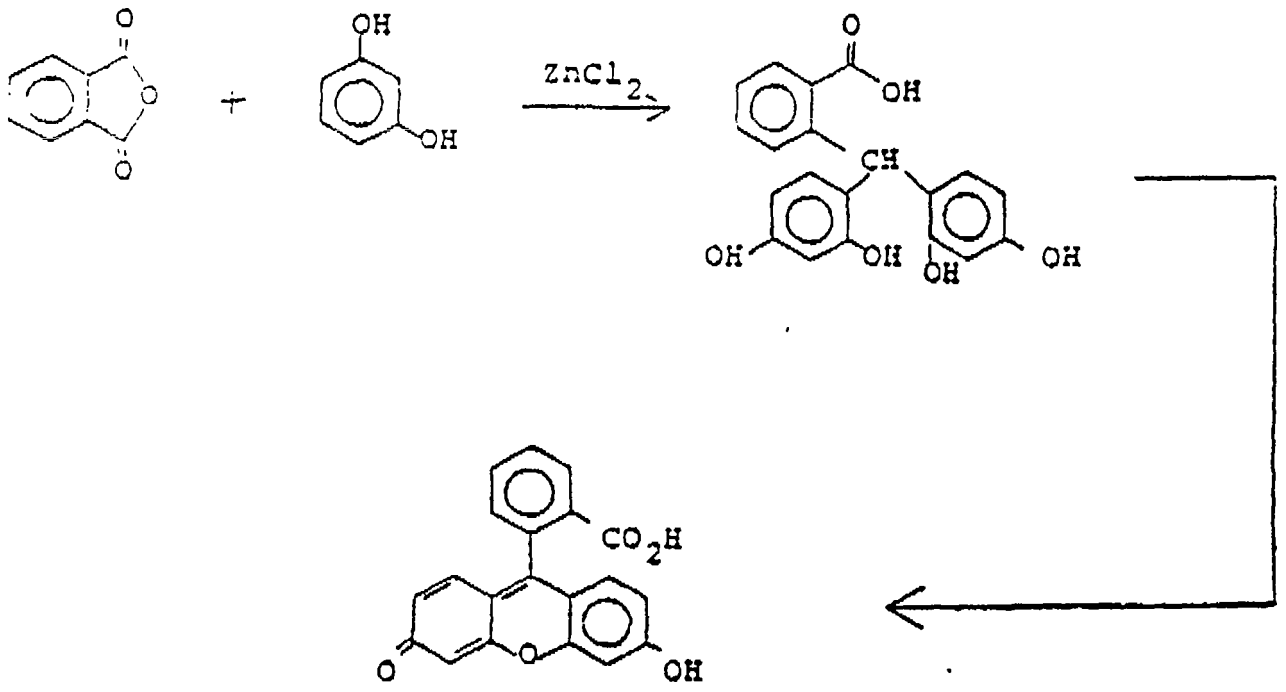
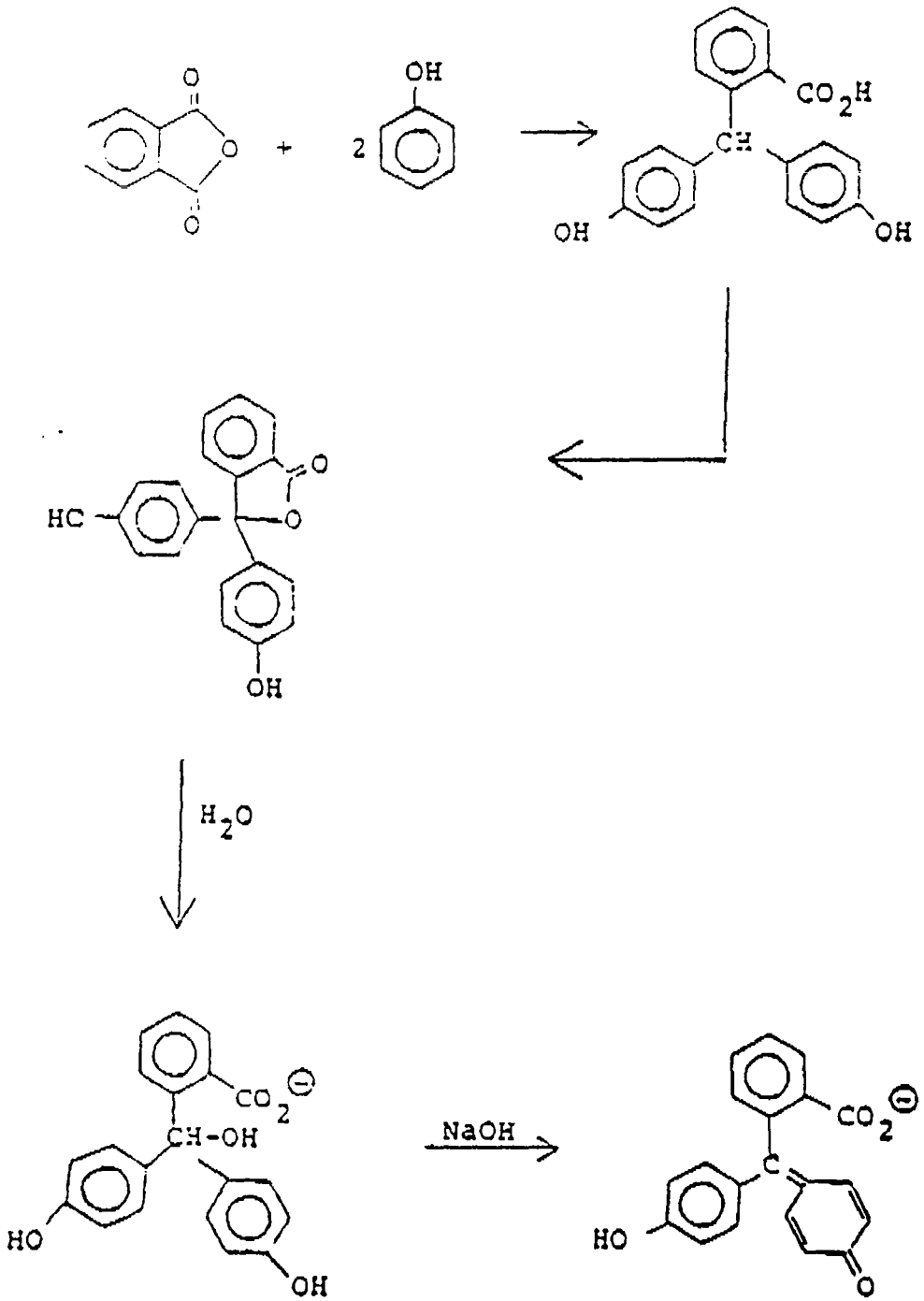


Phenolphthalein[8] is also made by this process using phenol instead of resorcinol.



colorless red

These background data give some important clues as to reaction mechanisms as will be whown later in the report.

DOW 267740

In order to understand the pathway of TCX formation, a series of ampoule tests were performed to determine which chemicals and/or combinations give rise to TCX. Table 3 summarizes the results of this study. A series of ampoules (25 ml capacity) were charged with 3-6 gms of mixtures in molar ratios as shown inTable 3 and were heated in an oil bath fo 72 hours at 160°C. The sources of the chemicals were as follows:

2,4-D: High Purity Rhone-Progil Acid
DCP : Doubly distilled 948 Bldg material
Perc :
NaOH :
Glyoxal :
Glyoxylic acid :
Tetrachloroethane :
(50:50 1,1,2,2- & 1,1,1,2-isomers)

} Reagent materials

Table 3: The Formation of TCX from Synthetic Mixtures Heated at 160° for 72 hrs.

Several compounds other than those found in the process were tested. The tetrachloroethane mixture is a known contaminant in the 941 Bldg. chloroacetylchloride that is used to make MCAA. 2,5-Dichlorosalicylic acid is a proposed intermediate from the reactions suggested below:

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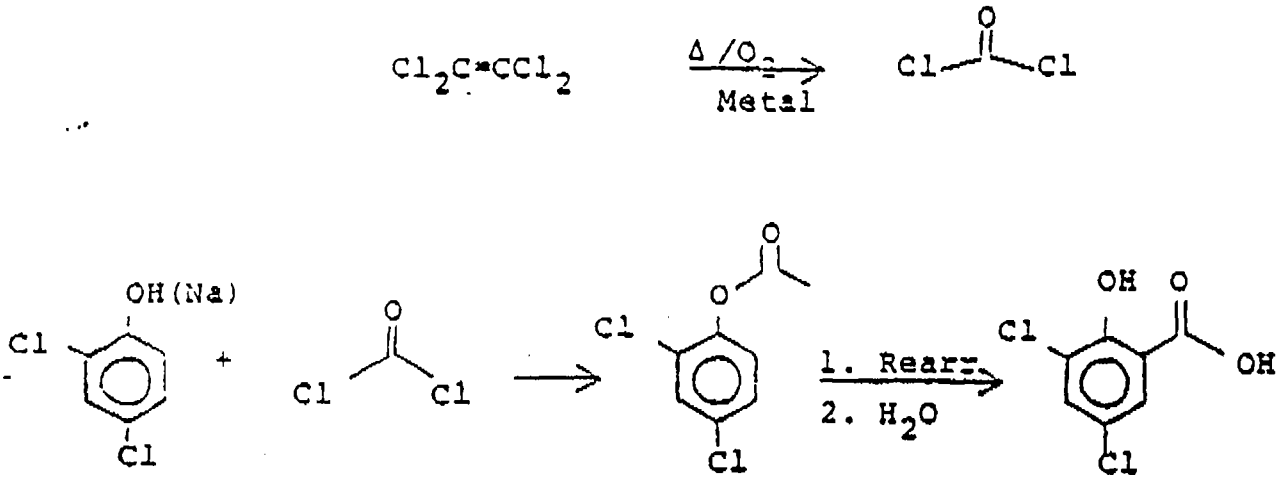
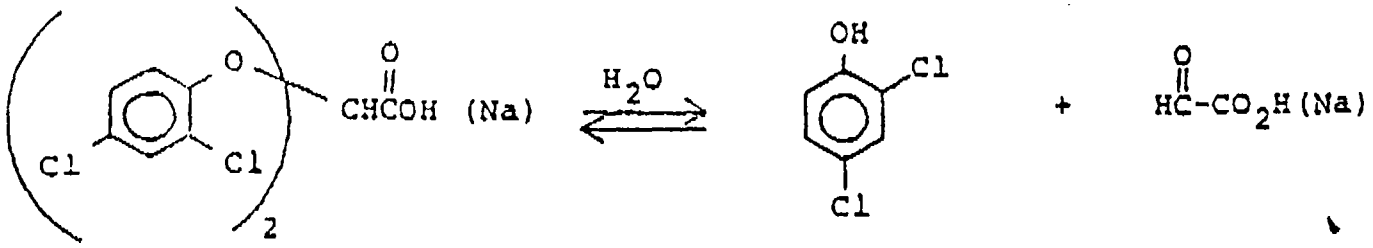


The decomposition of perc to yield phosgene is known[9] but the second reaction is only speculated.

The glyoxylic acid is postulated to come from bis 2,4-D as shown below:



which is a well known acetal hydrolysis. The glyoxal was included to show the general nature of the reaction whose mechanism is suggested later in this report.

Several tentative conclusions can be made from the data in Table 3.

(a) TCX can be made by several routes
a NaOH and/or NaDCP is necessary for the formation of TCX.
b bis-2,4-D appears to be a key intermediate.
c Perc is a source of TCX.

(b) Significant amounts of TCX are probably made only in the reactor crude storage tank in the plant since strong base is required. Run 14 (Table 3) simulates the Na 2,4-D storage tank (V-501: 948 Bldg) and Run 1 (Table 3) simulates the product storage tank (V-602: 948 Bldg) in which no TCX was observed.

In order to study the formation of TCX as a function of reaction parameters, a series of 2,4-D reactions were performed in the laboratory. These reactions were run to evaluate the effect on the amount and rate of TCX formation. The data are summarized in Table 4. In these experiments, 1.1 mol of DCP was treated wth 0.6 mol of caustic and the mixture was heated to 130°C. The majority of the water that was formed was boiled off. To this mixture, 0.5 mol of NaOH and 0.5 mol of MCAA were con-added during 1 hr at 130° and the crude product was heated an additional 1 hr. Water was continuously distilled out during the con add step. At this point the desired number of ampoules were charged with 5-10 gms of crude reaction mixture and were heated in oil baths at 130°, 145°, and/or 160° for 24, 48, and 72 hours.

DOW 2077750

Table 4: The Parameters Affecting the Formation of TCK in the Semi-Hydrous Process for Preparing 2,4-D

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	(°C)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	–	–	130 145 160	N.D. N.D. 14	TR 22 125	23 45 234	32 110 280	
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	1.1%	–	130 145 160	ND TR 6	13 32 76	29 83 132	44 127 288	
[illegible]	[illegible]	[illegible]	[illegible]	1.2	N_2	1.1%		130 145 160	ND ND TR	TR 20 54	17 57 111	18 104 166	
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	–	–	130 145 160	ND ND ND	9 21 52	12 – 93	13 39 94	
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	1.1%	–	130 145 160	– – –	14 24 49	22 57 96	53 96 144	
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	–	–	160	N.D.	49	91	–	DCP from the old Dow process direct chlorination; [illegible]
[illegible]	[illegible]	[illegible]	[illegible]	1.0	Air	–	–	160	N.D.	TR	52	125*	*After 15 hrs heating
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	–	–	160	ND	67	487	575	[illegible] with Dow
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	–	–	160	–	12	41	52	
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air & CO_2	–	–	130 160	5 –	7 81	12 219	29* 444*	*After 123 hrs heating. Initial reactor was [illegible] with 20 mole% NaOH. [illegible] with CO_2 during [illegible]
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	–	500	130 160	6 –	16 241	30 766	75 1002	
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	1.1%	500	130 160	ND –	9 197	28 505	42 728	
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	–	200	130 160	9 –	14 273	37 365	125* 932*	*After 120 hrs heating
[illegible]	[illegible]	[illegible]	[illegible]	1.2	Air	–	25	160	5	61	273	394	

The data in Table 4 show a number of interesting points. It must be emphasized that in view of the fact that these data are based on parts-per-million chemistry, the precision must be subject to some error. The data are reproducible to about 20%.

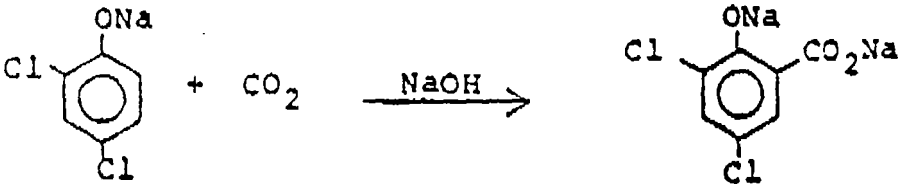
DOW 2617752

more facile route to TCX from perc whose effect is masked at the higher temperatures by a primary route (compare Table 4, Runs 1 & 2 and Runs 3 & 4).

(C) Effect of Atmosphere in the Reactor

Nitrogen blanketing appears to lower the TCX level to ~2/3 that observed in air. It is not certain that this result is significant and since the magnitude of the drop was low, further work was not warranted. Since CO_2 is known to be present[10] in the vapor space throughout the 2,4-D process, a run was made to determine its effect on TCX formation. Carbon dioxide comes into the process from the caustic and from perc decomposition.

The reaction was run as described earlier with 20 mol% of $NaHCO_3$ added before the boil down step and then blanketing the reaction mass with CO_2 during the post reaction heating step. Since this is a high temperature, nearly anhydrous process, the following reaction was thought possible which could eventually lead to TCX (See Table 3, Runs 15 and 16).



Comparing Runs 1 and 10 (Table 4) show that $NaHCO_3$ and/or CO_2 do not measurably affect the formation of TCX.

DOW 2017751

(D) Changing NaDCP/NaMCAA Ratio

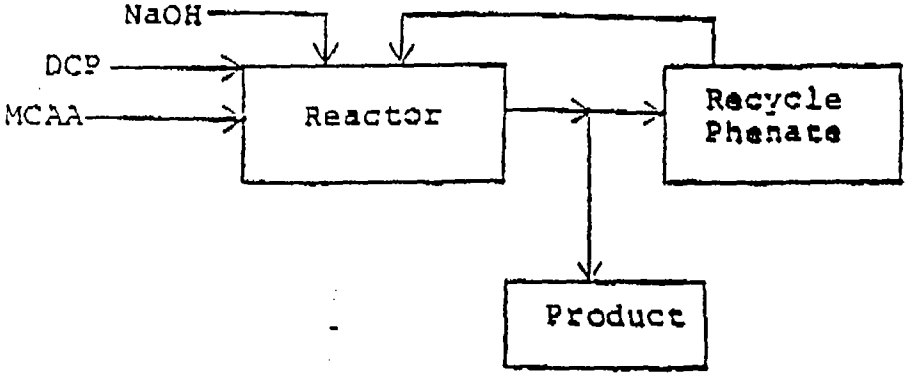
Comparing Runs 1 and 7 (Table 4) show that lowering the NaDCP/NaMCAA ratios significantly reduces the TCX levels as was also predicted from the data in Table 3. The effect was studied further and is discussed later in this report.

(E) Source of DCP

A run was made using the old lower purity DCP from the 349 Bldg process and assure that 948 Bldg, high purity, DCP was not a source of TCX. Run 6 shows that TCX formation is not associated with the source of DCP.

(F) Effect of Ferric Ion

Runs 11-14, Table 4, show that Fe^{+3} clearly increases the rate of TCX formation which suggest that alkylation step(s) are involved. D. Humbert and colleagues[7] performed a material balance of Fe in the following scheme.



They found that most of the iron is entering the process in the caustic and that the reactor normally contains 20 ppm of Fe^{+3}. A recurring problem for the past several months was how to explain the fact that the plant observed TCX formation rates that were 5 times greater than the lab. The iron results explain at least part of this discrepancy and suggest that efforts aimed at removing iron from the process are desirable.

Based upon the data presented up to this point, the mechanism shown in Figure 1 for TCX formation is suggested. This mechanism is consistent with the observations of the effect of caustic, the fact that TCX can be made from NaDCP and glyoxal or glyoxylic acid and the levels of bis-2,4-D. If this mechanism is correct, it is easy to see how perc can influence TCX formation when one considers the possible hydrolysis products using either NaOH or NaDCP. Some of these possibilities are shown in Figure 2 and many are known precursors to TCX.

In addition to TCX, OCSX and "8-5" are known to be formed in measurable quantities during the reaction to 2,4-D. It was initially assumed that TCX is the probable precursor to OCSX and "8-5". However, a series of ampoule experiments in which TCX was mixed with various ratios of DCP, 2,4-D, NaOH, and perc showed none formed in detectable amounts. In addition, a reaction was run in the presence of 500 ppm of added TCX and gave normal levels of the impurities when the 500 ppm of added TCX is subtracted out. It is apparent that OCSX, "8-5", and TCX are probably made by independent routes and proposed mechanisms are shown in Figures 3 and 4.

Figure 1: Proposed Mechanism of TCX Formation

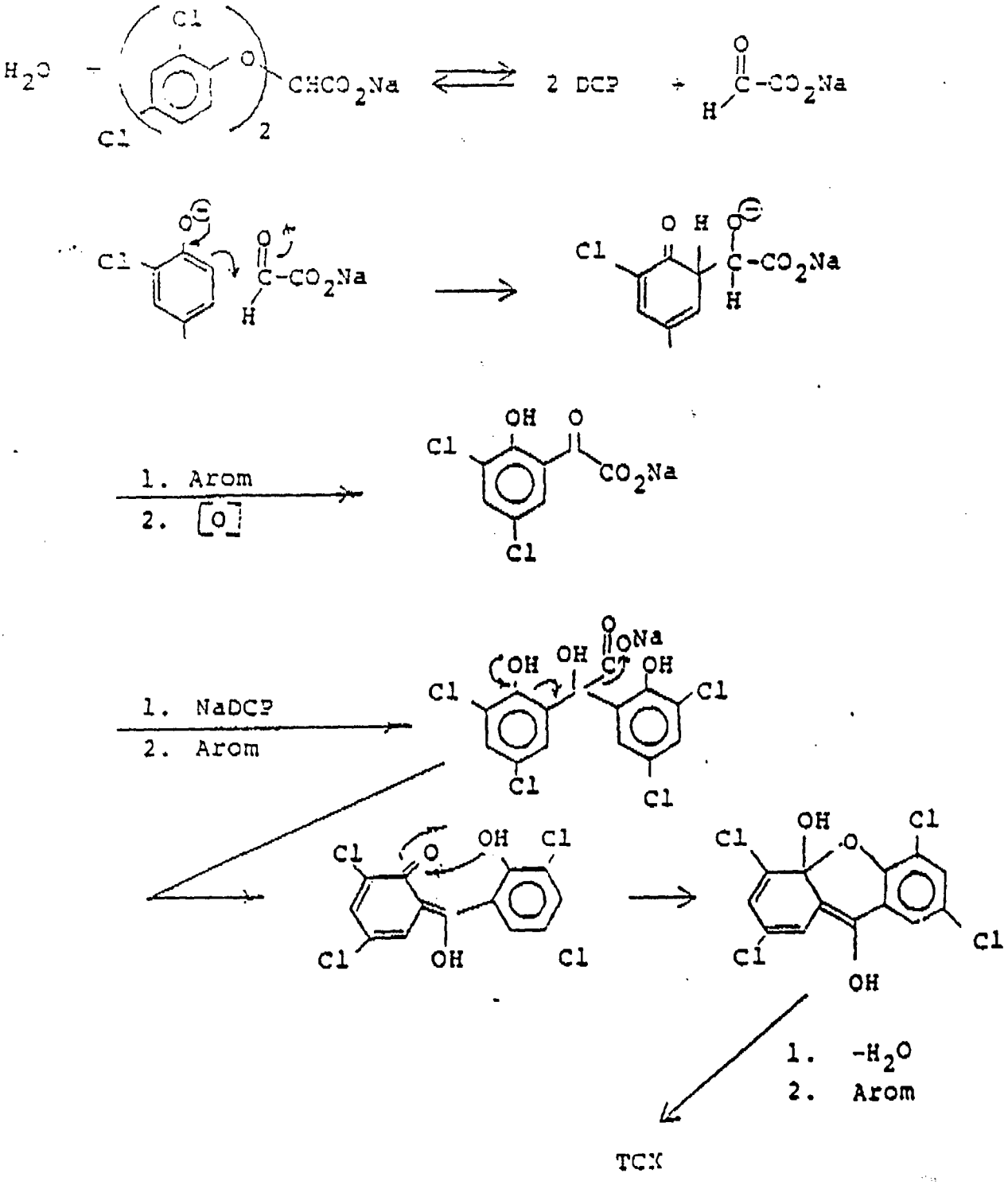


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Figure 2: Some of the Possible Products of the Hydrolysis of Perchloroethylene with NaOH or NaDCP

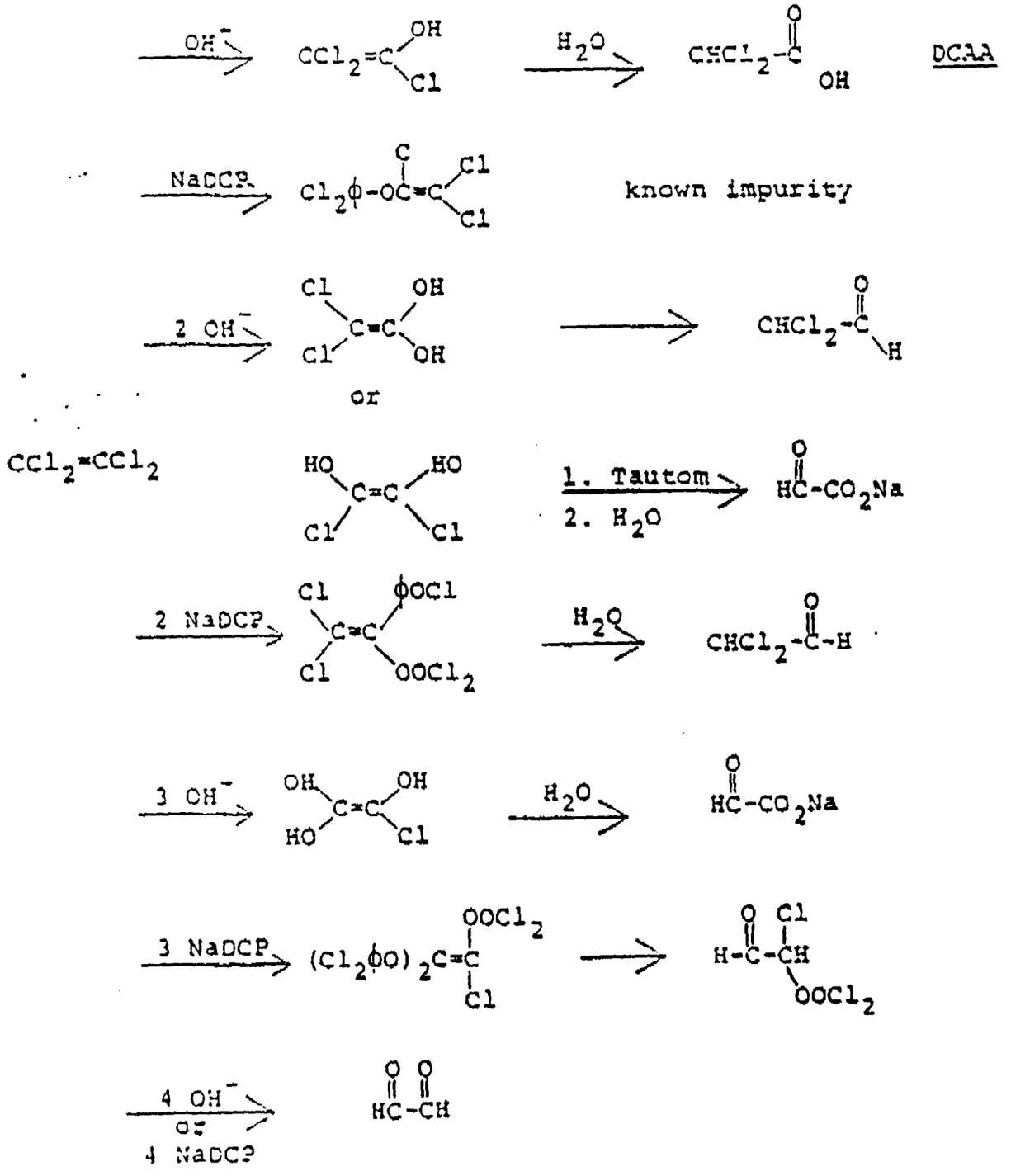

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Figure 3: Proposed Mechanism for the formation of OC by a Route That is Independent of TCX

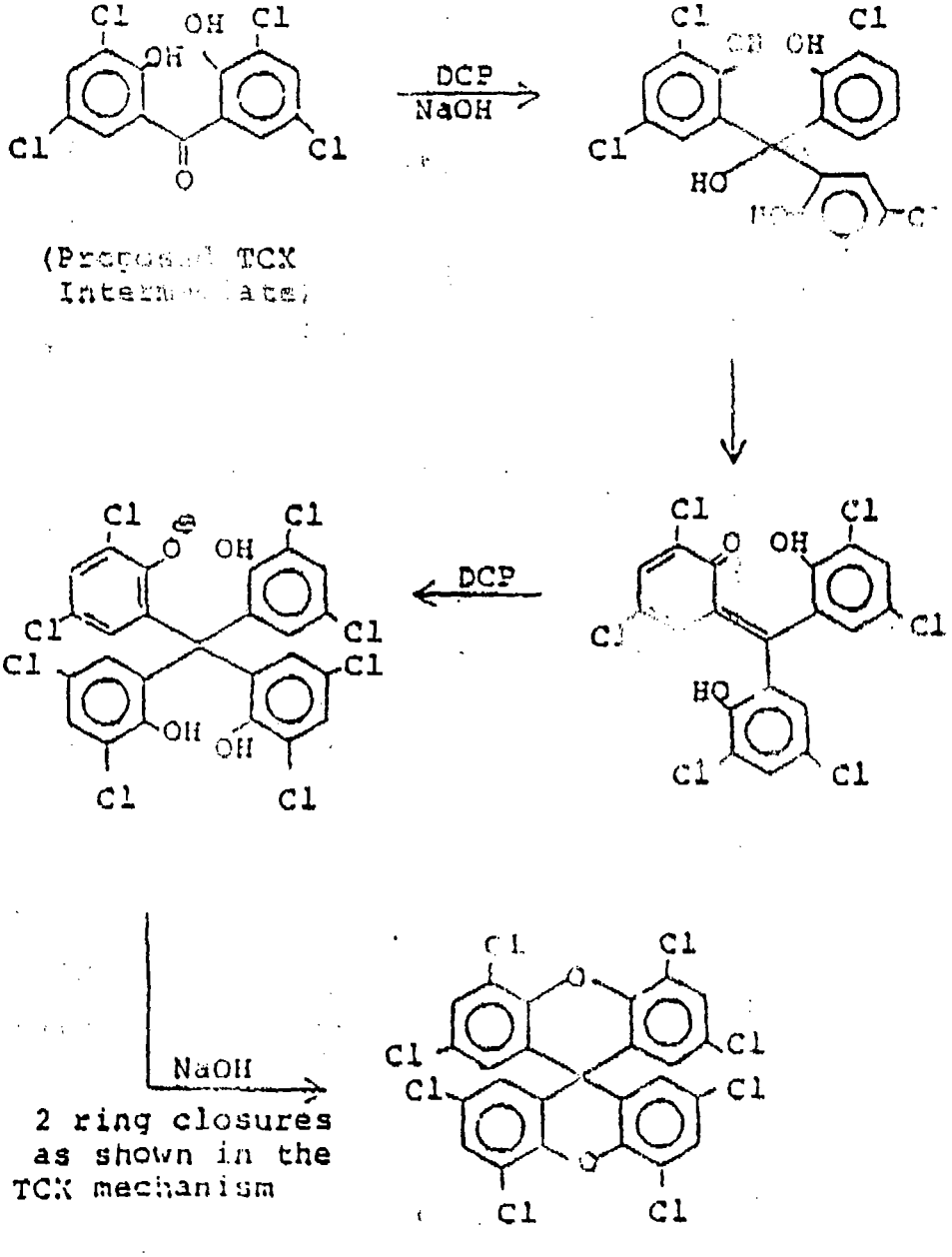
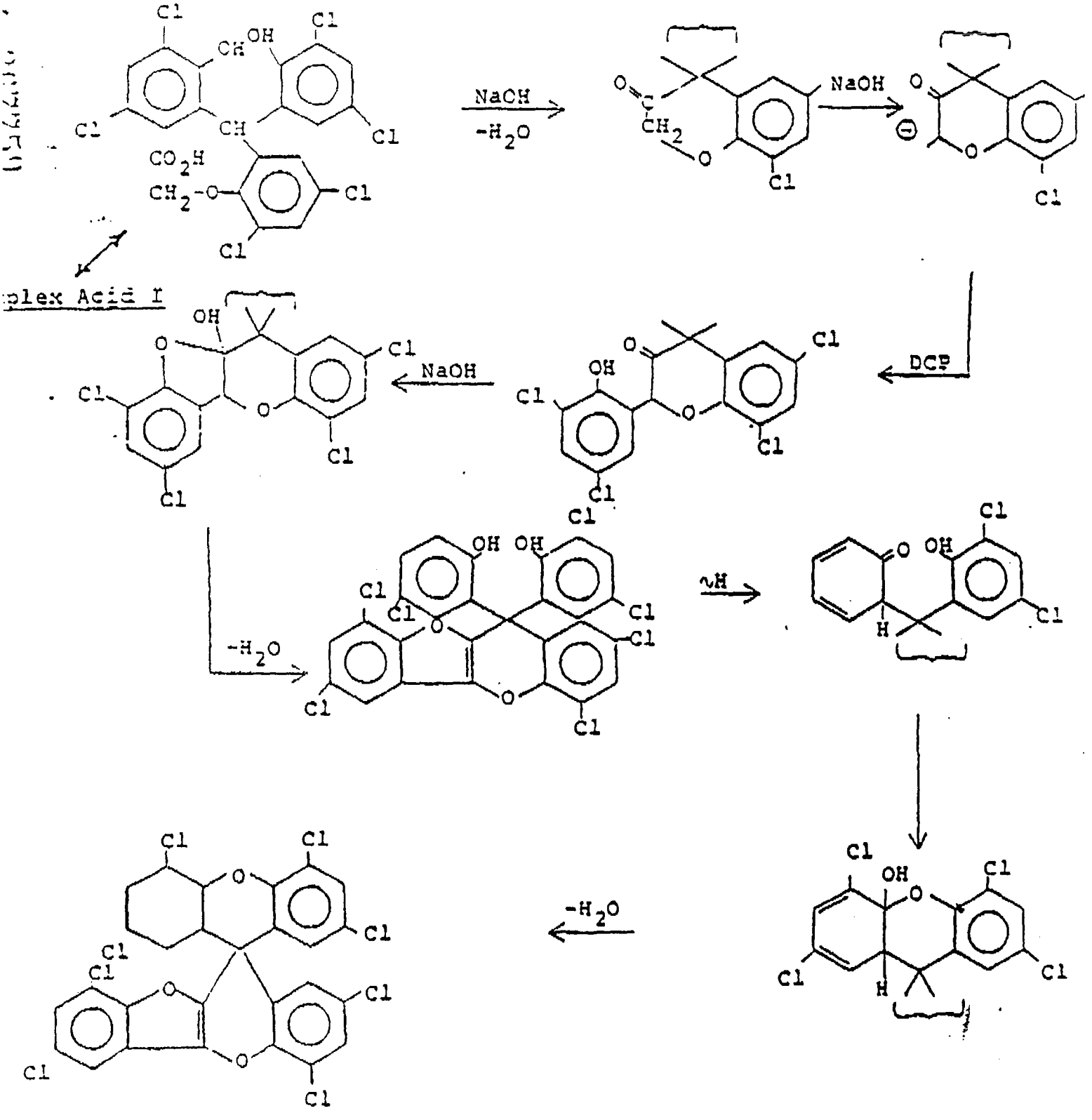


Figure 4: Proposed Mechanism for the Formation of "8-5" By a Route that is Independent of TCX



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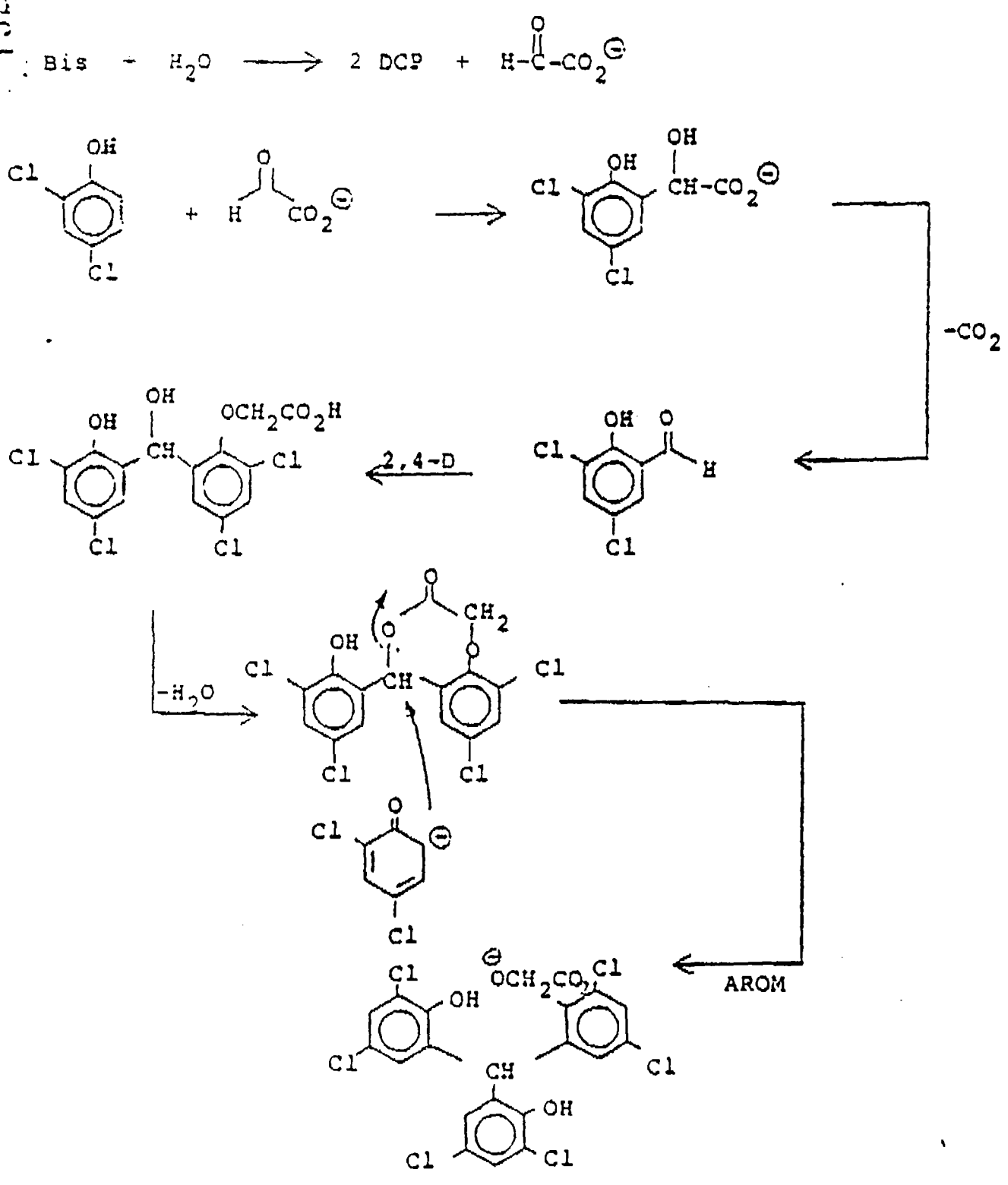
The formation of OCSX uses an intermediate in the TCX mechanism as its starting material. The apparent fact that TCX is not an intermediate suggests that the more activated dihydroxy ketone is necessary for alkylation. The mechanism for "8-5" formation involves a major component in the Complex I and II mixture as a starting material. Recent analytical results[10] have shown ~100 200 ppm of this mixture in the process. A proposed mechanism for the formation of Complex Acid I is shown in Figure 5. It must be emphasized that the mechanisms shown in Figures 3,4, and 5 are speculations and are only one of a number of possibilities. Much more work is necessary to prove their accuracy.

Figure 5: Proposed Mechanism for the Formation of the Major Impurity in Complex I mixture (Compound IV)



D-28

V-601: Final Product Storage Tank: Tests run at 120-175° on wet and dry 2,4-D[11] showed that there is an initial slow build up of about 20 ppm of TCX during the first 48 hrs at >160° that stabilizes out. This suggests a small amount of an unstable unknown species that decomposes in acidic media. Molten 2,4-D can be treated for at least 100 hrs under the above conditions without affecting product performance.

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Since TCX is formed in the reactor and was found throughout 948 Bldg process, a laboratory study of the distribution was requested. In this experiment a reaction was carried out and the crude reaction mass was spiked with TCX. The purification process was then simulated and the fate of the TCX was determined. Figure 6 summarizes the results of the extraction study performed at 90°/atm.

These data show an excellent TCX recovery in which, using clean perc, all the detectable TCX is removed from the Na 2,4-D solution. The fact that the plant observes some TCX in the product suggests that some entrained perc is carried overhead so that the impurities carried with it end in the product. The extraction of the perc/DCP mixture with caustic to recover the NaDCP also extracts about 5% of the TCX which is recycled to the reactor. This scheme was followed in a second experiment that was performed at 125°/ 35 psig which more closely follows the plant conditions. Under these conditions the aqueous solutions can be more concentrated in Na 2,4-D, NaCl, and DCP which could affect the distribution of TCX.

A high pressure, mechanically stirred glass reactor was constructed and was charged with partially neutralized material from V-301 (the DCP neutralizer). The molten material was extracted six times with perc at 125°C and the molten 2,4-D was isolated. The TCX and "8-5" levels were monitored throughout and the analytical results for the products are summarized in Table 5 for the two runs. The data show that TCX is effectively removed at the more drastic conditions.

Table 5: The Analysis of the Product from the High Temperature Extraction of Crude Na 2,4-D with Clean Perchloroethylene

	TCX (ppm)		"8-5" (ppm)		Metals (ppm)			
Run	init	final	init	final	Na	Fe	Ca	Mg
1	292	13	54	52	84	5	40	13
2	178	2	N.D.	25	91	3	50	16

It is interesting to note that "8-5" is not efficiently removed with perc extraction. Hence most of what is made goes out with the product. OCSX was not detected in these samples.

In summary, TCX is formed in the reactor and most of it remains in the recirculating perchloroethylene system. A certain amount of TCX spills into the product and the magnitude is directly related to the level in the perc. TCX is easily separated by distillation in the perc still so by increasing the rate of distillation one would achieve a lower steady state concentration of TCX in the perc.

Assuming a rate of TCX formation of 0.5-1.0 #/hr in the plant (based upon analyses of plant samples) K. E. First[4] has taken distribution coefficient data and has modeled the process in terms of TCX content in various streams as a function of % of perc distilled in the perc still. To date, there is not enough in-plant data to verify this model.

(C) Reduction of TCX by Chemical Means

Two approaches for chemical reduction of TCX were studied. These were methods for inhibiting its formation during the reaction step and methods for reducing it from process streams. The following approaches were studied and each will be discussed in detail.

1. Changing NaDCP/NaMCAA ratio.
2. Post reaction neutralization.
3. Effect of DCAA.
4. Bleaching Na 2,4-D solutions.

(1) Changing NaDCP/NaMCAA ratio

Excess caustic or NaDCP was shown earlier to have a significant qualitative effect on the increased production of TCX. The 2,4-D reaction as developed by H. Brust[12] used a ratio of NaDCP/NaMCAA = 1.2. As described earlier in the discussion, at this ratio the product contains theoretically ~6.3 mole % excess alkalinity as NaDCP as shown on the following page.

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Sta Mat'l		Product
0.5 mol DCP		0.5 mol DCP
0.6 mol NaDCP	⟶	0.1 ml NaDCP
0.5 ml NaMCAA		0.5 mol Na 2,4-D
		0.5 mol NaCl

Dhingra[13] and Fear[14] evaluated the effect of this ratio on the yield and kinetics of this reaction and concluded: (a) lower ratios (below 1.2 lead to lower yields based on MCAA and, (b) low H_2O in solution gives higher 2,4-D yields. The effect of changing the NaDCP/NaMCAA was restudied in order to determine if the lower yield from MCAA could be justified by reduced TCX formation due to less excess caustic.

The runs were carried out by using a constant amount of NaMCAA and varying the amounts of NaDCP which was done by adding differing amounts of caustic in the initial boil down step. Tables 6 and 7 and Figure 7 summarizes the results of this study. These data show that lowering the ratio from 1.2 to 1.1 results in a two fold reduction of TCX along with a 1% loss in MCAA yield. This is reasonable and was tested in the plant. After three weeks of operation, they did not note a measurable reduction for reasons that are not understood at this time. Any further reduction is not practical since the yield rapidly approaches that of the old plant thereby losing much of the advantage of the 948 Bldg process. It is interesting to note that at ratios below 1.0 there is still a measurable amount of NaDCP which explains why formation of TCX is still observed. All of the data to date indicate that formation of TCX cannot be limited to much less than 60 ppm (in the standard 72 hr/160°C ampoule test).

TABLE 6

EFFECT OF NaDCP/NaMCAA RATIO ON TCX FORMATION & YIELD ON MCAA

RUN	REF	Moles			Mol Ratio NaDCP / NaMCAA	ppm HOG	MCAA YIELD	CRUDE ANALYSIS		
		DCP	NaDCP	NaMCAA				Na 2,4-D	DCP	NaDCP
1	OC 417-5-143	0.50	0.60	0.50	1.2	951	96.4%	45.4	31.2	8.9
2	OC 417-5-144	0.55	0.55	0.50	1.1	1514	94.2	45.5	38.0	6.0
3	OC 417-5-146	0.60	0.50	0.50	1.0	3808	86.8	41.3	40.3	2.2
4	OC 640-1-1	0.61	0.49	0.50	0.98	3606	86.2	43.0	41.7	2.5

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TABLE 7

THE RATE OF TCX FORMATION AS A FUNCTION OF TIME, TEMPERATURE & $\frac{NaDCP}{NaHCAA}$ RATIO

RUN	REF	TEMP	TCX/OCSX			
			18 HRS	42 HRS	66 HRS	114 HRS
1	417-5-143	130	---	---	19	53
		145	37	34	70	218
		160	29	86	118/107	240
			18	42	66	114 Hrs
2	417-5-144	130	0	19	33	52
		145	27	39	64	93
		160	42	74	93	142
						90 Hrs
3	417-5-146	130	<10	<10	15	30
		145	15	20	41	59
		160	29	47	55	67
						90 Hrs
4	640-1	130	17	28	22	18
		145	23	31	34	52
		160	36	61	65	77

FIGURE 7 : THE YIELD OF 2,4-D BASED UPON MCAA & THE FORMATION OF TCX AS A FUNCTION OF THE $\frac{Na.DCP}{Na.MCAA}$ RATIO

K Kumar
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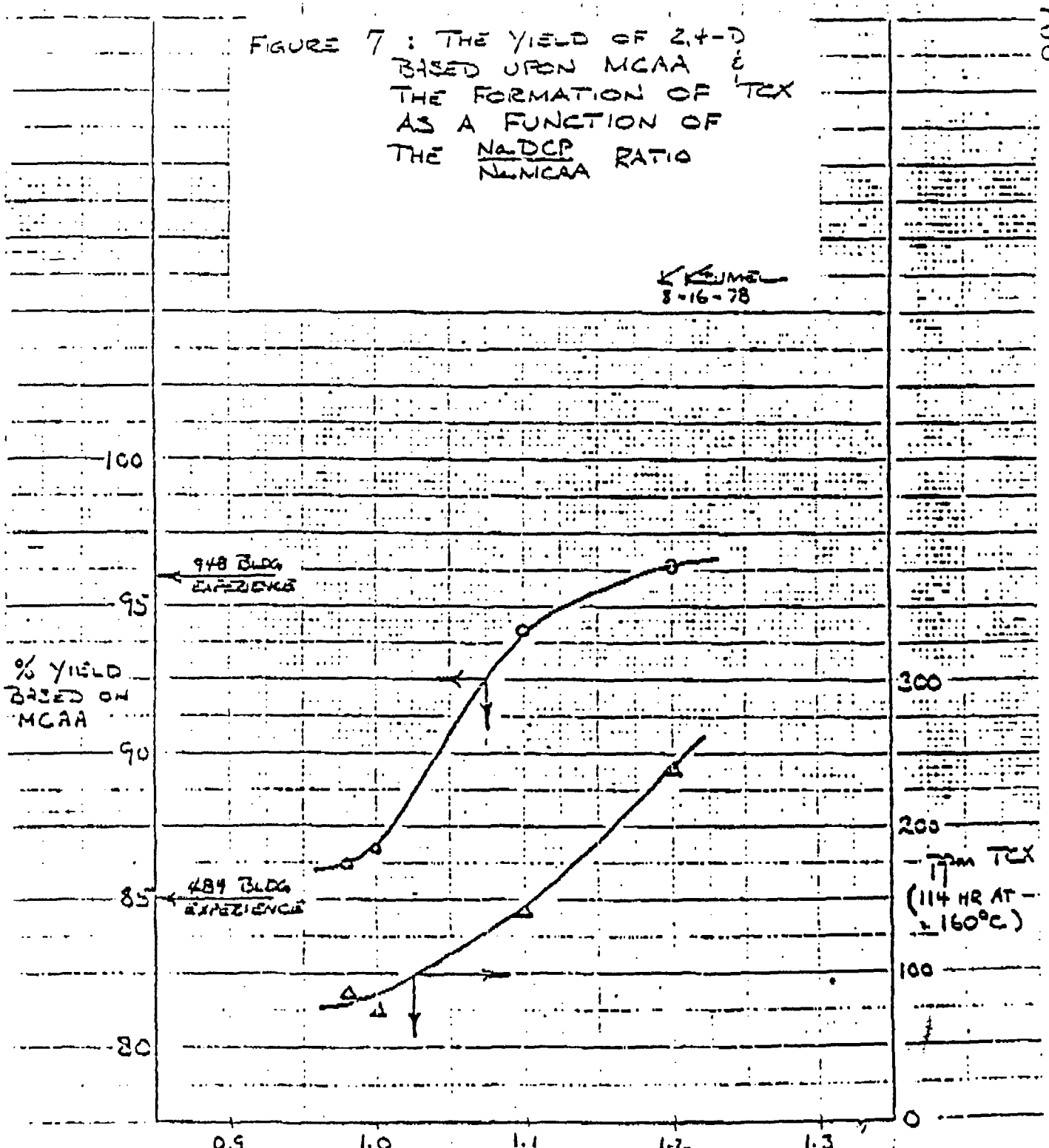

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(2) Post Reaction Neutralization

F. G. Aerstin[15] suggested that if the reactor crude were immediately treated with enough acid to neutralize the NaDCP after the post reaction before transfer to the reactor storage tank (V-202), TCX formation might be greatly reduced. This concept was tested using 32% HCl, and dry and wet 2,4-D as the neutralizing acid. The first experiment used enough dry 2,4-D to completely neutralize the residual NaDCP. The neutralized crude showed 1.4% NaDCP and a rate of TCX formation as shown below that is consistent with the data shown in Tables 6 & 7.

	ppm TCX		
Temp	24 hr	48 hr	72 hr
160°	24	51	62

The use of wet, molten 2,4-D (25% H_2O or 32% aqueous HCl has some serious physical handling problems.

As was discussed in an earlier report[16], water added to 2,4-D raises the freezing point of the mass creating a material similar to cottage cheese in consistency. In addition, the added salts (either Na 2,4-D or NaCl) also raised the freezing point of the reactor batch from a range of 115-120°C to 118-125°C.

In summary, whereas post reaction neutralization reduces TCX by a factor of four, it offers several disadvantages:

(a) it would add at least 30 min - 1 hr to the reaction cycle in a plant already reactor limited near capacity operation.

(b) Addition of acid could cause corrosion problems in the Incoloy 800 decanter .

(c) The possibility of precipitates forming in the reactor would put excessive stresses on the agitator. Their formation could not be avoided

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in the laboratory even by very slowing adding the aqueous acid.

(d) Control of the acid addition would be difficult and, in addition, the plant would have to run a slightly smaller batch size in order to provide room for the acid. Further work on this concept is not warranted at this time.

(3) DCAA Content of MCAA

The effect of DCAA was discussed earlier.

(4) Bleaching Na 2,4-D Solutions

The major chemical difference between 948 Bldg and 489 Bldg techniques for processing crude 2,4-D is that 489 Bldg uses a bleach step in which residual DCP is oxidized out of the Na 2,4-D solution with 8-12% NaOCl at pH 10.5/100°C. Several experiments were performed to determine if bleach would effect the impurity levels and/or improve the ability of the plant to consistently produce 2,4-D that passes the formulation dilution test. The results of these experiments are shown in Table 8.

The results of the first experiment appeared very encouraging since the dilution test solids, the TCX and the "8-5" were all significantly reduced. The second series of runs showed a consistent improvement in dilution test solids when near or out of spec, but not much effect on the impurities. A capital estimate performed by K. E. First[4] showed the cost of implementing a bleach step in 2,4-D to be $500 M which immediately eliminated any further interest in this project in view of the marginal benefits. It is assumed, posthumously, that the main effect of the bleach was to reduce residual DCP which is a known contributor to poor dilution test results.

Table 8: The Treatment of Na 2,4-D Solutions with Bleach

Na 2,4-D Solution Source	pH	Mol Ratio $\frac{NaOCl}{Na\ 2,4\text{-}D}$	ml solids		Impurities (ppm.		
			DMA-4	F-40	TCX	OCSX	"8-
V-501 (4-7-78) 948 Bldg.	starting material		---	0.18	58	N.D.	127
	10.5	0.1	---	0.02	25	N.D.	N.D
V-501 (6-5-78) 948 Bldg	starting material		0.01	TR	80	N.D.	31
	10.5	0.1	TR	TR	85	"	10
	10.5	0.2	TR	TR	85	"	26
	10.5	0.05	---	---	104	"	23
	10.5	0.1	---	---	94	"	16
	5	0.1	---	---	72	"	47

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(D) Removal of TCX by Physical Means

To date, a stage has been reached in 948 Bldg. where the 2,4-D plant can be run to consistently produce in-spec material and has demonstrated an ability to run at near capacity of 100-120 M#/day. With the perc still running at ∿15 GPM, the 2,4-D product contains ∿20 ppm of TCX and ∿20 ppm of "8-5".

A numberof attempts have been made to see if the levels of TCX can be reduced by physical means that include:

1. Carbon treatment of the recycling perc and the molten 2,4-D.
2. Removing perc from the reaction step.
3. Improved washing of the molten 2,4-D.
4. Recrystallization of Na 2,4-D and recrystallization of 2,4-D acid.

The details of each alternative are discussed below. In all cases, these experiments were short term, range finding efforts and not comprehensive. Further work is justified only if the levels of impurities presently found in the product prove unacceptable in the future from a toxicity, environmental, or performance standpoint.

(1) Removal of TCX with Activated Carbon

The removal of TCX with activated carbon from perchloroethylene from V-402 ("clean" perc storage tank) was evaluated by a standard isotherm method. A 100 ml portion of perc was treated with ground Pittsburg SGL carbon at 70°C/72 hrs. The data, summarized in Table 9, were evaluated by a known technique[18] that is summarized below. A plot was made of X/M vs. C on log-log paper as shown in Figure 5. By extrapoling C to incoming TCX concentration, the corresponding X/M value gives the amount of impurity absorbed per unit weight of carbon when that carbon is in equilibrium with the incoming concentration and represents the ultimate capacity of the carbon. The

theoretical volume of liquid to be completely freed by TCX/gram of carbon is calculated from the following equation:

$$V_{Co} = \frac{\left(\frac{X}{M}\right)_{Co}}{Co} \cdot V$$

V_{Co} = theoretical volumn to be treated

$\left(\frac{X}{M}\right)_{Co}$ = capacity/gm at incoming concentration

V = volume of liquid used in test

Co = incoming concentration

For this experiment:

$$V_{Co} = \frac{400}{241} \times 100 = 166 \text{ ml/g of Carbon}$$

or 19.9 gal of perc/# C

or 265 # perc/# C

Carbon loading at 241 ppm of TCX in feed = 166 ml/g C x 1.6 g ml x .00024
64 mg/gC

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Table 9: The Absorption Isotherm for TCX Removal from Perchloroethylene with Pittsburg SGL Activated Carbon

Sample	Impurity (ppm) TCX	OCSX	"8-9"	(M) WTC/100ml Perc	(C) Resid ppm TCX	(X) ppm TCX Removed	(X/M) ppm TCX removed / gm Carbon
STG. Mat'l	241	N.D.	19	0	241	0	---
1	159	"		0.25	159	82	328
2	108	"		0.50	108	133	266
3	57	"	17	1.00	57	184	184
4	40	"		1.50	40	201	134
5	29	"	17	2.00	29	212	106

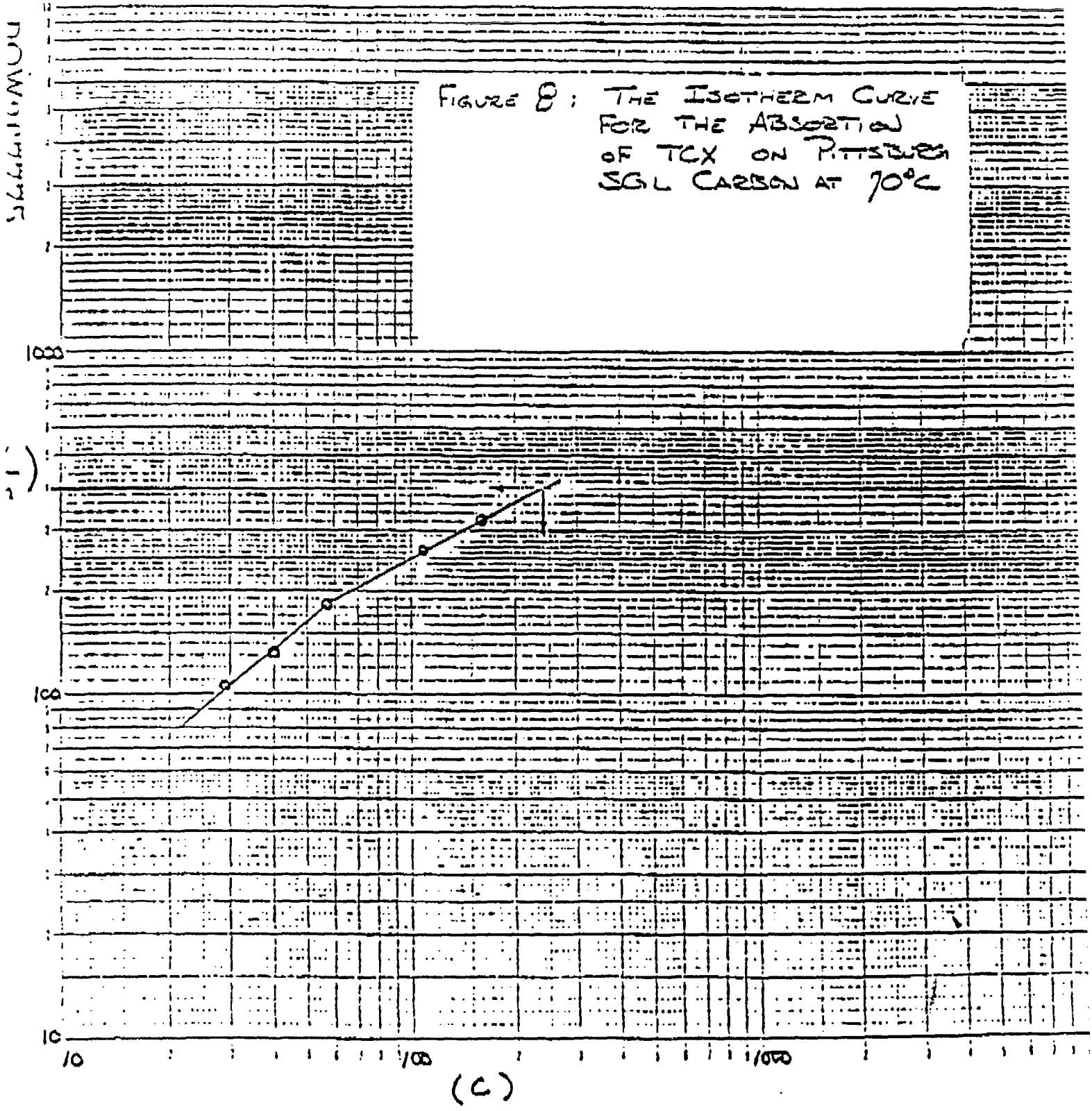

FIGURE 8 : THE ISOTHERM CURVE FOR THE ABSORTION OF TCX ON PITTSBURG SGL CARBON AT 70°C

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This is a low loading level and at the present rates of TCX production in the plant, about 15-20 # of carbon per hour would be required to remove the impurity. The data shown in Table 9 indicate that carbon does not remove "8-5" from perc. The shape of the isotherm curve indicates that more than one species is being absorbed onto the carbon. No effort was made to determine the identity of that compound although it was probably perc.

A run was made to remove impurities from wet molten 2,4-D. Since molten 2,-D is so difficult to handle at atmospheric pressure, pressurized system was built using a capillary feeder for controlling the continuous flow of molten 2,4-D at 100°/25 psig onto a vertical 2' x 0.5" column that was maintained liquid full. The flow rate was 10 ml/min down the column for a mass flux of ~1.0 gpm/ft.^{2} The results are summarized in Table 10.

Table 10: The Treatment of Molten 2,4-D with Activated Carbon

nple #	Temp (°C)	Pressure psig	Approx feed rate ml/hr	Approx. Prod. cut volume (ml)	Product Analysis (ppm)			F-40* solids (ml)
					TCX	OCSX	"8-5"	
ed	112				42	N.D.	32	.005
	110±2	33±2	300	100	--	--	--	
	110	33	600	375	14	N.D.	29	.04
	110	33	600	375	28	N.D.	38	.005
	110	33	600	376	32	N.D.	42	
	110	33	600	375	30	N.D.	36	

ormulation contains 2% Versene & 0% PG 4000

ese data are fairly crude in that the column was shorter than is desirable optimum column work (2' vs the recommended 5-6'[18]) and the flow through e column was a little faster than the more desirable 0.5 gpm/ft^2 recommended.

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The data show that TCX loading is rather low. Breakthrough occurred after 900 ml molten D (~935g pure 2,4-D) was treated. From the analyses, the 59.8 gm of Pittsburg SGL 8 x 30 granular carbon charged to the column absorbed 281 mg of TCX for a loading of ~0.5 mg/g of carbon which is quite low. Again, "8-5" was not absorbed by the carbon. Based upon these preliminary experiments, carbon absorption of these impurities is not an attractive purification technique.

(2) Remove Perchloroethylene From the Reactor

Since perc is known to give rise to TCX, several methods were examined to eliminate its recycle to the reactor. At present, since perc is soluble to 1.2% in the recycle NaDCP solution, there are about 350# returning to the reactor in each batch. Since a continuous percphenate phase separation is performed in V-401 just before recycle to the reactor, a brief study was undertaken to evaluate the phase separation to determine the time required for complete layer separation and the solubility of perc in NaDCP solution.

A solution of 62% NaDCP and 2% NaOH in water was slurried with an excess of perc and vigorously stirred for 30 min at 75°. The stirring was stopped and the phenate layer was analyzed for % perc as a function of time. The results are summarized in Table 11. These data show that the solubility of perc in NaDCP is 1.3±0.1% at 75°C and that layer separation is complete within 15 minutes. The residence time in V-401 is ~40 minutes so that with proper operation, no layer separation problems should result. The question was also asked if the perc was entrained in the NaDCP solution as an emulsion or was it in solution? A sample was centrifuged at 60° (minimum temperature) for 30 min at ~4000 rpm and 1.2% perc was found in the phenate. It is concluded that the present equipment gives optimum layer separation and the 1.2% of perc is soluble.

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Table 11: The Solubility and Separation Rate of Perchloroethylene and 62% NaDCP in Water at 75°C

TIME*	% Perc in Phenate Layer
5 min	1.9
15 "	1.3
30 "	1.4
1 hr	1.5
2 "	1.4
4 "	1.4
6 "	1.2
24 "	1.3

*Time zero is when the vigorous stirring of the two layers is stopped.

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Several attempts were made to strip perc from the reaction mass and from the NaDCP solution. The plant tried to strip perc from the reaction mass during the normal boil down step. Whereas normal operation involves returning the distilled organic layer to the reactor, in this experiment the recovered organic layer was discarded. Whereas normal boil down returns 350# of DCP to the reactor, in this experiment even after 4000# of DCP was distilled off, there was still detectable perc in the distillate. As a result, this approach was judged impractical. Two attempts were made to distill the 1.3% of perc from the 60% NaDCP-2% NaOH solution.

The first involved a batch distillation from a standard solution from V-403. A total of 65.9 gms were distilled out and 73.8% of the perc was removed. The reaction was then carried out as usual and samples were heated for 24, 48, and 72 hrs and the results are summarized below. These data suggest that distillation of 75% of the perc does not reduce TCX formation (See Table 4, Runs 4&5).

	Temp	24 hrs	48 hr	72 hrs
ppm TCX	160°	21	75	145

The second approach taken for stripping out perc was using a falling film still. The results of two experiments are shown in Table 12. The results show that, as before, 70-80% of the perc is easily removed but that the last 20% is likely to be quite difficult. No more work is planned in this area until it can be better proven that removing perc offers any real advantage in reducing rates of TCX formation.

(3) Improved Washing of 2,4-D Acid

Several experiments were run to see if improved washing would affect impurity levels in the 2,4-D product. A sample of 2,4-D product was taken from V-602 (948 Bldg) and was treated in the following ways:

(a) A 250 gm sample of molten acid was washed 3 times with 200 ml of water per wash at 100°C.

TABLE 12

Preliminary Data for Falling Film Distillation of Perc From NaDCP Solution

Still: 1" x 12" Tube

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	Run 1	Run 2
Pressure		
Temp (col'm)	120°	ATM.
" (feed)	75°	75°
Feed Rate (ave.)	10 ml/min	10 ml/min
Overhead Temp	85° → 90°	90° → 95°
Feed analysis		
% Perc	1.0	1.1
% DCP	51.5	50.1
Wt. Charged (Feed)	725 gms	738 gms
Product: Wt	652 gms	645 gms
% Perc	0.3%	0.2%
% DCP	53.9%	61.6%
Overhead: Wt	46.7 gms	75.0 gms
% Perc	1.5%	3.3%

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(b) Another sample was reacidified to pH 0.5 with conc HCl and rewashed 2 times with water at 100°C.

(c) A synthetic V-501 mixture was made up using Rhone Progil 2,4-D to determine if any impurities are made in the washing step. The synthetic mixture was acidified and washed and the 2,4-D was recovered for analysis. This experiment was repeated in the presence of 2750 ppm of added TCX.

The results of these experiments are shown in Table 13. Based upon these experiments, it is shown that the impurities are not made or reduced by improved washing. If anything, they are slightly increased in the product due to the greater solubility of 2,4-D in the hot water or brine.

(d) Recrystallization of Na 2,4-D and 2,4-D Acid

An attempt was made to determine if the impurities could be removed by recrystallization of Na 2,4-D from water and 2,4-D acid from organic solvents. Na 2,4-D was recrystallized by taking 500 gms of material from V-501 and adding enough water (350 ml) to form a homogeneous solution at 100°C. The solution was cooled and the precipitated Na 2,4-D was filtered and washed with 5% brine. The Na 2,4-D was redissolved in hot water and the 2,4-D was isolated and analyzed. The results are shown in Table 14.

In two separate experiments, 2,4-D from V-602 was recrystallized from perchloroethylene and ethylbenzene. A weight ratio of 3 parts solvent to 1 part 2,4-D was heated to boiling, the water contained in the molten 2,4-D was boiled out as an azetrope (the organic distillate was returned) and the solution was cooled. The 2,4-D was recovered by filtration and the solvent removed by heating in a vacuum oven at ~60°C. The results are summarized in Table 14.

Table 13: The Effect of Improved Washing of Molten 2,4-D on Levels of Impurities

Material	Impurities		
	TCX	OCSX	"8-5"
V-602 Starting Mat'l	56	N.D.	58
Wash three times	73	N.D.	60
Reacidify, wash two times	96	34	68
Synthetic V-501 Na 2,4-D: 21.5% NaCl 7.0% DCP 0.2%			
After Acidif. & Wash	N.D.	N.D.	N.D.
Repeat the synthetic V-501 spiked with 2750 ppm TCX			
After Acidif & wash	3150	N.D.	10

Note: Rhone Progil 2,4-D shows no detectable TCX, OCSX & "8-5"

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Table 14: The Effect of Recrystallization of Na 2,4-D and 2,4-D Acid on Impurity Levels

Treatment		Impurity Level (ppm) TCX	OCSX	"8-5"	F-40** Dilution Test	Comme
Recrystallize Na 2,4-D	Before*	58	---	127	0.18	Produc Highly lored
	After	81	53	54	0.3+	
Recrystallize 2,4-D From Perc	Before	52	N.D.	46	***	91% Re very o 2,4-D
	After	1	N.D.	N.D.		
Recrystallize 2,4-D From Ethylbenzene	Before	52	N.D.	46	***	87% Re very o 2,4-D
	After	N.D.	N.D.	N.D.		

*The impurities analysis was performed on a sample of 2,4-D acid isolated from Na 2,4-D without any extra treatment.

**20:1 dilution in 1000 ppm hard water, formulation contained 2% Versene and no P-4000.

***The recrystallized product behaved like the high purity Rhone Progil 2,4-D which is difficult to formulate as was mentioned earlier in this report.

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GENERAL CONCLUSIONS

TCX and other non-acidic impurities are formed chiefly in the reaction step of the 2,4-D by several routes.

A number of attempts to chemically and physically remove these species have met with limited success.

SAFETY & ECOLOGY

2,4-Dichlorophenol, 50% NaOH, and chloroacetic acid are highly toxic and corrosive raw materials. When handling, the protective clothing included lab coat, rubber gloves and goggles, and when possible, all operations were performed in a fume hood. A number of operations were carried out at elevated pressure which required the use of a face shield and secondary shielding in the hood. All waste samples and solutions were sent to the burner for disposal.

DOE ARCHIVE

EXPERIMENTAL

The Preparation and Workup of 2,4-D

The following is a general description of the procedure used to prepare and isolate 2,4-D when simulating 948 Bldg. A 1 liter round bottom flask equipped with a bottom drain, two dropping funnels, a mechanical stirrer, a thermometer, and a distillation head was charged with 179g (1.1 moles) of 2,4-DCP and 48 g (0.6 moles) of 50% NaOH. The flask was heated with a heating mantel attached to an I^2R Thermowatch controller.

The reactor contents were heated while stirring and a DCP-water azetrope was distilled out. The distillation was continued until enough water was removed so that a temperature of 130°C could be achieved. Normally 9-10 ml of H_2O and 2-3 ml of DCP were removed. The DCP was returned to the pot. Then 47.3g (0.5 moles) of melted MCAA and 40.0g (0.5 moles) of 50% caustic were con-added from the two dropping funnels during 50-60 minutes at 130°C. The rates of addition were carefully controlled so that neither added reactant was significantly in excess of the other. Water and DCP continuously distilled out during the con-add and the DCP was returned to the reactor. After the addition was complete, the reaction was heated an additional 60 minutes. About 43-47 gms of H_2O was recovered in the con-add step. At the end of the post reaction samples of the viscous crude reaction melt were taken into ampoules, if desired.

The work up procedure for isolating the 2,4-D is as follows: (The amounts used assumes no samples were taken after reaction). The reaction mass was diluted with about 500 ml of water, heated to boiling to ensure complete dissolution and the pH was adjusted to 5.2±0.2 with about 12 ml of conc HCl. The solution was then extracted with six 150 ml portions of perc at a temperature of >90°C to remove the DCP. Occasionally 50-100 ml of additional H_2O was necessary to keep all of the solids dissolved. The extracted Na 2,4-D solution was heated

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to boiling and any traces of perc were distilled off. The pH of the solution was then lowered to 0.5-0.7 with about 55 ml of conc HCl added rapidly and the molten 2,4-D layer was separated and drained into a beaker. The resulting brine was discarded. The 2,4-D was reslurried in 250 ml of hot distilled H_2O in the pot and washed in this manner two times. The final pH of the aqueous layer was 2.7-2.9. The 2,4-D was recovered and dried overnight at ambient temperatures.

The analyses of product and intermediate streams were performed by personnel in the 948 Bldg quality control laboratory. The analyses for TCX, OCSX, and "8-5" were performed as described earlier[8].

The Carbon Clean up of Molten 2,4-D

A glass pressure apparatus was assembled in which molten 2,4-D was pumped onto a carbon column (downflow). The apparatus is shown schematically in Figure 10. The flow of 2,4-D was controlled by controlling the pressure drop across a capillary tube. To handle

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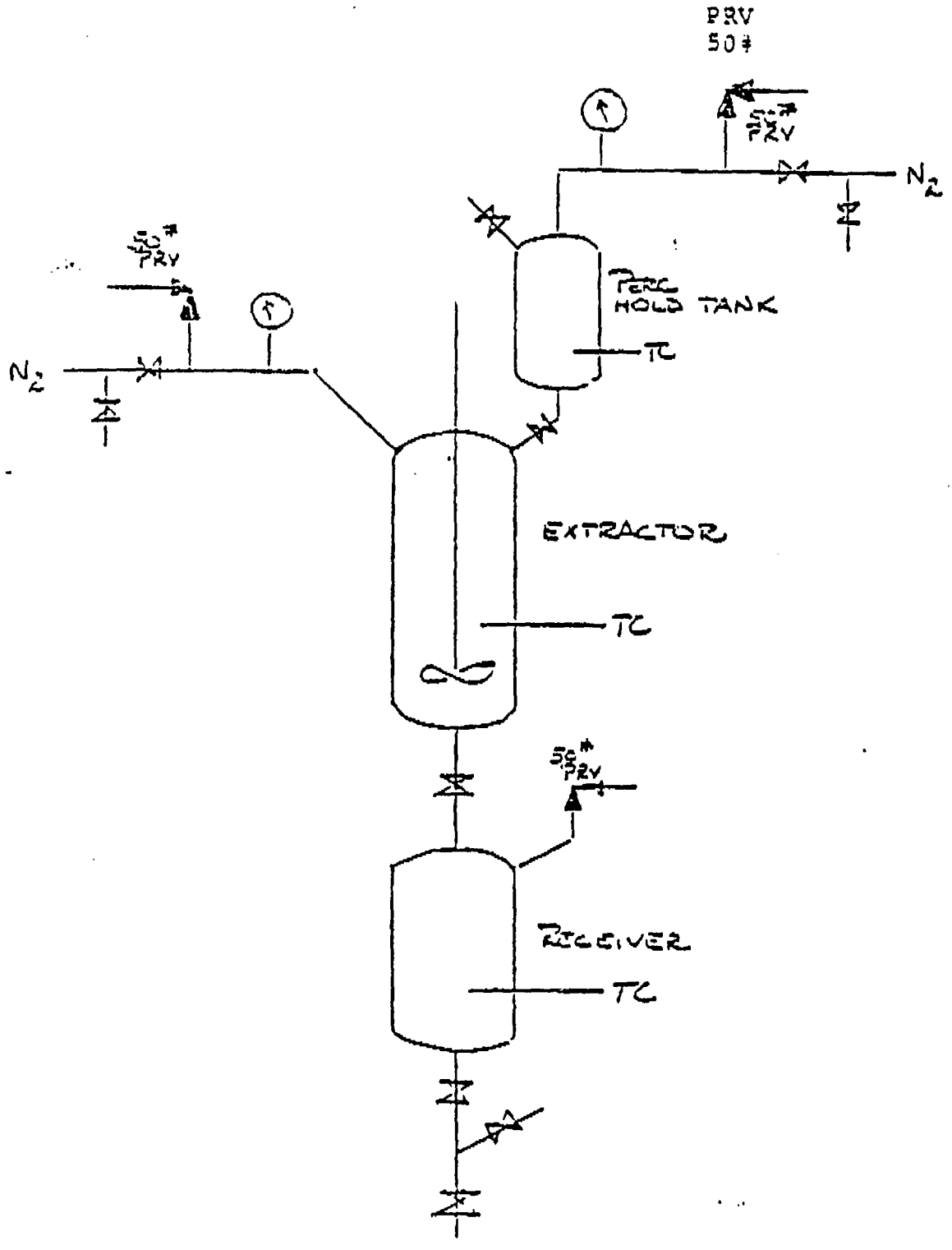
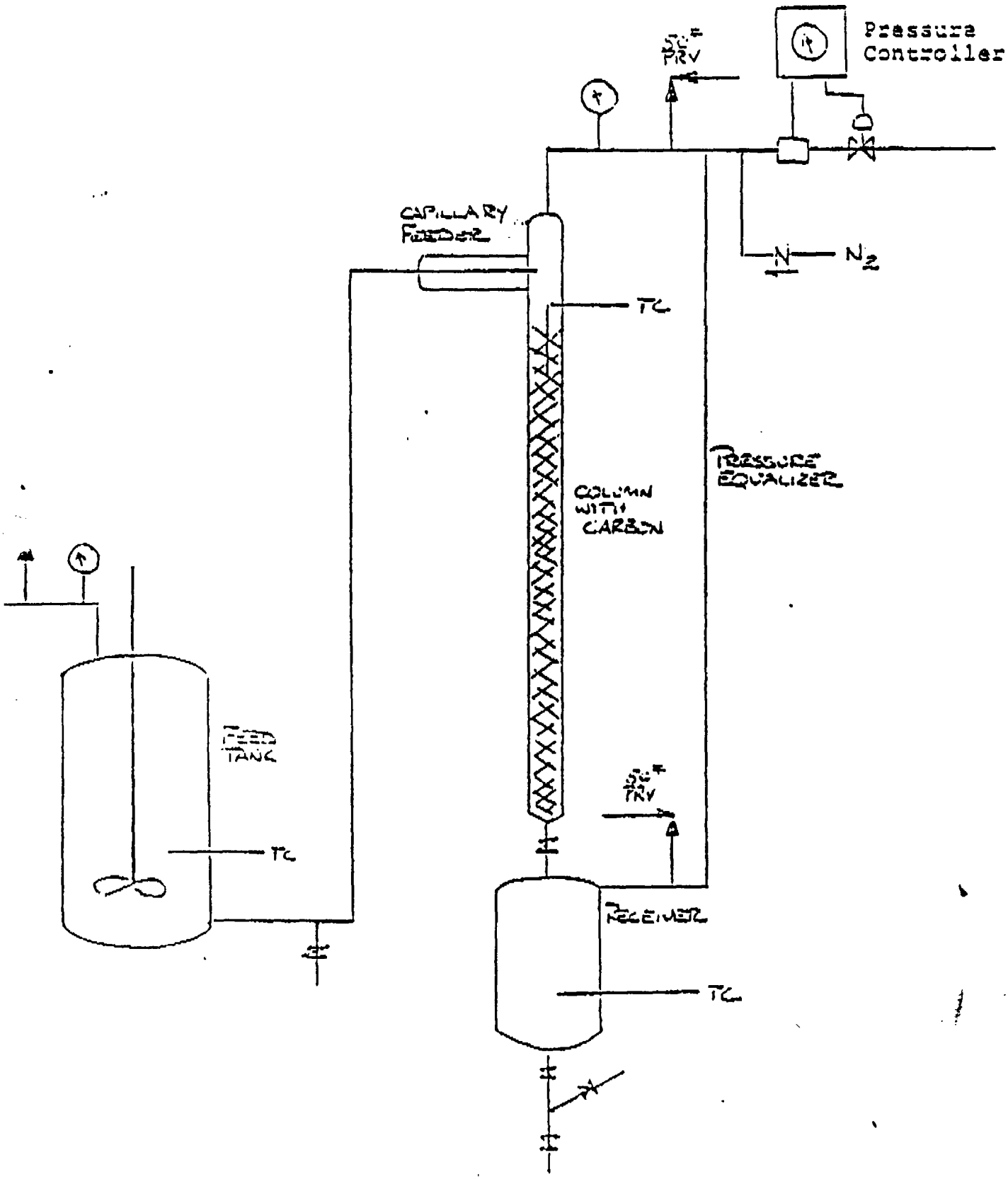


Figure 9: A Schematic Drawing of the apparatus used for Extracting DCP from Na 2,4-D with Perchloroethylene.

Figure 10: A Schematic Drawing of the apparatus used to treat Molten 2,4-D with activated carbon



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molten 2,4-D reliably and effectively, required at least 10 psig/ ~100-105°C to avoid flashing and freezing problems.

The 2,4-D and a slight excess of water were placed in the feed tank and heated to 110°C. When the entire contents were melted the valve on the bottom of the column was closed, the column was filled with molten acid to 1" above the top of the carbon, and the system stood for 60 min. The pressure drop across the capillary was adjusted to 7 psi (~10 ml/min flow) and the valve on the bottom of the column was adjusted so as to maintain the liquid level above the carbon bed. The results are shown in Table 10.

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ACKNOWLEDGEMENTS

The authors wish to thank D. Humbert, R. MacLachlan, T. Evans, G. Jewett, P. Schloemann, and their colleagues for their analytical support. The assistance of K. First and his process modeling efforts are also acknowledged.

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K. L. Krumel OC 559, Pg. 95-131.

THE DOW CHEMICAL COMPANY

MIDLAND DIVISION
April 25, 1967

1599

K. E. Coulter
Midland Division Research & Development
566 Building

DOW12329910

MN0697B9

CHLORACNE RESEARCH PROGRAM

History of Chloracne Incidences at Dow:

Historically, Dow Chemical has been involved in chloracne incidences ever since Dow began the production of chlorophenols. At first, the commercial production of chlorophenols was conducted at 206 Building. During the period 1934-36 there was a severe outbreak among the employees which resulted in an unsuccessful lawsuit. The chloracne incidents were traced back to poor working conditions and the manufacture of Dowicide P. The manufacture of Dowicide P has since been terminated. New and improved working facilities for the Dowicide group were constructed at 265 Building in 1940.

Na SALTS OF Dow. 3 + Dow. 6

In the late 1930's, Wes Stoesser in 20A lab got a serious chloracne attack from chlorinated diphenylene oxide. Drastic treatments were used to cure this incident and no further work was done on this series of compounds. It is suspected that many of the other incidences of chloracne are caused by chlorinated diphenylene oxides or analogues thereof.

In the next ten years, another unfortunate situation occurred in the chloracne situation. Some of the Dow customers complained about dermatitis and/or chloracne from the use of Dow's Dowicide 3. I understand financial adjustments were made and the production of Dowicide 3 terminated. A purified material of related structure is now sold as Dowicide 31 and 32.

Dow 31 + MONO CHLORO-PHENOL

During the period 1940-65, the product 6X (diphenyl oxide chlorinated to the hexa level) was manufactured at 206 Building and at least one severe case of chloracne occurred because of this product. The production of 6X has been terminated.

In the research lab at 172 Building, there were some cases of chloracne from research exposures. In one case, a severe case resulted from the recycling of residues from the manufacture of 2,4,5-trichlorophenol using glycol as a solvent. In another case, several mild cases occurred hydrolyzing polychlorobenzenes using aqueous caustic at high temperature. The Chemical Physics Lab had several incidences of chloracne from the recycling of caustic insolubles in the alcoholic caustic hydrolysis of tetrachlorobenzene.

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In 1963, the 2,4,5-trichlorophenol hydrolysis step at 199 Building was modified for economy and safety reasons from the use of 100% caustic to 23% caustic. The rabbit test for chloracnigens in the caustic insolubles obtained from a pilot run at this time indicated that the test response for chloracnigens showed no difference between caustic insolubles obtained by either procedure. During the latter part of 1963, the production department, in order to increase capacity, raised the reaction temperature and increased the throughput. This meant that more caustic insolubles were produced, and more Dempster loadings had to be made. This meant that employees had more exposures to the caustic insolubles, and the caustic insolubles due to the higher temperature had larger concentrations of chloracnigens. Thus the higher concentration of chloracnigens and the more frequent exposure caused many mild incidences of chloracne in 199 Building and two severe cases (LTI's) In 1966, a new process (Boehringer) was put into operation using a batch reactor at low temperature, and so far has operated satisfactorily.

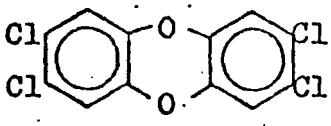
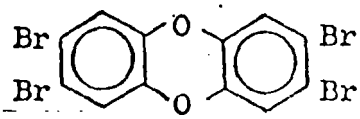
After they started up their Dowicide plant, the Canadians began to experience chloracne incidences in their employees. In Midland, more than half of the Dowicide employees have chloracne of varying intensity and it is impossible to say when or where these incidences occurred.

Research Program in Progress for Chloracne Reduction:

Because of the prevailing existence of chloracne in the Dowicide plants and a sincere desire to reduce or eliminate this, research has been initiated in 1966 on this problem. Progress has been slow due to the complexity of the problem. The problem involves isolation and determination of the identity of the chloracnigens. After being properly identified, work can progress on its reduction or elimination in the process.

In commenting on chloracne, we must keep in mind that chloracne is a cosmetic evidence of the attack and serious liver damage. is an invisible effect of the attack. Rabbit ear tests are a positive sensitive method of determining the chloracne activity of chlorophenol impurities.

Present Knowledge of Chloracnigens:

Compound	Activity
	2,3,7,8 Tetrachloro - Very positive Cl_{1-3} - Not active Cl_{5-7} - Possibly some cpds. active Cl_8 - Not active
	Very active

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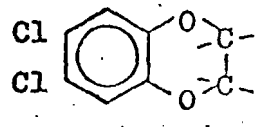
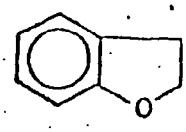
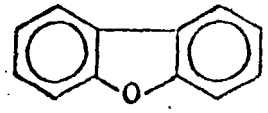
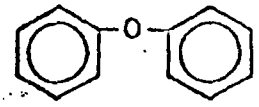
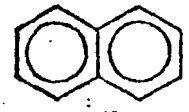
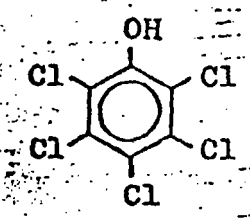
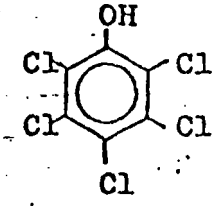
Compound	Activity
	Very active
	Cl_{1-X} - Unknown activity
	Cl_{1-2} - Unknown activity Cl_{3-6} - Some very active
	Cl_{4-6} - Some activity?
	Cl_3 + - Some activity

Materials possessing unexplained chloracne activity:



Some Midland batches are mildly reactive

Many Canadian batches are mildl reactive



$\xrightarrow{NaOH}$ Dowicide G

All sludges are active

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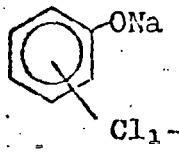
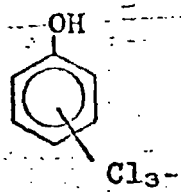
Compound	Activity
	All decompositions are active
	Some have activity

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Midland Research Program on Chloracne:

The following chloracne activity fractions are being examined for isolation, identification, and minimization of chloracne activity. Unfortunately, due to shortage of technical help, the program is proceeding quite slowly.

1. Dichlorophenol still residue.
2. Pentachlorophenol process samples.
   a. Dowicide 6 and 7 "active" batches.
   b. Dowicide G sludge.
   c. Dowicide G scrubber sludge.

The method of research is to first concentrate the sample (remove chlorophenols); then fractionate by chromatography; test fraction on rabbits, then further fractionate by chromatography, then test fraction on rabbits; etc., then determine structure by micro analysis; then determine method of analysis in original sample; and then investigate process changes which will minimize the chloracnigens in the process.

The Benzene Research Lab and the Biochem Research Lab are collaborating in this project. The Benzene Research Lab does the chemical research and the Biochem Research Lab does the testing on the rabbits on their charge.

Alex Widiger

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Benzene Research Laboratory
474 Building

je

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E. C. Staehling, 258 Bldg.
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R & D REPORT

DOW CHEMICAL U.S.A.

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CRI NUMBER

LABORATORY REPORT CODE: OC/78-85

DATE ISSUED: October 27, 1978

DEPARTMENT: ORGANIC CHEMICALS RESEARCH

LAB. NO. | PROBLEM NO.: 0 5 0 9 0 0 0 0 0 0

TITLE: A STUDY OF THE FORMATION AND REMOVAL OF IMPURITIES IN THE SEMI-HYDROUS PROCESS FOR 2,4-D

57 PAGES IN FUL REPOR

AUTHOR(S): K. L. Krumel & R. F. Arnold

AUTHOR(S) SIGNATURE(S): Karl L. Krumel R.F. Arnold (by KLK)

REVIEWER'S SIGNATURE: Peter W. Owen

This report is: [X] INTERIM [ ] FINAL and mainly: [X] NEW [ ] REVIEW

CRI NUMBER

DESCRIPTIVE SUMMARY WITH CONCLUSIONS: (Include in this space references to data books, and to earlier related reports, patents and publications.)

Shortly after the startup of the new 2,4-D process in 948 Building, a new and unexpected class of nonacidic impurities were isolated in which two of the major components were tetrachloroxanthone and octachlorospirobixanthene. These impurities were causing problems in the subsequent formulation of 2,4-D as amine salts.

A project was started to learn the source of these impurities and methods for controlling them. It was found that the impurities are formed mainly in the 2,4-D reaction step by several different routes and that the rate of formation is increased by increased caustic ratios, perchloroethylene, heat and iron.

A number of techniques were evaluated for removing the impurities including carbon treatment, recrystallization, bleaching, varying reaction conditions, and improved washing. None of the treatments were totally successful.

In the plant, the impurities tend to concentrate in the recirculating perchloroethylene system. It has been found that by increasing the capacity of the perchloroethylene distillation column from 0.7 to 15 gpm, the steady state concentration of impurities is reduced to where they do not adversely affect general product quality or the ability of the plant to operate at optimum rates.

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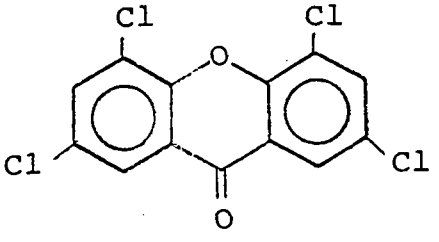
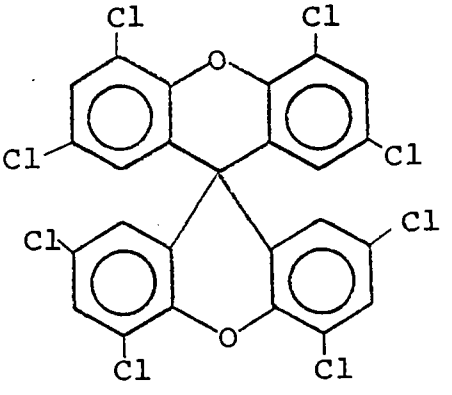
DOW 267736

INTRODUCTION

A new process for preparing high purity 2,4-D was started in May 1977 at 948 Building. The high purity molten acid is transferred by pipeline from 948 Building to 489 Building where it is formulated into esters and water soluble amine salts. Starting in late October 1977, precipitates were observed regularly in diluted amines formulations that were found to be made up of a number of impurities associated with the process but that were never detected during laboratory or pilot plant development work. In addition, these impurities were not found in the old 489 Building aqueous 2,4-D process. R. McLachlan[1] analyzed the precipitates and found 1,3,6,8-tetrachloroxanthone (I: TCX), 1,1'3,3'6,6'8,8'-octachloro-9,9'-spirobixanthene (II: OCSX), and marginally soluble salts of 2,4-D.



(I)



(II)

A screening program in the plant showed TCX at levels of 200-500 ppm in the crude reaction mass, the recycle sodium dichlorophenate (NaDCP) solution, and in the final product. Levels of 1000-2000 ppm were found in the perchloroethylene (Perc) solvent and as much as 10% in the perc still tars.

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McLachlan[1] analyzed a sample of perc still tars and his results are summarized in Table 1.

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Table 1: An Analysis of One Perc Tar Sample

Structure	Approximate Percentage	Comment
Perc	60%	Main Component
Diethylbenzene	25%	From a heat exchanger leak (Dowtherm J)
DCP	0.5%	raw material
2,4-D	0.01%	Product
TCX (I)	1.5%	
OCSX (II)	1.1%	
Dichlorophenyl-dichlorovinyl ether	1.2%	Rxn product of NaDCP & perc & its impurities
Dichlorophenyl-trichlorovinyl ether	0.8%	

Plus:

at least eleven other minor components structurally similar to the above. See Ref. 1 for details.

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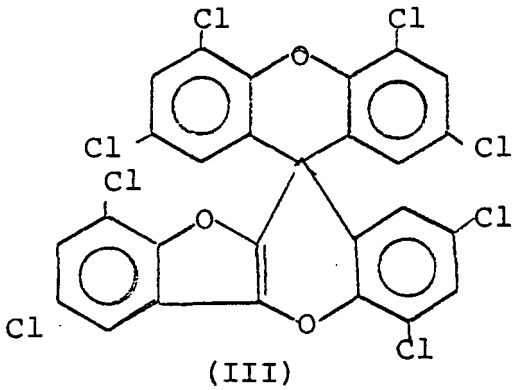
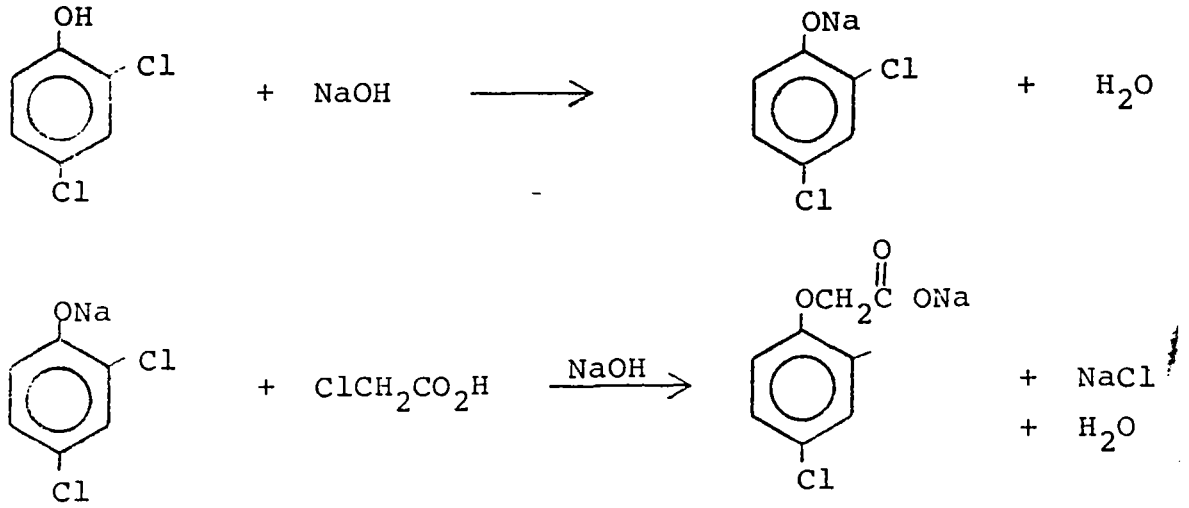
A project was started to study the formation of TCX and OCSX in some detail to learn more about their formation and fate in the process because it is not obvious how they are made. Several months after starting this study, another significant impurity was found in the product and, to a lesser extent, in the perc tars. It was identified as (III: "8-5") 2,2',4,4',5',7,7',9-octachlorospiro-(benzofuro(3,2-b)-benzopyran-11,9'-xanthene).



(III)

A description of the 2,4-D process in 948 Building is as follows:

Main Reactions



Na 2,4-D

Important Side Reactions

$$ClCH_2CO_2Na + NaOH \longrightarrow HOCH_2CO_2Na + NaCl$$

Glycolic Acid

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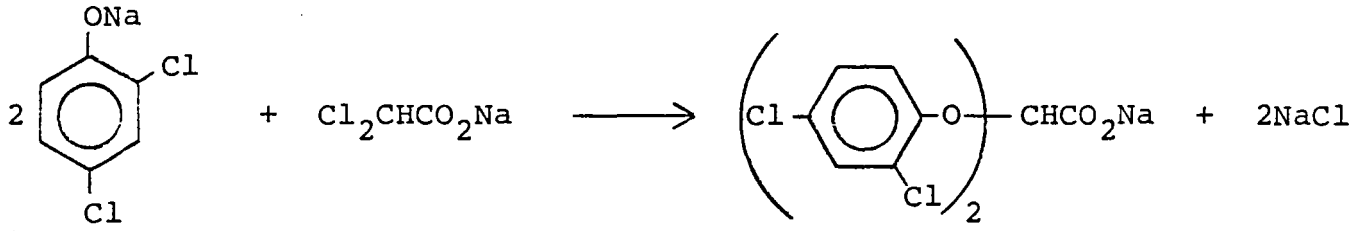

"Bis 2,4-D"

The reaction is performed in two stages by first reacting 2.2 moles of DCP with 1.2 moles of caustic (added as 50% NaOH) to form a solution of NaDCP in DCP.

High purity 2,4-dichlorophenol (2,4-DCP) made by the chlorination of phenol with sulfuryl chloride in the presence of $FeCl_3$/Diphenyl sulfide catalyst is used with chloroacetic acid (MCAA) made by the oxidation of vinylidine chloride to make 2,4-D as shown above. The typical raw materials analyses for each is shown in Table 2.

Table 2: Typical Raw Material Analyses for the 2,4-D Process

	DCP		MCAA
2,4-DCP	98.5%	MCAA	99.0%
2,6-DCP	∿0.8%	Dichloroacetic acid	0.3%
Other Chlorophenols	∿0.5%	Chloromaleic acid	∿0.05%
		H_2O	<1.0%

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The solution is then boiled down to remove most of the water. Then, 1.0 moles of NaOH (added as 50% NaOH) and 1.0 moles of MCAA are added to the solution at 130° and the water formed is continuously boiled off. The crude product, whose approximate analysis is shown below, is transferred to a storage tank that feeds the continuous purification equipment.

DOW 267740

Approximate 2,4-D Crude Product Analysis

Na 2,4-D	45%
Na DCP	10%
DCP	30%
NaCl	12%
H_2O	3%

The 2,4-D is purified by partial acidification to selectively neutralize the DCP, extraction with Perc to remove the DCP, and then final acidification to liberate molten 2,4-D which is decanted from the brine and washed with water. A schematic flow sheet of the process is shown below.

A rapid initial screening of the toxicity of purified TCX and perc tars gave the following results.

	Oral LD_{50} (single dose)	Skin/Eye
Perc Tar (contains 3-5% TCX + OCSX)	>5g/Kg	slight transient initiation. Chloracne response after 10 applications of neat tars.
Purified TCX	>4g/Kg	not irritating. Chloracne response after 10 applications of 1% solution in $CHCl_3$.

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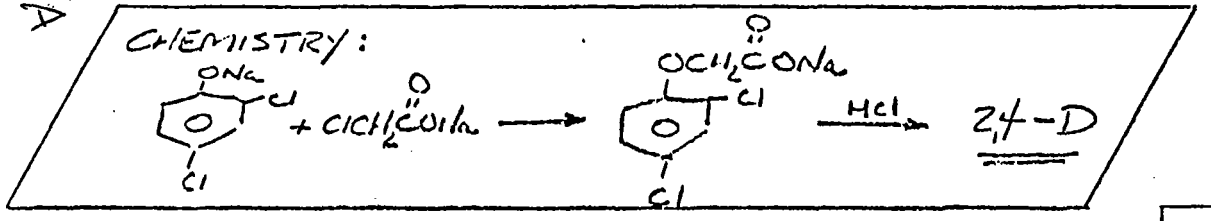
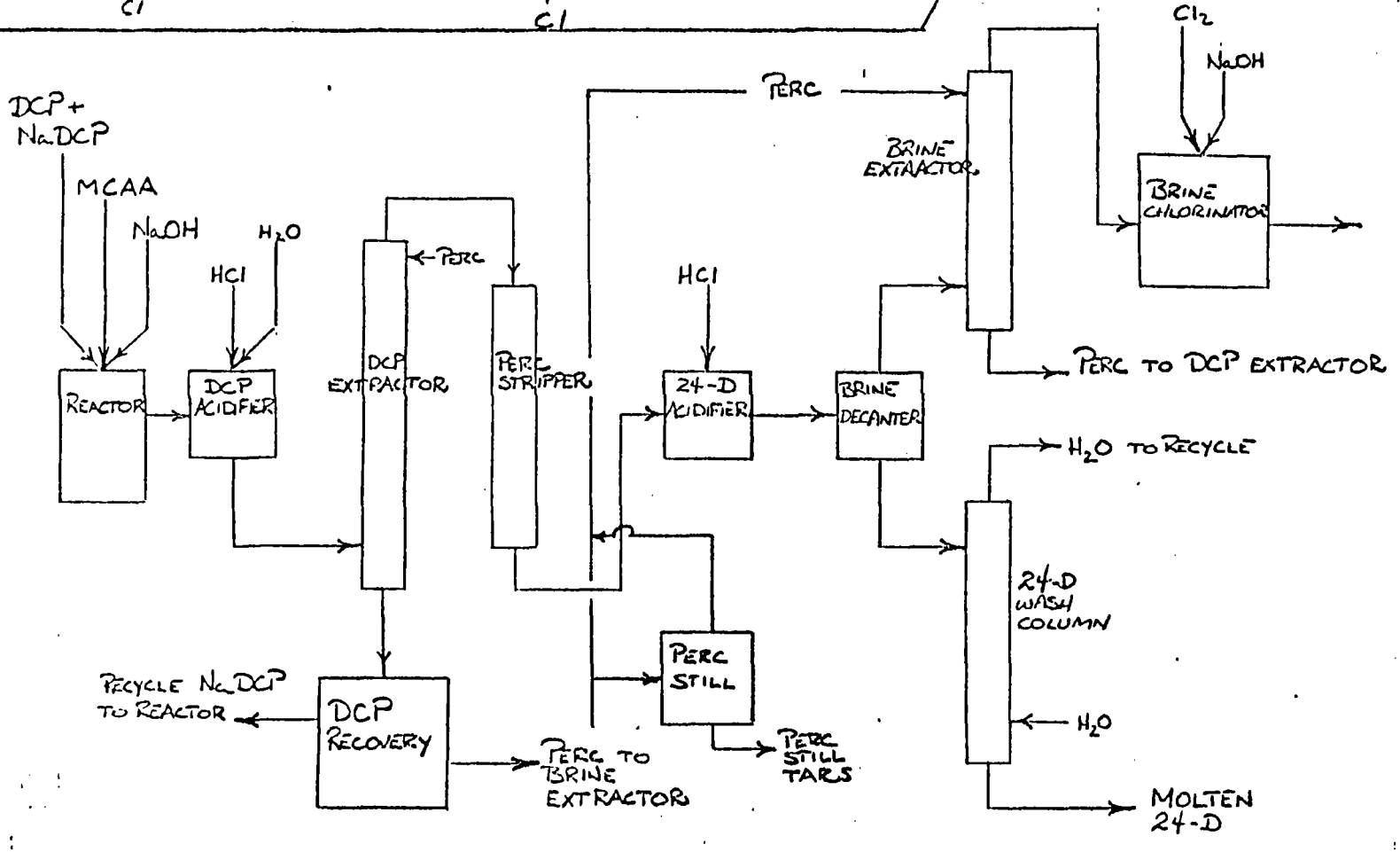


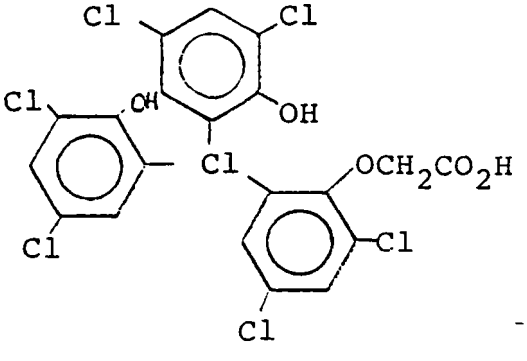


2,4-D PROCESS

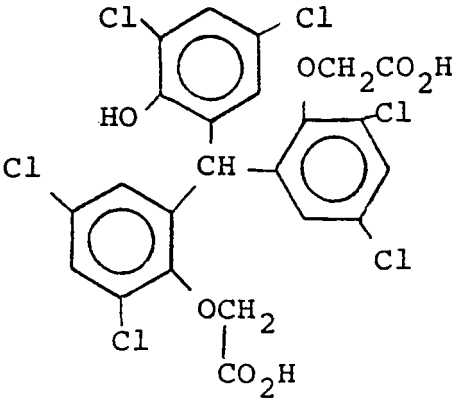
DOW 2677742

These results are encouraging from a plant hygiene standpoint, but more data is necessary regarding long term effects. When the impurities were first discovered in the plant, the perchloroethylene still was used very occasionally and at a rate of <1 gpm vs a total perc flow of 40 gpm. The still was originally added to the process as a way of purging contaminants out of the stream to maintain high quality recycle solvent. At this point, perc tar impurities made up 60-75% of the precipitates formed in diluted amines formulations.

About February 1978, the capacity of the perc still was increased to 3 gpm and the average levels of TCX levels dropped to ~50 ppm in the crude reaction mass and product and to 200-500 ppm in the recycled perc. From the period of March-May 1978, the ability to produce quality 2,4-D continued to improve and the amount of perc tar impurities found in the dilution test precipitates dropped to 10% of the total[3]. The balance were sparingly soluble metal salts of 2,4-D and some new impurities called Complex 1 and Complex 2, two of which are shown below (IV & V).



IV



V

In July 1978, the perc still capacity was increased to 15 gpm and efforts gained at understanding the parameters affecting formulation quality by S. Siegel (OCR), S. Schell (Production 489), and J. King (Formulation - 9001 Bldg) and their co-workers have greatly improved

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DOW 2677743

the consistency with which 948 Bldg. 2,4-D can be formulated. Based upon partition coefficients and data on the rate of formation of TCX to be discussed later in this report, K. E. First[4] (Process Engineering) generated a computer program which predicted that by distilling 15 gpm of recycle perc, the steady state level of TCX in the product would be ∿10 ppm and in the recycled perc the TCX level would be ∿40 ppm.

The purpose of this report is to present data on the formation and fate of the impurities in the 2,4-D process. In addition, the results of experiments aimed at reducing or eliminating the impurities by chemical and physical methods will be presented.

RESULTS AND DISCUSSION

This study was divided into the following sections and the results of each are discussed separately.

(A) The mechanism of TCX formation.
(B) The distribution of TCX in the process.
(C) Reduction of TCX by chemical means.
(D) Reduction of TCX by physical means.

Although there are many impurities formed in this process, it was decided to focus the research on TCX for several reasons: (1) The rate and mode of formation of TCX was the most predicable of the major multicyclic impurities; (2) it was a major impurity; (3) a pure sample was readily obtained (by D. Humbert, Anal. Lab); (4) the analysis is not complicated; and; (5) structurally, it is the simplest of the multicyclic impurities.

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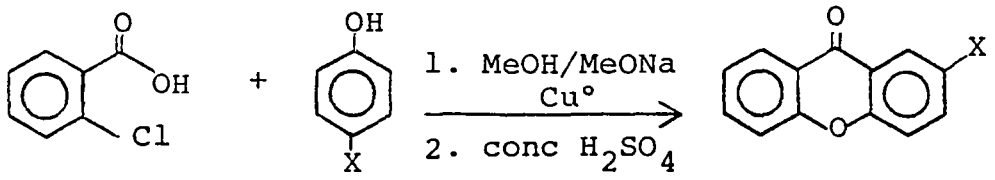
(A) The Mechanism of TCX Formation

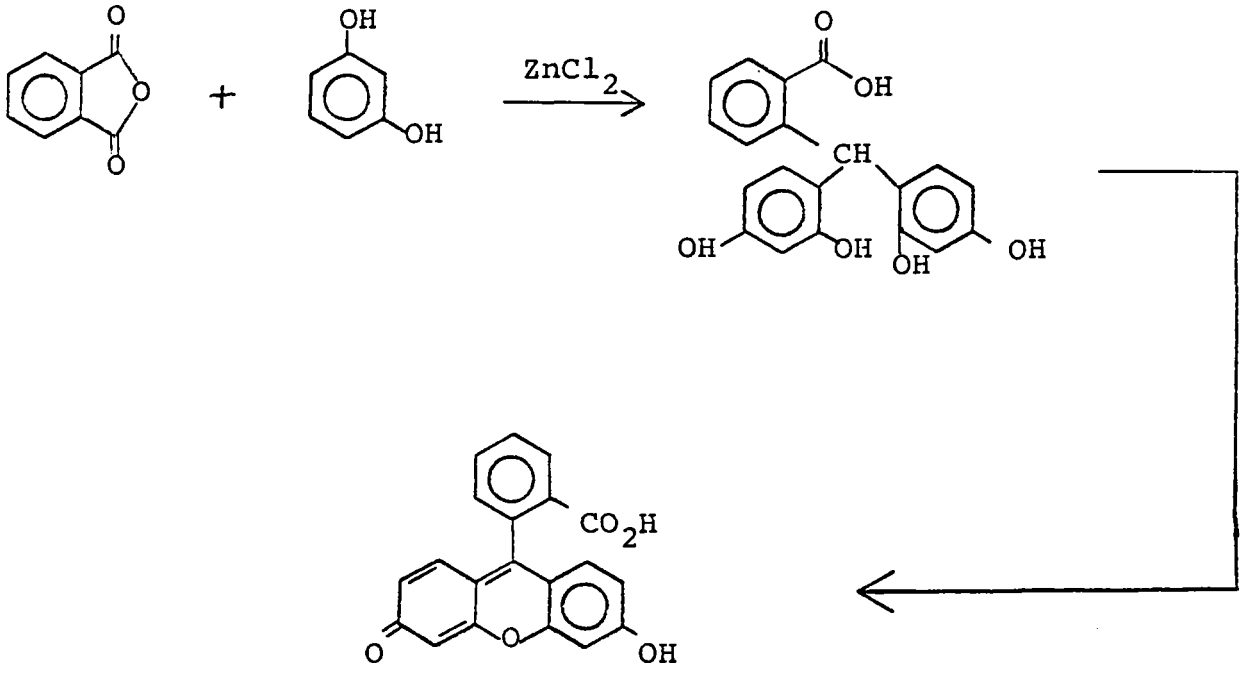
A brief search of the literature including Chemical Abstracts showed that the xanthone ring system is formed from a number of reactions.[5] A common synthetic reaction is shown below in which the -X is included



to show the orientation of reaction. Xanthone is formed along with other products from the pyrolysis of o-chlorobenzoic acid, salicylic acid, aspirin, o-phenoxybenzoic acid, and salts of the carboxylic acids. Most of these cyclizations take place in the presence of acidic catalysts such as P_2O_5, $AlCl_3$, Acetic anhydride, or sulfuric acid. Xanthone is prepared in reasonable yield[6] by the pyrolysis of phenol salicylate with or without a catalyst.

The ease of formation of ring systems that are structurally similar to xanthones is most clearly shown by the formation of fluorescein and fluorescein dyes. Fluorescein[7] is made by reaction of phthalic anhydride and resorcinol as shown on the following page.

DOW 2677745



Phenolphthalein[8] is also made by this process using phenol instead of resorcinol.

71A
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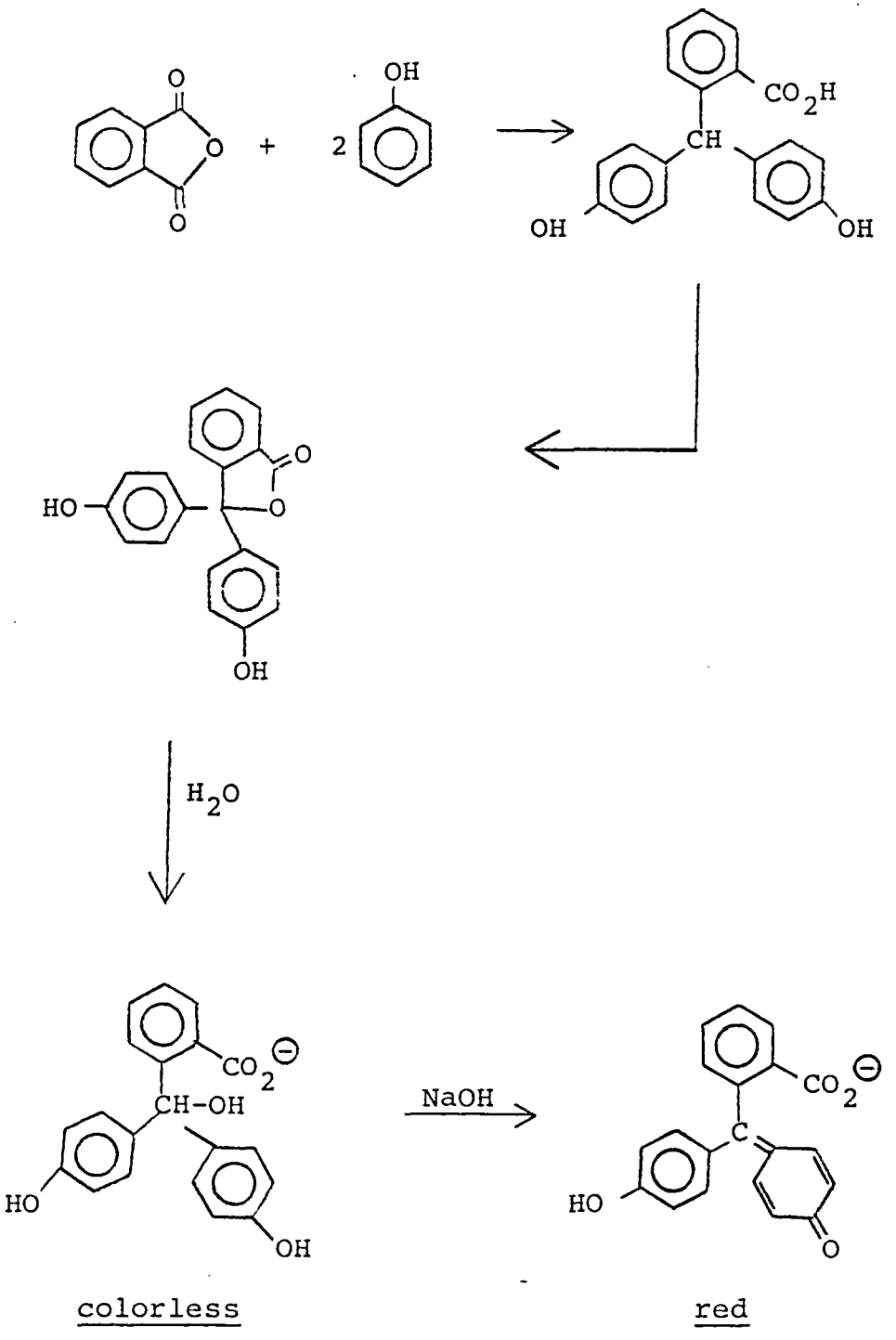

colorless red

These background data give some important clues as to reaction mechanisms as will be whown later in the report.

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In order to understand the pathway of TCX formation, a series of ampoule tests were performed to determine which chemicals and/or combinations give rise to TCX. Table 3 summarizes the results of this study. A series of ampoules (25 ml capacity) were charged with 3-6 gms of mixtures in molar ratios as shown inTable 3 and were heated in an oil bath fo 72 hours at 160°C. The sources of the chemicals were as follows:

2,4-D: High Purity Rhone-Progil Acid
DCP : Doubly distilled 948 Bldg material
Perc :
NaOH :
Glyoxal :
Glyoxylic acid :
Tetrachloroethane :
(50:50 1,1,2,2- & 1,1,1,2-isomers)

} Reagent materia

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Run #	Molar Ratio						rpm TCX
	2,4-D	DCP	NaOH	Perc	Bis 2,4-D	Other	
1	1.0						N.D.
2	1.0	1.0					N.D.
3	1.0		1.0				N.D.
4	1.0		2.0				N.D.
5		1.0	1.0				N.D.
6					1.0		N.D.
7	1.0	1.2	1.16				8(
8	1.0	1.4	1.16				28:
9	1.0	1.2	1.16	0.06			244
10		1.0	0.26	0.25			245
11	1.0	1.2	1.16			TCE mixture*: 0.11	218
12			1.15		1.0		127
13		4.7	1.5		1.0		189:
14	1.0		1.0			NaCl:1.5, H_2O: 26.0	-ND-
15		1.0	0.16			3,5-dichlorosalicylic acid: 0.16	109
16		1.0				" "	N.D.
17		1.0	0.26			Glyoxal: 0.26	104
18		1.0	0.26			Glyoxylic Acid: 0.55	211

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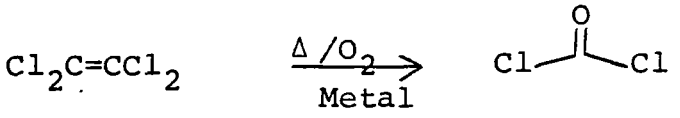
*TCE Mixture: 50:50 Mixture of 1,1,1,2- & 1,1,2,2-Tetrachloroethane

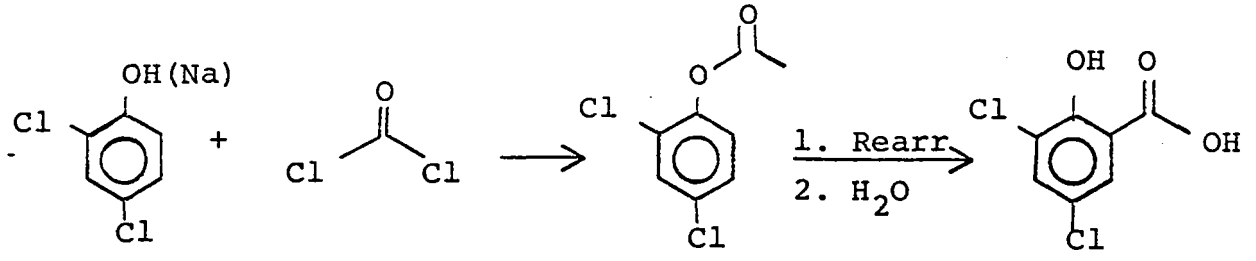
Table 3: The Formation of TCX from Synthetic Mixtures Heated at 160° for 72 hrs.

D-77

Several compounds other than those found in the process were tested. The tetrachloroethane mixture is a known contaminant in tne 941 Bldg. chloroacetylchloride that is used to make MCAA. 2,5-Dichlorosalicylic acid is a proposed intermediate from the reactions suggested below:

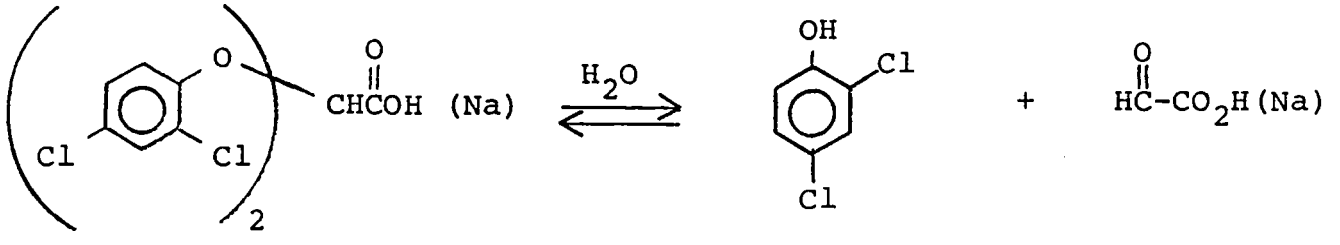
DOW 2677749





The decomposition of perc to yield phosgene is known[9] but the second reaction is only speculated.

The glyoxylic acid is postulated to come from bis 2,4-D as shown below:



which is a well known acetal hydrolysis. The glyoxal was included to show the general nature of the reaction whose mechanism is suggested later in this report.

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Several tentative conclusions can be made from the data in Table 3.

(a) TCX can be made by several routes
- NaOH and/or NaDCP is necessary for the formation of TCX.
- bis-2,4-D appears to be a key intermediate.
- Perc is a source of TCX.

(b) Significant amounts of TCX are probably made only in the reactor crude storage tank in the plant since strong base is required. Run 14 (Table 3) simulates the Na 2,4-D storage tank (V-501: 948 Bldg) and Run 1 (Table 3) simulates the product storage tank (V-602: 948 Bldg) in which no TCX was observed.

In order to study the formation of TCX as a function of reaction parameters, a series of 2,4-D reactions were performed in the laboratory. These reactions were run to evaluate the effect of different raw materials, perc, air/N_2, and iron on the amount and rate of TCX formation. The data are summarized in Table 4. In these experiments, 1.1 mol of DCP was treated wth 0.6 mol of caustic and the mixture was heated to 130°C. The majority of the water that was formed was boiled off. To this mixture, 0.5 mol of NaOH and 0.5 mol of MCAA were con-added during 1 hr at 130° and the crude product was heated an additional 1 hr. Water was continuously distilled out during the con add step. At this point the desired number of ampoules were charged with 5-10 gms of crude reaction mixture and were heated in oil baths at 130°, 145°, and/or 160° for 24, 48, and 72 hours.

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Table 4: The Parameters Affecting the Formation of TCX in the Semi-Hydrous Process for Preparing 2,4-D

Run / Reference	Raw Material Source DCP	MCAA	% DCAA in MCAA	Mol DCP / Mol MCAA Ratio	Air or N_2 Purge	% Added Feed	Stirrer Speed ft^{-3}	Heat-Age Tests in Ampoules — Ppm of TCX at Time: Test Temp. (°C)	Initial	24 hrs	48 hrs	72 hrs	Comments
1/ OC 417-5-130	Dow 948 Bldg	Dow	0.4	1.2	Air	–	–	130	N.D.	TR	23	32	
								145	N.D.	22	48	110	
								160	14	125	234	280	
2/ OC 417-5-118	Dow 948 Bldg	Dow	0.4	1.2	Air	1.1%	–	130	ND	13	29	49	
								145	TR	32	83	127	
								160	6	86	132	230	
3/ OC 417-5-120	Dow 948 Bldg	Dow	0.4	1.2	N_2	1.1%		130	ND	TR	17	18	
								145	ND	20	59	104	
								160	TR	56	111	160	
4/ OC 417-5-125	Dow 948 Bldg	Hoechst	0.2	1.2	Air	–	–	130	ND	8	12	13	
								145	ND	24	–	39	
								160	ND	52	93	94	
5/ OC 417-5-135	Dow 948 Bldg	Hoechst	0.2	1.2	Air	1.1%	–	130	–	14	22	53	
								145	–	24	58	96	
								160	–	49	96	144	
6/ OC 417-5-137	Dow 349 Bldg	Hoechst	0.2	1.2	Air	–	–	160	N.D.	49	91	–	DCP from the old Dow process Direct chlorination; lower assay
7/ OC 417-5-135	Dow 948 Bldg	Hoechst	0.2	1.0	Air	–	–	160	N.D.	TR	52	125*	*After 96 hrs heating
8/ OC 415-5-131	Dow 948 Bldg	Dow Technical Grade DCAA	10%	1.2	Air	–	–	160	ND	167	487	575	Spiked MCAA with DCAA
9/ OC 640-10	Dow 948 Bldg	High Purity	N.D.	1.2	Air	–	–	160	–	12	41	56	
10/ OC 640-68	Dow 948 Bldg	Dow	0.4	1.2	Air & CO_2	–	–	130	5	7	12	29 *	*After 120 hrs heating. Initial reactor was spiked with 20 mol% $NaHCO_3$ & purged with CO_2 during post reaction
								160	–	81	219	444 *	
11/ OC 640-64	Dow 948 Bldg	Dow	0.4	1.2	Air	–	500	130	6	16	30	75	
								160	–	241	766	1002	
12/ OC 640-66	Dow 948 Bldg	Dow	0.4	1.2	Air	1.1%	500	130	ND	9	28	42	
								160	–	177	555	908	
13/ OC 640-67	Dow 948 Bldg	Dow	0.4	1.2	Air	–	200	130	9	14	37	126 *	*After 120 hrs heating
								160	–	273	365	932 *	
14/ OC 640-73	Dow 948 Bldg	Dow	0.4	1.2	Air	–	25	160	5	61	273	394	

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The data in Table 4 show a number of interesting points. It must be emphasized that in view of the fact that these data are based on parts-per-million chemistry, the precision must be subject to some error. The data are reproducible to about 20%.

DOW 267752

(A) Effect of Dichloroacetic Acid in MCAA

Runs 1,4,8, and 9 show that DCAA affects TCX formation presumably through the formation and decomposition of bis-2,4-D. Run 9 was especially interesting because not only was TCX made but bis 2,4-D was observed as shown below:

	Hrs at 160°C		
	24	48	72
ppm TCX	12	41	56
% Bis	0.4	0.3	0.2

These data indicate there is another route to bis-2,4-D besides reaction of NaDCP with dichloroacetic acid since the monochloroacetic acid used in this experiment showed no detectable DCAA (< 100 ppm) by liquid chromatography.

(B) Effect of Perchloroethylene

Whereas Perc showed a significant increase in TCX levels in the ampoule experiments, its effect in the reactions is uncertain. In most of the runs, the reactions contaminated with perc showed more TCX at 130°C and similar amounts at 160°C.

K. E. First, Process Engineering,[4] ran a computer analysis of the data which gave the best fit when calculated as two consecutive first order reactions with an Ea = ∿30 Kcal/mol. In the presence of perc the Ea dropped to ∿15 Kcal/mol. These data suggest that there is another

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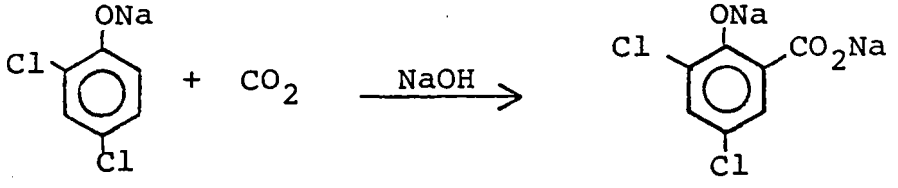
DOW 267753

more facile route to TCX from perc whose effect is masked at the higher temperatures by a primary route (compare Table 4, Runs 1 & 2 and Runs 3 & 4).

(C) Effect of Atmosphere in the Reactor

Nitrogen blanketing appears to lower the TCX level to ∿2/3 that observed in air. It is not certain that this result is significant and since the magnitude of the drop was low, further work was not warranted. Since CO_2 is known to be present[10] in the vapor space throughout the 2,4-D process, a run was made to determine its effect on TCX formation. Carbon dioxide comes into the process from the caustic and from perc decomposition.

The reaction was run as described earlier with 20 mol% of $NaHCO_3$ added before the boil down step and then blanketing the reaction mass with CO_2 during the post reaction heating step. Since this is a high temperature, nearly anhydrous process, the following reaction was thought possible which could eventually lead to TCX (See Table 3, Runs 15 and 16).



Comparing Runs 1 and 10 (Table 4) show that $NaHCO_3$ and/or CO_2 do not measurably affect the formation of TCX.

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(D) Changing NaDCP/NaMCAA Ratio

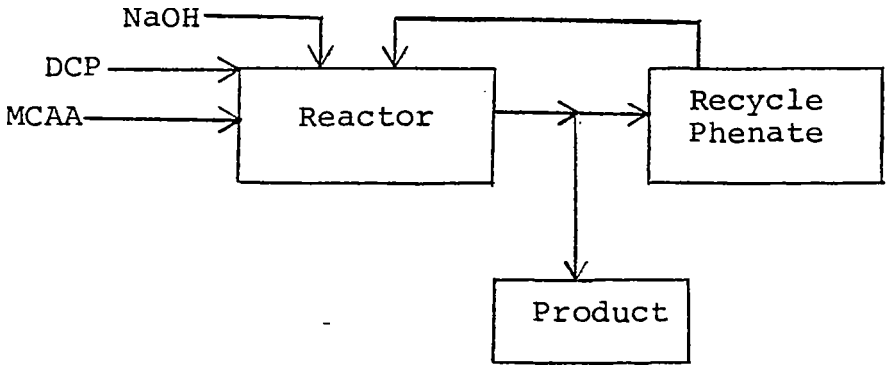
Comparing Runs 1 and 7 (Table 4) show that lowering the NaDCP/NaMCAA ratios significantly reduces the TCX levels as was also predicted from the data in Table 3. The effect was studied further and is discussed later in this report.

(E) Source of DCP

A run was made using the old lower purity DCP from the 349 Bldg process and assure that 948 Bldg, high purity, DCP was not a source of TCX. Run 6 shows that TCX formation is not associated with the source of DCP.

(F) Effect of Ferric Ion

Runs 11-14, Table 4, show that Fe^{+3} clearly increases the rate of TCX formation which suggest that alkylation step(s) are involved. D. Humbert and colleagues[7] performed a material balance of Fe in the following scheme.



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They found that most of the iron is entering the process in the caustic and that the reactor normally contains 20 ppm of Fe^{+3}. A recurring problem for the past several months was how to explain the fact that the plant observed TCX formation rates that were 5 times greater than the lab. The iron results explain at least part of this discrepancy and suggest that efforts aimed at removing iron from the process are desirable.

Based upon the data presented up to this point, the mechanism shown in Figure 1 for TCX formation is suggested. This mechanism is consistent with the observations of the effect of caustic, the fact that TCX can be made from NaDCP and glyoxal or glyoxylic acid and the levels of bis-2,4-D. If this mechanism is correct, it is easy to see how perc can influence TCX formation when one considers the possible hydrolysis products using either NaOH or NaDCP. Some of these possibilities are shown in Figure 2 and many are known precursors to TCX.

In addition to TCX, OCSX and "8-5" are known to be formed in measurable quantities during the reaction to 2,4-D. It was initially assumed that TCX is the probable precursor to OCSX and "8-5". However, a series of ampoule experiments in which TCX was mixed with various ratios of DCP, 2,4-D, NaOH, and perc showed none formed in detectable amounts. In addition, a reaction was run in the presence of 500 ppm of added TCX and gave normal levels of the impurities when the 500 ppm of added TCX is subtracted out. It is apparent that OCSX, "8-5", and TCX are probably made by independent routes and proposed mechanisms are shown in Figures 3 and 4.

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Figure 1: Proposed Mechanism of TCX Formation

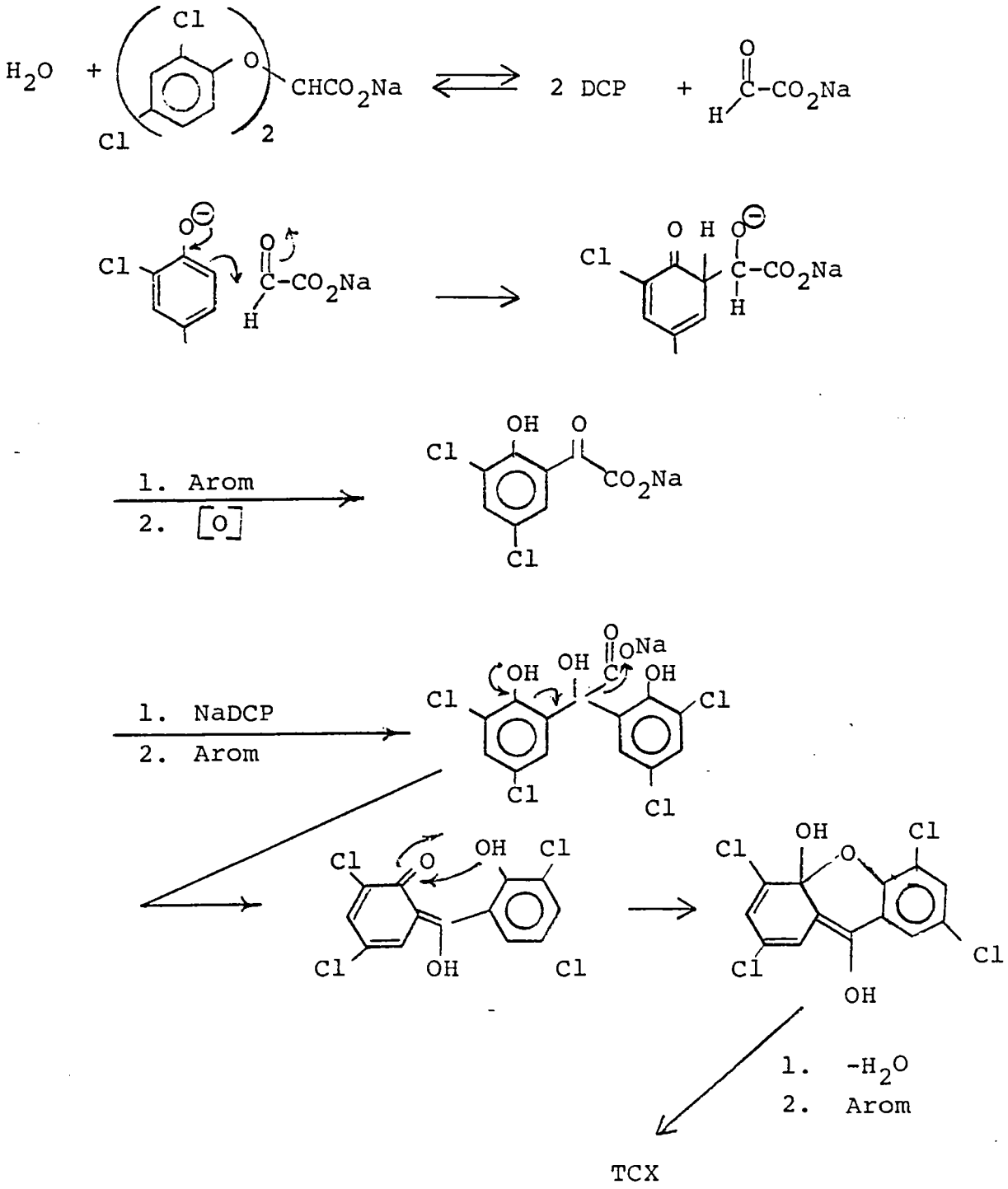

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Figure 2: Some of the Possible Products of the Hydrolysis of Perchloroethylene with NaOH or NaDCP

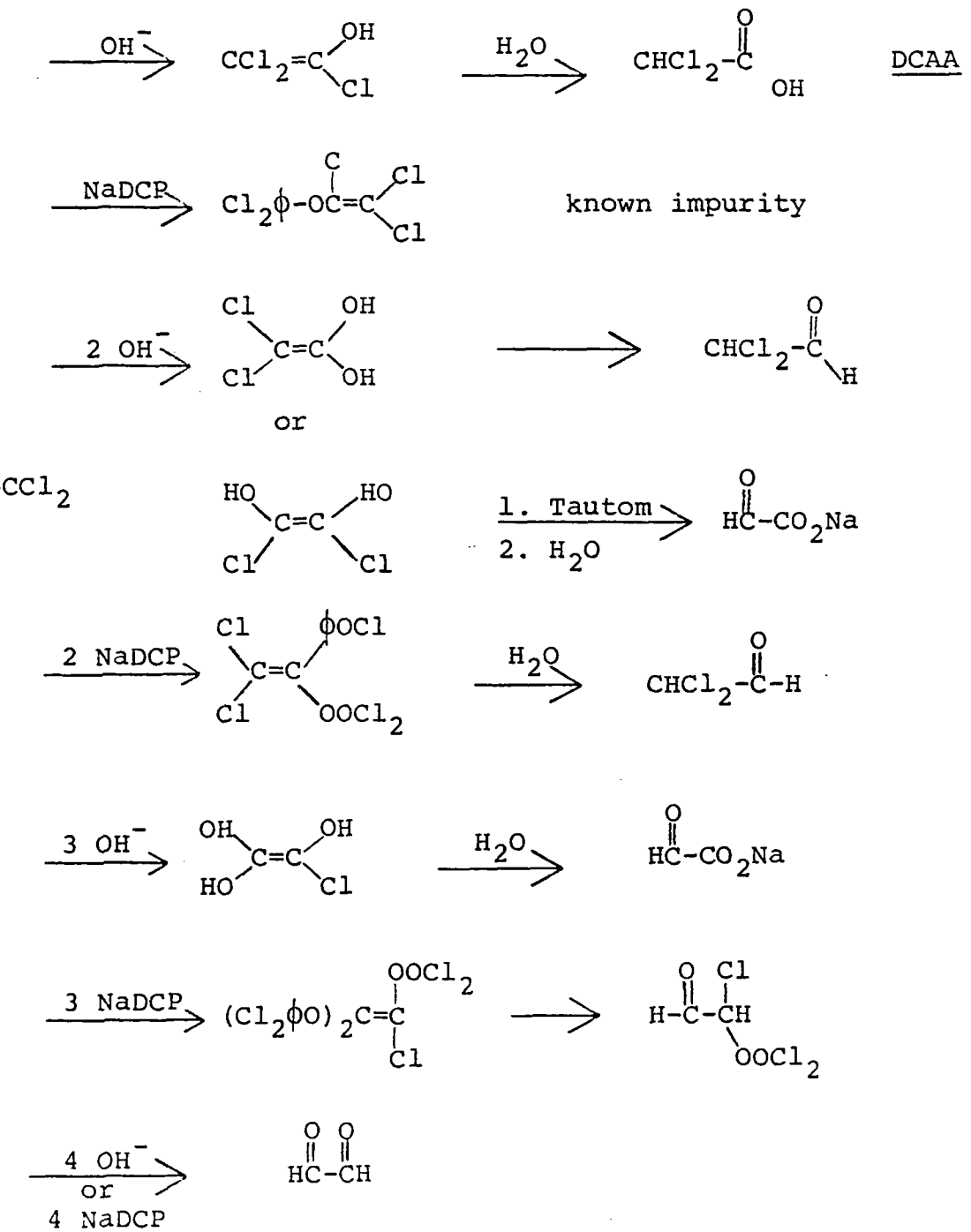

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Figure 3: Proposed Mechanism for the Formation of OCSX By a Route That is Independent of TCX

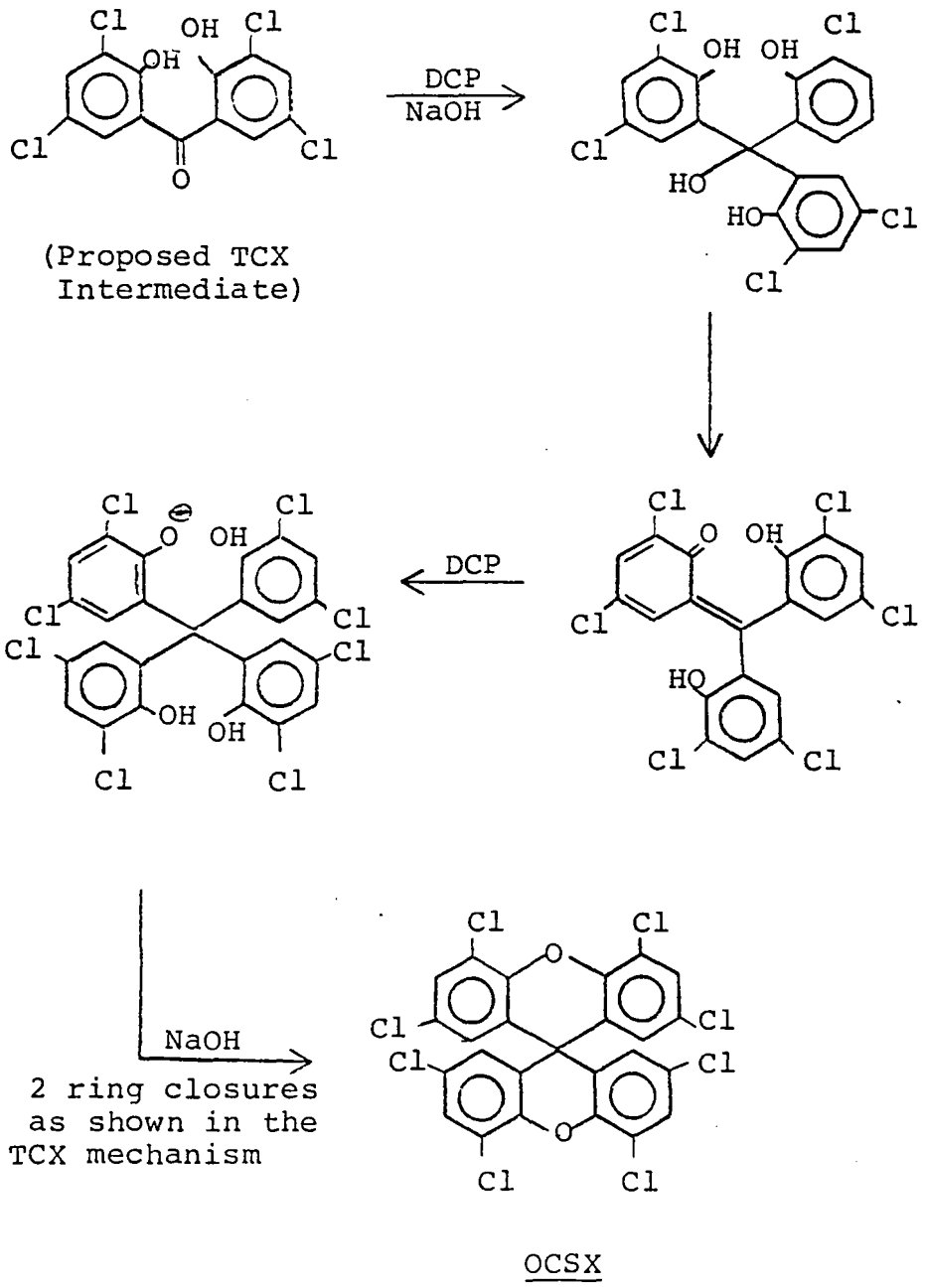

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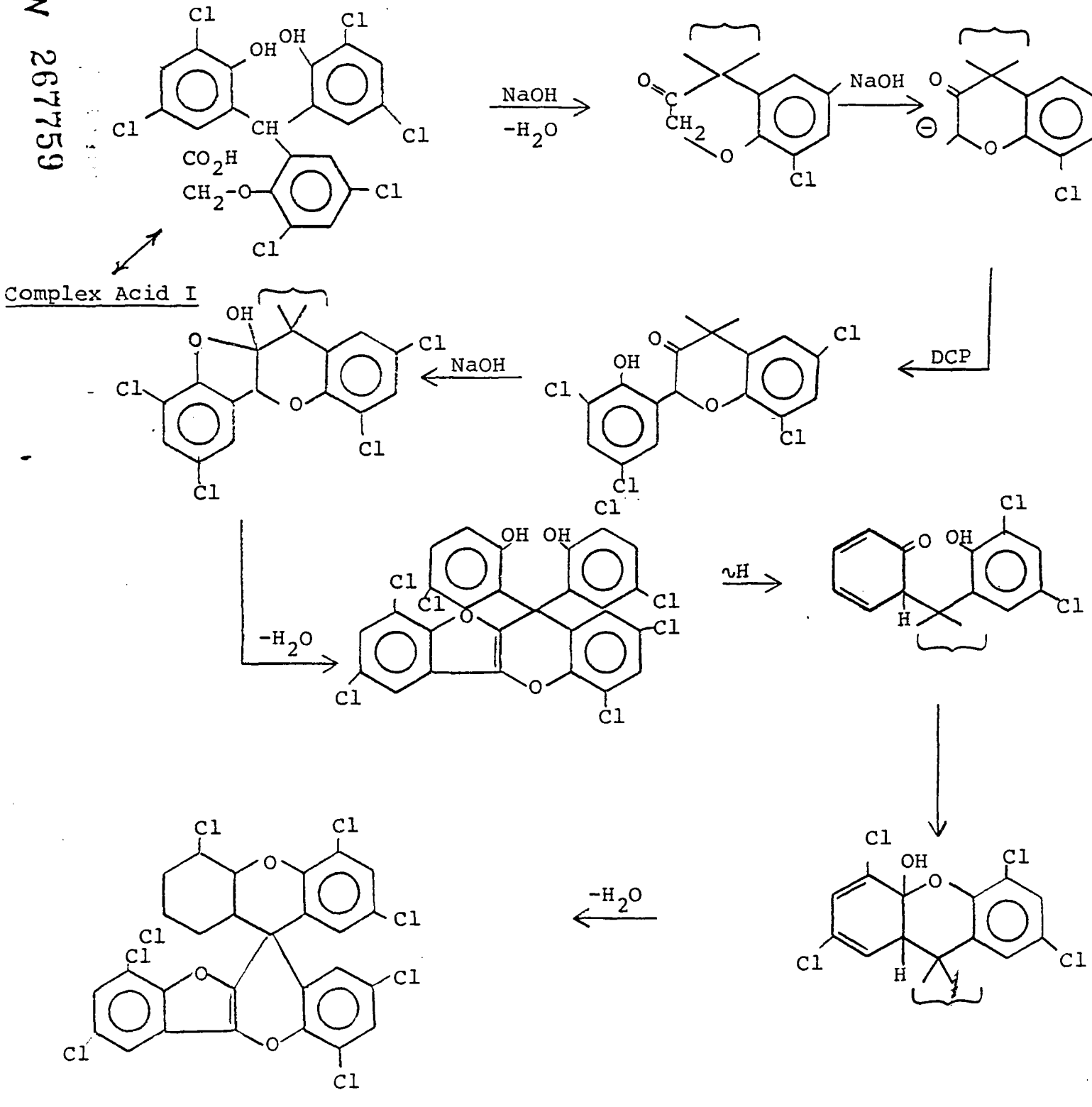
Figure 4: Proposed Mechanism for the Formation of "8-5" By a Route that is Independent of TCX



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The formation of OCSX uses an intermediate in the TCX mechanism as its starting material. The apparent fact that TCX is not an intermediate suggests that the more activated dihydroxy ketone is necessary for alkylation. The mechanism for "8-5" formation involves a major component in the Complex I and II mixture as a starting material. Recent analytical results[10] have shown ∿100-200 ppm of this mixture in the process. A proposed mechanism for the formation of Complex Acid I is shown in Figure 5. It must be emphasized that the mechanisms shown in Figures 3,4, and 5 are speculations and are only one of a number of possibilities. Much more work is necessary to prove their accuracy.

(B) The Distribution of TCX in the Process

As mentioned earlier, TCX appears to be formed only in the reactor section of the process. Each of the process hold tanks were tested using either synthetic mixtures and/or actual plant material under normal operating conditions and the results are shown below:

V-201 and V-202: Reactor & crude reactor hold tank. Tables 3&4 summarize these results.

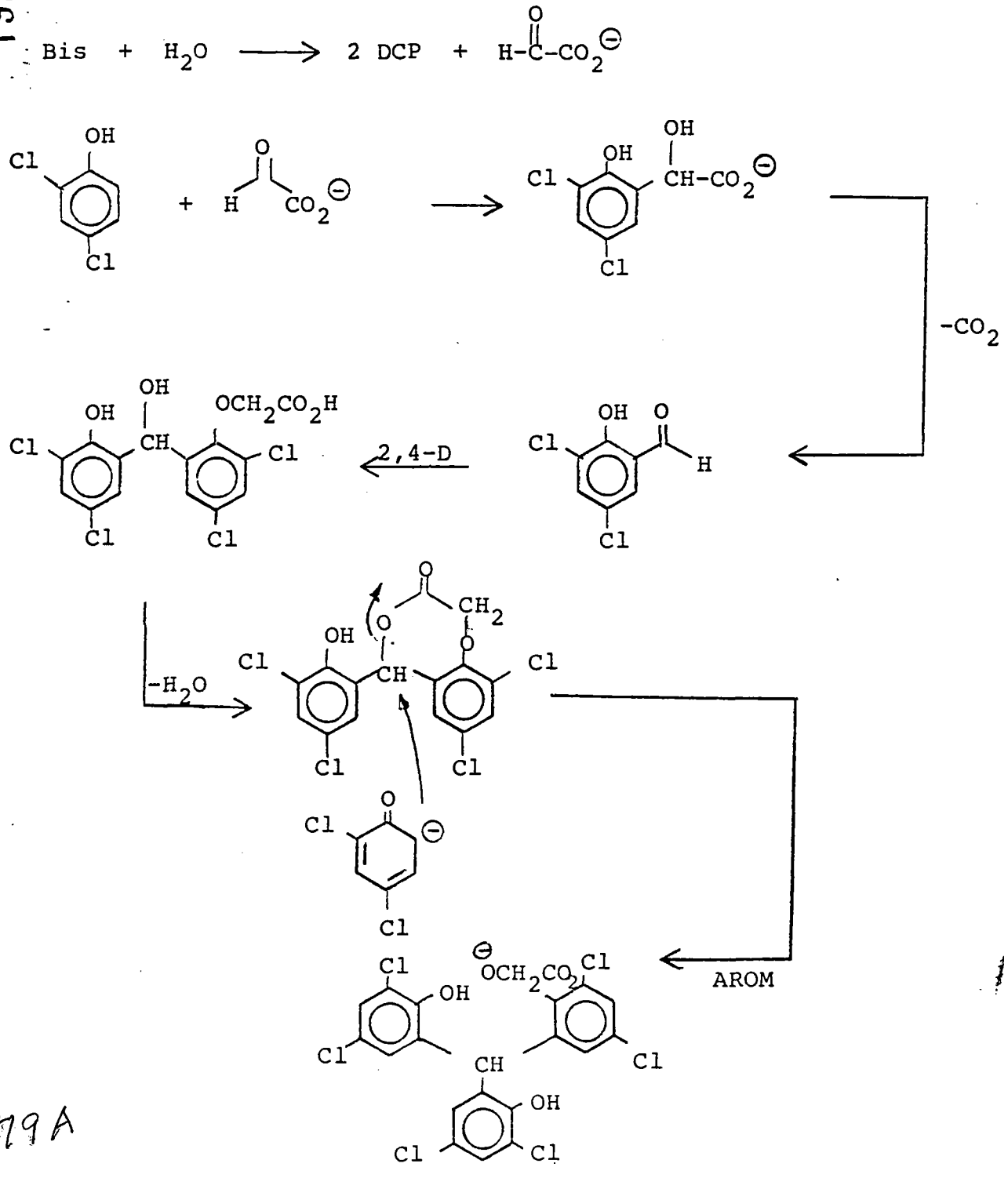
V-403: Phenate Recycle Storage Tank. 60% NaDCP was heated for up to 7 days in presence and absence of air in presence and absence of steel at 90°c and showed no detectable TCX.

V-501: Na 2,4-D Storage Tank
Mixtures of Na 2,4-D, NaCl & H_2O were heated at 145-160° for 3 days in presence and absence of traces of perc and DCP: no detectable TCX was formed.

D-84

DOW 267761

Figure 5: Proposed Mechanism for the Formation of the Major Impurity in Complex I mixture (Compound IV)



COMPLEX ACID I

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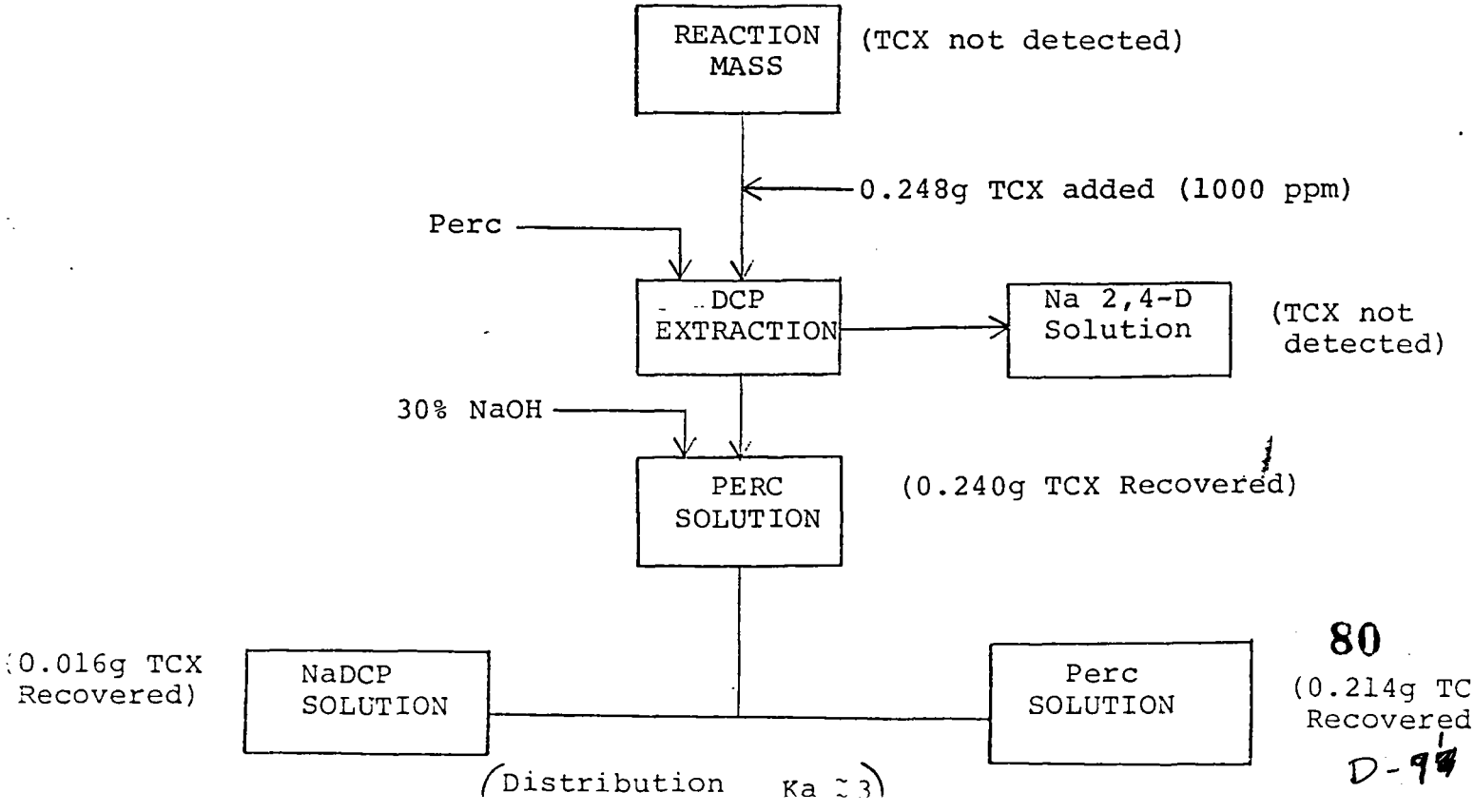
V-602: Final Product Storage Tank: Tests run at 120-175° on wet and dry 2,4-D[11] showed that there is an initial slow build up of about 20 ppm of TCX during the first 48 hrs at >160° that stabilizes out. This suggests a small amount of an unstable unknown species that decomposes in acidic media. Molten 2,4-D can be treated for at least 100 hrs under the above conditions without affecting product performance.

Since TCX is formed in the reactor and was found throughout 948 Bldg process, a laboratory study of the distribution was requested. In this experiment a reaction was carried out and the crude reaction mass was spiked with TCX. The purification process was then simulated and the fate of the TCX was determined. Figure 6 summarizes the results of the extraction study performed at 90°/atm.

Figure 6: The Distribution of TCX in a Laboratory Simulation of the 948 Bldg 2,4-D Process



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These data show an excellent TCX recovery in which, using clean perc, all the detectable TCX is removed from the Na 2,4-D solution. The fact that the plant observes some TCX in the product suggests that some entrained perc is carried overhead so that the impurities carried with it end in the product. The extraction of the perc/DCP mixture with caustic to recover the NaDCP also extracts about 5% of the TCX which is recycled to the reactor. This scheme was followed in a second experiment that was performed at 125°/ 35 psig which more closely follows the plant conditions. Under these conditions the aqueous solutions can be more concentrated in Na 2,4-D, NaCl, and DCP which could affect the distribution of TCX.

A high pressure, mechanically stirred glass reactor was constructed and was charged with partially neutralized material from V-301 (the DCP neutralizer). The molten material was extracted six times with perc at 125°C and the molten 2,4-D was isolated. The TCX and "8-5" levels were monitored throughout and the analytical results for the products are summarized in Table 5 for the two runs. The data show that TCX is effectively removed at the more drastic conditions.

Table 5: The Analysis of the Product from the High Temperature Extraction of Crude Na 2,4-D with Clean Perchloroethylene

	TCX (ppm)		"8-5" (ppm)		Metals (ppm)			
Run	init	final	init	final	Na	Fe	Ca	Mg
1	292	13	54	52	84	5	40	13
2	178	2	N.D.	25	91	3	50	16

It is interesting to note that "8-5" is not efficiently removed with perc extraction. Hence most of what is made goes out with the product. OCSX was not detected in these samples.

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In summary, TCX is formed in the reactor and most of it remains in the recirculating perchloroethylene system. A certain amount of TCX spills into the product and the magnitude is directly related to the level in the perc. TCX is easily separated by distillation in the perc still so by increasing the rate of distillation one would achieve a lower steady state concentration of TCX in the perc.

Assuming a rate of TCX formation of 0.5-1.0 #/hr in the plant (based upon analyses of plant samples) K. E. First[4] has taken distribution coefficient data and has modeled the process in terms of TCX content in various streams as a function of % of perc distilled in the perc still. To date, there is not enough in-plant data to verify this model.

(C) Reduction of TCX by Chemical Means

Two approaches for chemical reduction of TCX were studied. These were methods for inhibiting its formation during the reaction step and methods for reducing it from process streams. The following approaches were studied and each will be discussed in detail.

1. Changing NaDCP/NaMCAA ratio.
2. Post reaction neutralization.
3. Effect of DCAA.
4. Bleaching Na 2,4-D solutions.

(1) Changing NaDCP/NaMCAA ratio

Excess caustic or NaDCP was shown earlier to have a significant qualitative effect on the increased production of TCX. The 2,4-D reaction as developed by H. Brust[12] used a ratio of NaDCP/NaMCAA = 1.2. As described earlier in the discussion, at this ratio the product contains theoretically ∿6.3 mole % excess alkalinity as NaDCP as shown on the following page.

DOW 2674765

Stg Mat'l		Product
0.5 mol DCP		0.5 mol DCP
0.6 mol NaDCP	⟶	0.1 ml NaDCP
0.5 ml NaMCAA		0.5 mol Na 2,4-D
		0.5 mol NaCl

Dhingra[13] and Fear[14] evaluated the effect of this ratio on the yield and kinetics of this reaction and concluded: (a) lower ratios (below 1.2 lead to lower yields based on MCAA and, (b) low H_2O in solution gives higher 2,4-D yields. The effect of changing the NaDCP/NaMCAA was restudied in order to determine if the lower yield from MCAA could be justified by reduced TCX formation due to less excess caustic.

The runs were carried out by using a constant amount of NaMCAA and varying the amounts of NaDCP which was done by adding differing amounts of caustic in the initial boil down step. Tables 6 and 7 and Figure 7 summarizes the results of this study. These data show that lowering the ratio from 1.2 to 1.1 results in a two fold reduction of TCX along with a 1% loss in MCAA yield. This is reasonable and was tested in the plant. After three weeks of operation, they did not note a measurable reduction for reasons that are not understood at this time. Any further reduction is not practical since the yield rapidly approaches that of the old plant thereby losing much of the advantage of the 948 Bldg process. It is interesting to note that at ratios below 1.0 there is still a measurable amount of NaDCP which explains why formation of TCX is still observed. All of the data to date indicate that formation of TCX cannot be limited to much less than 60 ppm (in the standard 72 hr/160°C ampoule test).

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TABLE 6

EFFECT OF NaDCP/NaMCAA RATIO ON TCX FORMATION & YIELD ON MCAA

RUN	REF	Moles			Mol Ratio $\frac{\text{NaDCP}}{\text{NaMCAA}}$	ppm HOG	MCAA YIELD	CRUDE ANALYSIS			
		DCP	NaDCP	NaMCAA				Na 2,4-D	DCP	NaDCP	NaCl
1	OC 417-5-143	0.50	0.60	0.50	1.2	951	96.4%	45.4	31.2	8.9	10.0
2	OC 417-5-144	0.55	0.55	0.50	1.1	1514	94.2	45.5	38.0	6.0	7.4
3	OC 417-5-146	0.60	0.50	0.50	1.0	3808	86.8	41.3	40.3	2.2	7.4
4	OC 640-1-1	0.61	0.49	0.50	0.98	3606	86.2	43.0	41.7	2.5	7.9

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TABLE 7

THE RATE OF TCX FORMATION AS A FUNCTION OF TIME, TEMPERATURE & $\frac{\text{NaDCP}}{\text{NaMCAA}}$ RATIO

RUN	REF	TEMP	TCX/OCSX			
			18 HRS	42 HRS	66 HRS	114 HRS
1	417-5-143	130	---	---	19	53
		145	37	34	70	218
		160	29	86	118/107	240
			18	42	66	114 Hrs
2	417-5-144	130	0	19	33	52
		145	27	39	64	93
		160	42	74	93	142
						90 Hrs
3	417-5-146	130	<10	<10	15	30
		145	15	20	41	59
		160	29	47	55	67
						90 Hrs
4	640-1	130	17	28	22	18
		145	23	31	34	52
		160	36	61	65	77

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in the laboratory even by very slowing adding the aqueous acid.

(d) Control of the acid addition would be difficult and, in addition, the plant would have to run a slightly smaller batch size in order to provide room for the acid. Further work on this concept is not warranted at this time.

(3) DCAA Content of MCAA

The effect of DCAA was discussed earlier.

(4) Bleaching Na 2,4-D Solutions

The major chemical difference between 948 Bldg and 489 Bldg techniques for processing crude 2,4-D is that 489 Bldg uses a bleach step in which residual DCP is oxidized out of the Na 2,4-D solution with 8-12% NaOCl at pH 10.5/100°C. Several experiments were performed to determine if bleach would effect the impurity levels and/or improve the ability of the plant to consistently produce 2,4-D that passes the formulation dilution test. The results of these experiments are shown in Table 8.

The results of the first experiment appeared very encouraging since the dilution test solids, the TCX and the "8-5" were all significantly reduced. The second series of runs showed a consistent improvement in dilution test solids when near or out of spec, but not much effect on the impurities. A capital estimate performed by K. E. First[4] showed the cost of implementing a bleach step in 2,4-D to be $500 M which immediately eliminated any further interest in this project in view of the marginal benefits. It is assumed, posthumously, that the main effect of the bleach was to reduce residual DCP which is a known contributor to poor dilution test results.

Table 8: The Treatment of Na 2,4-D Solutions with Bleach

Na 2,4-D Solution Source	pH	Mol Ratio $\frac{NaOCl}{Na\ 2,4\text{-}D}$	ml solids		Impurities (ppm)		
			DMA-4	F-40	TCX	OCSX	"8-
V-501 (4-7-78) 948 Bldg.	starting material		---	0.18	58	N.D.	127
	10.5	0.1	---	0.02	25	N.D.	N.D.
V-501 (6-5-78) 948 Bldg	starting material		0.01	TR	80	N.D.	31
	10.5	0.1	TR	TR	85	"	10
	10.5	0.2	TR	TR	85	"	26
	10.5	0.05	---	---	104	"	23
	10.5	0.1	---	---	94	"	16
	5	0.1	---	---	72	"	7

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(D) Removal of TCX by Physical Means

To date, a stage has been reached in 948 Bldg. where the 2,4-D plant can be run to consistently produce in-spec material and has demonstrated an ability to run at near capacity of 100-120 M#/day. With the perc still running at ∿15 GPM, the 2,4-D product contains ∿20 ppm of TCX and ∿20 ppm of "8-5".

A numberof attempts have been made to see if the levels of TCX can be reduced by physical means that include:

1. Carbon treatment of the recycling perc and the molten 2,4-D.
2. Removing perc from the reaction step.
3. Improved washing of the molten 2,4-D.
4. Recrystallization of Na 2,4-D and recrystallization of 2,4-D acid.

The details of each alternative are discussed below. In all cases, these experiments were short term, range finding efforts and not comprehensive. Further work is justified only if the levels of impurities presently found in the product prove unacceptable in the future from a toxicity, environmental, or performance standpoint.

(1) Removal of TCX with Activated Carbon

The removal of TCX with activated carbon from perchloroethylene from V-402 ("clean" perc storage tank) was evaluated by a standard isotherm method. A 100 ml portion of perc was treated with ground Pittsburg SGL carbon at 70°C/72 hrs. The data, summarized in Table 9, were evaluated by a known technique[18] that is summarized below. A plot was made of X/M vs. C on log-log paper as shown in Figure 5. By extrapoling C to incoming TCX concentration, the corresponding X/M value gives the amount of impurity absorbed per unit weight of carbon when that carbon is in equilibrium with the incoming concentration and represents the ultimate capacity of the carbon. The

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theoretical volume of liquid to be completely freed by TCX/gram of carbon is calculated from the following equation:

$$V_{Co} = \frac{\left(\frac{X}{M}\right)_{Co}}{Co} \cdot V$$

V_{Co} = theoretical volumn to be treated

$\left(\frac{X}{M}\right)_{Co}$ = capacity/gm at incoming concentration

V = volume of liquid used in test

Co = incoming concentration

For this experiment:

$$V_{Co} = \frac{400}{241} \times 100 = 166 \text{ ml/g of Carbon}$$

or 19.9 gal of perc/# C
or 265 # perc/# C

Carbon loading at 241 ppm of TCX in feed = $166 \text{ ml/g C} \times \frac{1.6 \text{ g ml}}{64 \text{ mg/gC}} \times .00024$

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Table 9: The Absorption Isotherm for TCX Removal from Perchloroethylene with Pittsburg SGL Activated Carbon

Sample	Impurity (ppm)			(M) WTC/100ml Perc	(C) Resid ppm TCX	(X) ppm TCX Removed	(X/M) ppm TCX removed / gm Carbon
	TCX	OCSX	"8-9"				
STG. Mat'l	241	N.D.	19	0	241	0	---
1	159	"		0.25	159	82	328
2	108	"		0.50	108	133	266
3	57	"	17	1.00	57	184	184
4	40	"		1.50	40	201	134
5	29	"	17	2.00	29	212	106

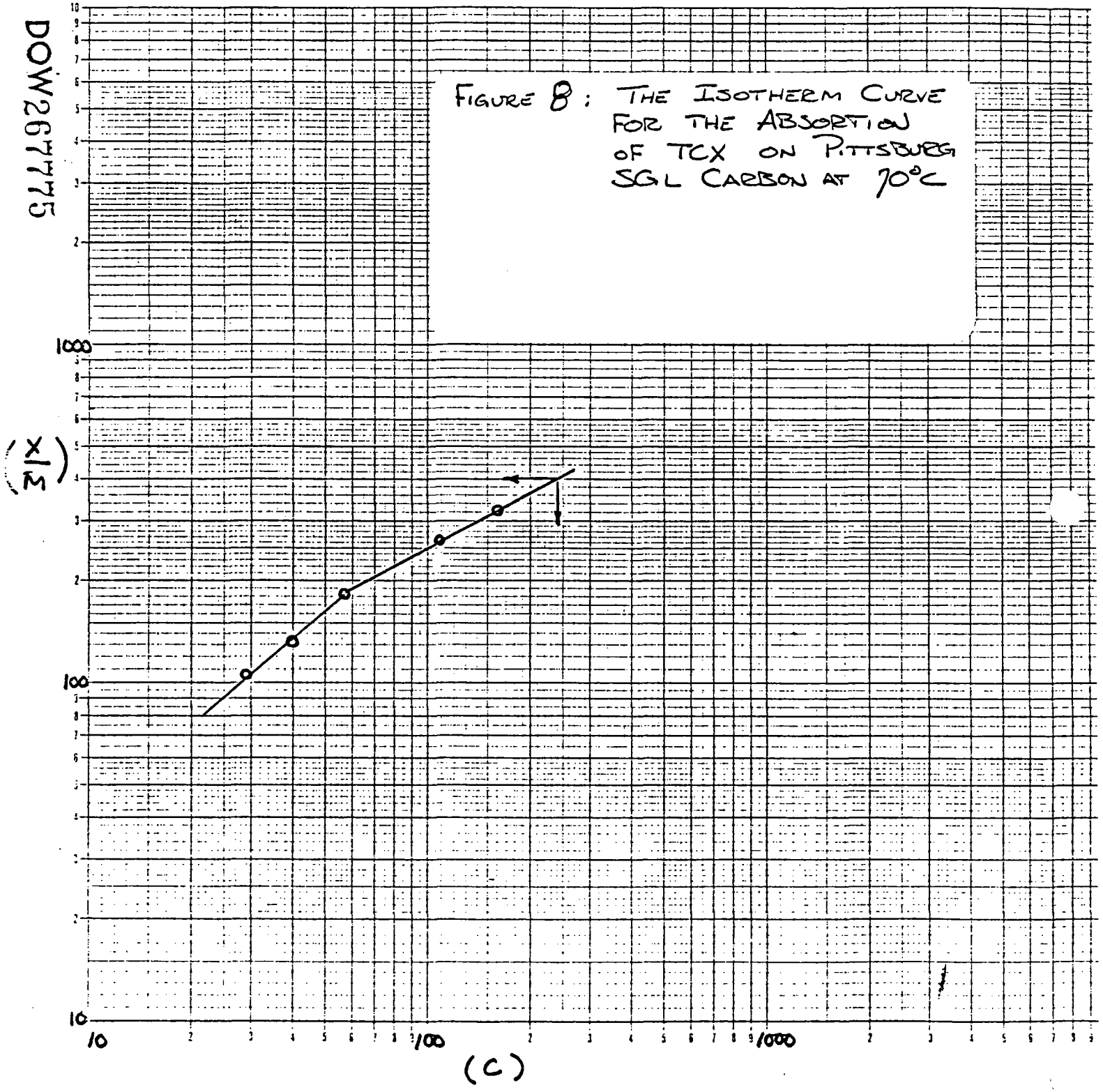

FIGURE 8: THE ISOTHERM CURVE FOR THE ABSORTION OF TCX ON PITTSBURG SGL CARBON AT 70°C

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This is a low loading level and at the present rates of TCX production in the plant, about 15-20 # of carbon per hour would be required to remove the impurity. The data shown in Table 9 indicate that carbon does not remove "8-5" from perc. The shape of the isotherm curve indicates that more than one species is being absorbed onto the carbon. No effort was made to determine the identity of that compound although it was probably perc.

A run was made to remove impurities from wet molten 2,4-D. Since molten 2,-D is so difficult to handle at atmospheric pressure, pressurized system was built using a capillary feeder for controlling the continuous flow of molten 2,4-D at 100°/25 psig onto a vertical 2' x 0.5" column that was maintained liquid full. The flow rate was 10 ml/min down the column for a mass flux of ∿1.0 gpm/ft.^{2} The results are summarized in Table 10.

Table 10: The Treatment of Molten 2,4-D with Activated Carbon

Sample #	Temp (°C)	Pressure psig	Approx feed rate ml/hr	Approx. Prod. cut volume (ml)	Product Analysis (ppm)			F-40* solids (ml)
					TCX	OCSX	"8-5"	
Feed	112				42	N.D.	32	.005
1	110±2	33±2	300	100	--	--	--	
2	110	33	600	375	14	N.D.	29	.04
3	110	33	600	375	28	N.D.	38	.005
4	110	33	600	376	32	N.D.	42	
5	110	33	600	375	30	N.D.	36	

*Formulation contains 2% Versene & 0% PG 4000

These data are fairly crude in that the column was shorter than is desirable for optimum column work (2' vs the recommended 5-6'[18]) and the flow through the column was a little faster than the more desirable 0.5 gpm/ft^2 recommended.[1]

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The data show that TCX loading is rather low. Breakthrough occurred after 900 ml molten D (∿935g pure 2,4-D) was treated. From the analyses, the 59.8 gm of Pittsburg SGL 8 x 30 granular carbon charged to the column absorbed 281 mg of TCX for a loading of ∿0.5 mg/g of carbon which is quite low. Again, "8-5" was not absorbed by the carbon. Based upon these preliminary experiments, carbon absorption of these impurities is not an attractive purification technique.

(2) Remove Perchloroethylene From the Reactor

Since perc is known to give rise to TCX, several methods were examined to eliminate its recycle to the reactor. At present, since perc is soluble to 1.2% in the recycle NaDCP solution, there are about 350# returning to the reactor in each batch. Since a continuous percphenate phase separation is performed in V-401 just before recycle to the reactor, a brief study was undertaken to evaluate the phase separation to determine the time required for complete layer separation and the solubility of perc in NaDCP solution.

A solution of 62% NaDCP and 2% NaOH in water was slurried with an excess of perc and vigorously stirred for 30 min at 75°. The stirring was stopped and the phenate layer was analyzed for % perc as a function of time. The results are summarized in Table 11. These data show that the solubility of perc in NaDCP is 1.3±0.1% at 75°C and that layer separation is complete within 15 minutes. The residence time in V-401 is ∿40 minutes so that with proper operation, no layer separation problems should result. The question was also asked if the perc was entrained in the NaDCP solution as an emulsion or was it in solution? A sample was centrifuged at 60° (minimum temperature) for 30 min at ∿4000 rpm and 1.2% perc was found in the phenate. It is concluded that the present equipment gives optimum layer separation and the 1.2% of perc is soluble.

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Table 11: The Solubility and Separation Rate of Perchloroethylene and 62% NaDCP in Water at 75°C

TIME*	% Perc in Phenate Layer
5 min	1.9
15 "	1.3
30 "	1.4
1 hr	1.5
2 "	1.4
4 "	1.4
6 "	1.2
24 "	1.3

*Time zero is when the vigorous stirring of the two layers is stopped.

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Several attempts were made to strip perc from the reaction mass and from the NaDCP solution. The plant tried to strip perc from the reaction mass during the normal boil down step. Whereas normal operation involves returning the distilled organic layer to the reactor, in this experiment the recovered organic layer was discarded. Whereas normal boil down returns 350# of DCP to the reactor, in this experiment even after 4000# of DCP was distilled off, there was still detectable perc in the distillate. As a result, this approach was judged impractical. Two attempts were made to distill the 1.3% of perc from the 60% NaDCP-2% NaOH solution.

The first involved a batch distillation from a standard solution from V-403. A total of 65.9 gms were distilled out and 73.8% of the perc was removed. The reaction was then carried out as usual and samples were heated for 24, 48, and 72 hrs and the results are summarized below. These data suggest that distillation of 75% of the perc does not reduce TCX formation (See Table 4, Runs 4&5).

	Temp	24 hrs	48 hr	72 hrs
ppm TCX	160°	21	75	145

The second approach taken for stripping out perc was using a falling film still. The results of two experiments are shown in Table 12. The results show that, as before, 70-80% of the perc is easily removed but that the last 20% is likely to be quite difficult. No more work is planned in this area until it can be better proven that removing perc offers any real advantage in reducing rates of TCX formation.

(3) Improved Washing of 2,4-D Acid

Several experiments were run to see if improved washing would affect impurity levels in the 2,4-D product. A sample of 2,4-D product was taken from V-602 (948 Bldg) and was treated in the following ways:

(a) A 250 gm sample of molten acid was washed 3 times with 200 ml of water per wash at 100°C.

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TABLE 12

Preliminary Data for Falling Film Distillation of Perc From NaDCP Solution

Still: 1" x 12" Tube

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	Run 1	Run 2
Pressure	ATM.	ATM.
Temp (col'm)	120°	
" (feed)	75°	75°
Feed Rate (ave.)	10 ml/min	10 ml/min
Overhead Temp	85° → 90°	90° → 95°
Feed analysis		
% Perc	1.0	1.1
% DCP	51.5	50.1
Wt. Charged (Feed)	725 gms	738 gms
Product: Wt	652 gms	645 gms
% Perc	0.3%	0.2%
% DCP	53.9%	61.6%
Overhead: Wt	46.7 gms	75.0 gms
% Perc	1.5%	3.3%

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(b) Another sample was reacidified to pH 0.5 with conc HCl and rewashed 2 times with water at 100°C.

(c) A synthetic V-501 mixture was made up using Rhone Progil 2,4-D to determine if any impurities are made in the washing step. The synthetic mixture was acidified and washed and the 2,4-D was recovered for analysis. This experiment was repeated in the presence of 2750 ppm of added TCX.

The results of these experiments are shown in Table 13. Based upon these experiments, it is shown that the impurities are not made or reduced by improved washing. If anything, they are slightly increased in the product due to the greater solubility of 2,4-D in the hot water or brine.

(d) Recrystallization of Na 2,4-D and 2,4-D Acid

An attempt was made to determine if the impurities could be removed by recrystallization of Na 2,4-D from water and 2,4-D acid from organic solvents. Na 2,4-D was recrystallized by taking 500 gms of material from V-501 and adding enough water (350 ml) to form a homogeneous solution at 100°C. The solution was cooled and the precipitated Na 2,4-D was filtered and washed with 5% brine. The Na 2,4-D was redissolved in hot water and the 2,4-D was isolated and analyzed. The results are shown in Table 14.

In two separate experiments, 2,4-D from V-602 was recrystallized from perchloroethylene and ethylbenzene. A weight ratio of 3 parts solvent to 1 part 2,4-D was heated to boiling, the water contained in the molten 2,4-D was boiled out as an azetrope (the organic distillate was returned) and the solution was cooled. The 2,4-D was recovered by filtration and the solvent removed by heating in a vacuum oven at ~60°C. The results are summarized in Table 14.

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Table 13: The Effect of Improved Washing of Molten 2,4-D on Levels of Impurities

Material	Impurities		
	TCX	OCSX	"8-5"
V-602 Starting Mat'l	56	N.D.	58
Wash three times	73	N.D.	60
Reacidify, wash two times	96	34	68
Synthetic V-501 Na 2,4-D: 21.5% NaCl 7.0% DCP 0.2%			
After Acidif. & Wash	N.D.	N.D.	N.D.
Repeat the synthetic V-501 spiked with 2750 ppm TCX			
After Acidif & wash	3150	N.D.	10

Note: Rhone Progil 2,4-D shows no detectable TCX, OCSX & "8-5"

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Table 14: The Effect of Recrystallization of Na 2,4-D and 2,4-D Acid on Impurity Levels

Treatment		Impurity Level (ppm) TCX	OCSX	"8-5"	F-40** Dilution Test	Commen
Recrystallize Na 2,4-D	Before*	58	---	127	0.18	Product Highly lored
	After	81	53	54	0.3+	
Recrystallize 2,4-D From Perc	Before	52	N.D.	46	***	91% Rec very of 2,4-D
	After	1	N.D.	N.D.		
Recrystallize 2,4-D From Ethylbenzene	Before	52	N.D.	46	***	87% Rec very f 2,4-D
	After	N.D.	N.D.	N.D.		

*The impurities analysis was performed on a sample of 2,4-D acid isolated from Na 2,4-D without any extra treatment.

**20:1 dilution in 1000 ppm hard water, formulation contained 2% Versene and no P-4000.

***The recrystallized product behaved like the high purity Rhone Progil 2,4-D which is difficult to formulate as was mentioned earlier in this report.

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Based upon these results, recrystallization of Na 2,4-D is not a good option since the TCX tends to concentrate in the product and the product was highly colored. It was also observed that the iron level in the product increased from 22 ppm to 91 ppm which could explain the off-color.

Recrystallization from an organic solvent clearly improves the product quality although it would be difficult and expensive to implement in the plant. No further work is planned in this area unless it is determined that extremely low levels of impurities are necessary from a toxicity or an environmental standpoint.

GENERAL CONCLUSIONS

TCX and other non-acidic impurities are formed chiefly in the reaction step of the 2,4-D by several routes. Additional caustic, perchloroethylene, elevated temperatures and iron all promote their formation. A number of attempts to chemically and physically remove these species have met with limited success. It was found that the impurities are concentrated the recirculating perchloroethylene system and that by increasing the capacity of the clean up distillation column from 0.75 to 15 gpm, the levels of impurities in the process do not cause serious operating or quality problems.

SAFETY & ECOLOGY

2,4-Dichlorophenol, 50% NaOH, and chloroacetic acid are highly toxic and corrosive raw materials. When handling, the protective clothing included lab coat, rubber gloves and goggles, and when possible, all operations were performed in a fume hood. A number of operations were carried out at elevated pressure which required the use of a face shield and secondary shielding in the hood. All waste samples and solutions were sent to the burner for disposal.

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EXPERIMENTAL

The Preparation and Workup of 2,4-D

The following is a general description of the procedure used to prepare and isolate 2,4-D when simulating 948 Bldg. A 1 liter round bottom flask equipped with a bottom drain, two dropping funnels, a mechanical stirrer, a thermometer, and a distillation head was charged with 179g (1.1 moles) of 2,4-DCP and 48 g (0.6 moles) of 50% NaOH. The flask was heated with a heating mantel attached to an I^2R Thermowatch controller.

The reactor contents were heated while stirring and a DCP-water azetrope was distilled out. The distillation was continued until enough water was removed so that a temperature of 130°C could be achieved. Normally 9-10 ml of H_2O and 2-3 ml of DCP were removed. The DCP was returned to the pot. Then 47.3g (0.5 moles) of melted MCAA and 40.0g (0.5 moles) of 50% caustic were con-added from the two dropping funnels during 50-60 minutes at 130°C. The rates of addition were carefully controlled so that neither added reactant was significantly in excess of the other. Water and DCP continuously distilled out during the con-add and the DCP was returned to the reactor. After the addition was complete, the reaction was heated an additional 60 minutes. About 43-47 gms of H_2O was recovered in the con-add step. At the end of the post reaction samples of the viscous crude reaction melt were taken into ampoules, if desired.

The work up procedure for isolating the 2,4-D is as follows: (The amounts used assumes no samples were taken after reaction). The reaction mass was diluted with about 500 ml of water, heated to boiling to ensure complete dissolution and the pH was adjusted to 5.2±0.2 with about 12 ml of conc HCl. The solution was then extracted with six 150 ml portions of perc at a temperature of >90°C to remove the DCP. Occasionally 50-100 ml of additional H_2O was necessary to keep all of the solids dissolved. The extracted Na 2,4-D solution was heated

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to boiling and any traces of perc were distilled off. The pH of the solution was then lowered to 0.5-0.7 with about 55 ml of conc HCl added rapidly and the molten 2,4-D layer was separated and drained into a beaker. The resulting brine was discarded. The 2,4-D was reslurried in 250 ml of hot distilled H_2O in the pot and washed in this manner two times. The final pH of the aqueous layer was 2.7-2.9. The 2,4-D was recovered and dried overnight at ambient temperatures.

The analyses of product and intermediate streams were performed by personnel in the 948 Bldg quality control laboratory. The analyses for TCX, OCSX, and "8-5" were performed as described earlier[8].

The Extraction of DCP and Impurities from Na 2,4-D Solution Under Pressure

A glass apparatus was designed and fabricated from heavy wall glass pipe as shown schematically in Figure 9 . The main pot was equipped with a mechanical stirrer and was loaded with 700g of material from V-301 (948 Bldg). The reactor was sealed and heated to 125°C. The perchloroethylene was added in 649 gm increments from the pressurized shot tank. The perc layer was drained into the bottom receiver where it was cooled before draining into a bottle. All analyses on the perc and Na 2,4-D layers were performed in the 948 Bldg Q. C. Laboratory.

The Carbon Clean up of Molten 2,4-D

A glass pressure apparatus was assembled in which molten 2,4-D was pumped onto a carbon column (downflow). The apparatus is shown schematically in Figure 10. The flow of 2,4-D was controlled by controlling the pressure drop across a capillary tube. To handle

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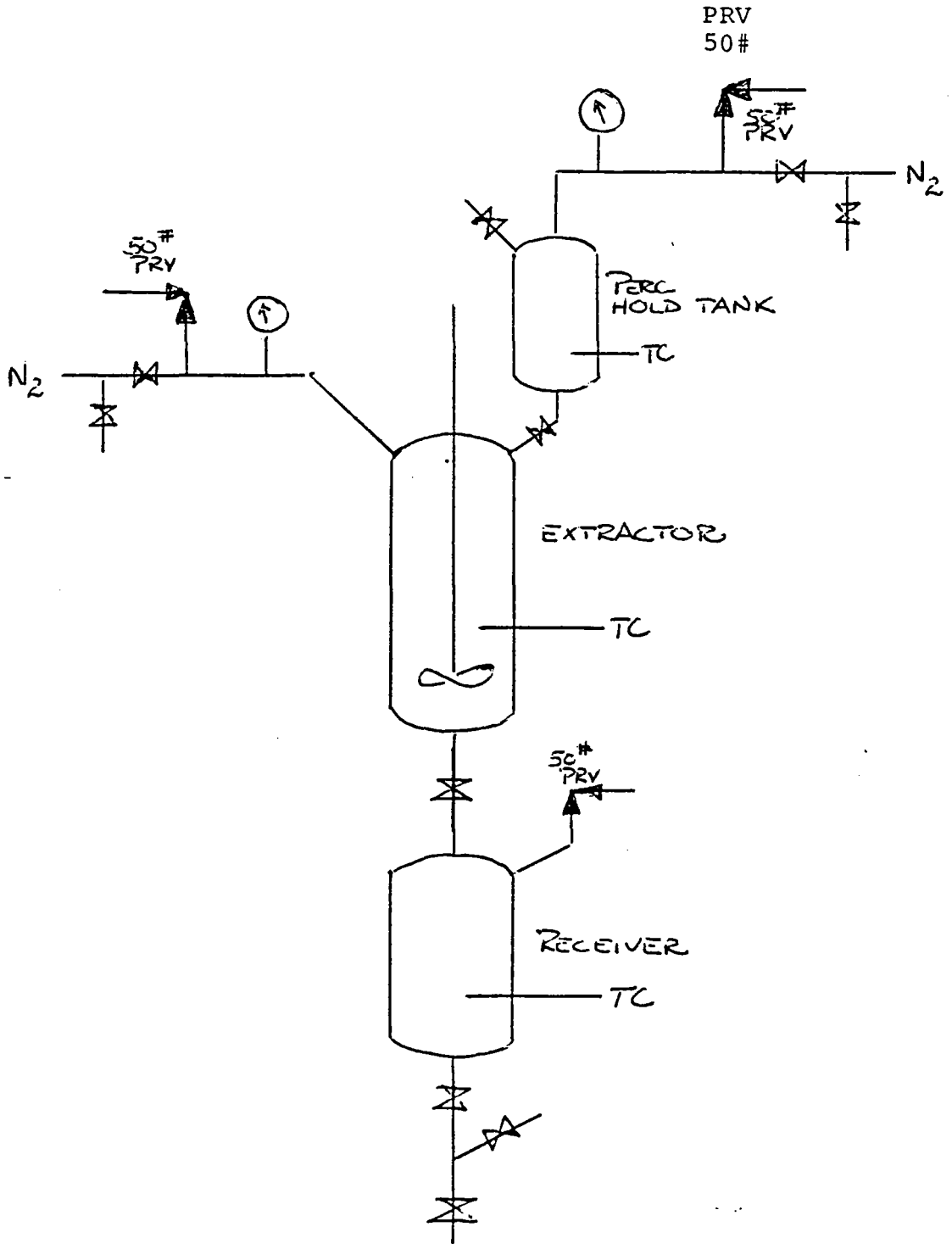

Figure 9: A Schematic Drawing of the apparatus used for Extracting DCP from Na 2,4-D with Perchloroethylene.

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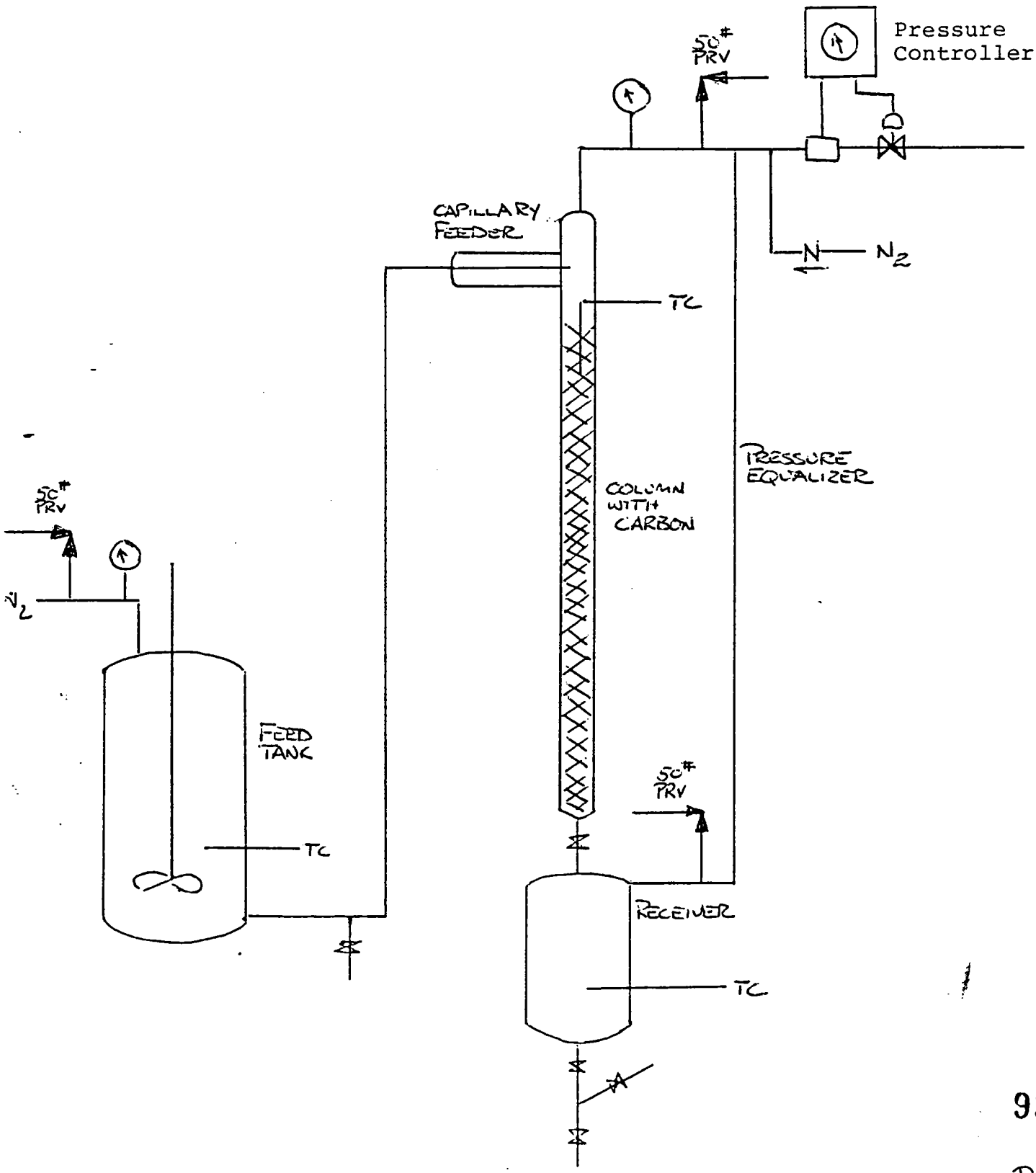
Figure 10: A Schematic Drawing of the apparatus used to treat Molten 2,4-D with activated carbon



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molten 2,4-D reliably and effectively, required at least 10 psig/ ∿100-105°C to avoid flashing and freezing problems.

The 2,4-D and a slight excess of water were placed in the feed tank and heated to 110°C. When the entire contents were melted the valve on the bottom of the column was closed, the column was filled with molten acid to 1" above the top of the carbon, and the system stood for 60 min. The pressure drop across the capillary was adjusted to 7 psi (∿10 ml/min flow) and the valve on the bottom of the column was adjusted so as to maintain the liquid level above the carbon bed. The results are shown in Table 10.

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*R. R. Bumb
*M. J. Mintz

633 Building

*J. Bleiweiss
K. E. First

W. Ward, 9008

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STATE OF FLORIDA)
) SS:
COUNTY OF ORANGE)

IN THE CIRCUIT COURT FOR ORANGE COUNTY, FLORIDA

KIMBERLY MOYER, as Personal Representative of the Estate of ROBERT W. MOYER, II, Deceased,	
Plaintiffs,	Case No. CI 89-8657 Div: 32 Thompson
vs.	
DOW CHEMICAL COMPANY, et al.,	
Defendants.	

The deposition upon oral examination of KARL KRUMEL, Ph.D., a deponent produced and sworn to before me, Aprille Rigsbee Lucas, RPR, a Notary Public at large in and for the State of Indiana, taken on behalf of the Plaintiff at DowElanco, 9001 Purdue Road, Quad III, Indianapolis, Marion County, Indiana, on March 10, 1993, at 9:30 a.m., taken pursuant to the Florida Rules of Civil Procedure in the above-captioned matter.

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E X H I B I T S

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KARL KRUMEL, Ph.D.,

having been first duly sworn to tell the truth, the whole truth and nothing but the truth, relating to said matter, was examined and testified as follows:

DIRECT EXAMINATION,

QUESTIONS BY MR. SCHULER:

Q Would you state your name, please.

A My name is Karl Krumel.

Q What is your professional address?

A My professional address is 1710 Building, the Dow Chemical Company, Midland, Michigan, 48674.

Q Are you employed?

A Yes, I am.

Q By whom are you employed?

A By the Dow Chemical Company.

Q What is your position with Dow Chemical Company?

A My title is associate scientist.

Q As associate scientist, just in general, now, what are your duties and responsibilities?

A Well, the associate scientist is a generic title for people in research who have reached a certain level in the company. It doesn't in any way

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define the job.

Q Tell me a little bit about the structure, to give me some understanding of how the research department is organized. And if you would, could you also tell me, and you don't have to be completely thorough about this, but just tell me in general what the structure is and the various positions that are within the research department.

MR. WAGNER: I object as to breadth, compound. You mean today?

MR. SCHULER: Right.

A Are you asking me about the structure of research within the total Dow or within the structure within my department, which is a small part of the overall?

Q Let's start with your department.

A The department I'm in is agricultural chemicals process research. This department, the name has changed several times over the years that I've been in it, but that's the current name. Our structure, we have a technical director. We have two research managers, and these research managers then control groups of on the order of 30

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technical professionals each. I happen to be in one of those groups as a senior scientist in the department.

Q So there are roughly 62 or 65 people in the department?

A In the current department, yes.

Q Now, to expand that to the, to give me some idea of how the department of agricultural chemicals process research fits into the overall scheme of things, what other departments are there, other than that, if you know?

A Oh, goodness, there are a number of departments located in Midland that support other areas of Dow R&D, you know, of the Dow Chemical Company, including pharmaceuticals, analytical, polymers, resins.

Q You're the only department that has to do with agricultural chemicals in --

A In the Midland, area, yes.

MR. WAGNER: You meant research, of course?

MR. SCHULER: Right.

Q Are there other research departments that deal

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with agricultural chemicals in other areas of the country?

A Well, we have small groups that will support the production of ag chemicals in other locations other than Midland, yes.

Q That are right within the factories, themselves, you mean?

A They're within the plant area, themselves, yes.

Q Who is the technical director presently?

A The gentleman's name is Jim Love, L-O-V-E.

Q How long has he been technical director at the agricultural chemicals process research department?

A He's been there since 1988.

Q Do you know who his predecessor was?

A His predecessor was, yes, the gentleman's name is Alex Vogel, V-O-G-E-L.

Q How long was he there, if you know?

A I can't give you the exact time frame. It's on the order of four years or so.

Q Would that position of technical director of the agricultural chemicals process research department have been in existence back in 1975, let's say?

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A In '75, the organization was pretty much the same. The name of the department at that point was different.

Q What was the name at that time?

A Organic chemicals research.

Q And who was the head of the department back in 1975, if you recall?

A 1975, the technical director was a gentleman named Don Morehouse.

Q Were there also residents or research managers back in 1975?

A Yes.

Q Do you recall who the research managers were in 1975?

A Well, I certainly recall my research manager at that point, which was Michael Mintz, M-I-N-T-Z.

Q Is Mr. Morehouse still with the company?

A No. He retired a number of years ago.

Q Is he still in Midland or has he moved away?

A He moved -- well, where he is today, I really don't know. He moved away to Florida, but I've lost track of him.

Q How about Mr. Mintz, it is he still with the

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company?

A Yes, he still works for Dow.

Q And what is his position now, the same?

A Oh, no, no, no. He's off in another area. I can't tell you exactly what his job is today.

Q What is your educational background, Dr. Krumel?

A In 1960, I received a Bachelor of Arts degree at Grinnell College, Grinnell, Iowa; in 1962, a Master in chemistry; in 1962, a Master of Arts in chemistry from DePauw University, D-E-P-A-U-W, in Greencastle; and then in 1965, Ph.D. in organic chemistry from Michigan State University.

MR. LUTZ: What year was that?

THE DEPONENT: 1965.

Q After '65, what did you do?

A I joined Dow in June of '65, right out of college.

Q So you have worked for Dow basically all of your working professional life?

A Correct, since graduation from college.

Q Trace for me, if you would, the positions that you've held at Dow, starting from when you began work there after graduating in 1965.

A From the standpoint of the departments in which I

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worked?

Q Yes, and the positions that you held.

A In 1965, I joined Dow as a research chemist, which was an entry-level position for a Ph.D. at that time. I joined the benzene research lab, which was part of the laboratory organization at that time known as organic chemicals production research.

In 1969, I moved over to an area of polymer chemistry, cellulose ether chemistry. The department I moved into was --

Q I'm sorry, that last statement was?

A Cellulose, C-E-L-L-U-L-O-S-E, cellulose ether chemistry.

Q Cellulose ether?

A Yes. And the name of that department changed a couple of times during the time I was there, but in 1975, I then moved into what was then known as organic chemicals research, and I've been in that department, or whatever that department was renamed, since that time.

Q So I can save myself some time here, prior to 1975, would it be fair to say that you did not

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have any experience, within Dow Chemical Company, with the agricultural chemicals that the company was producing?

A No, because I hired into benzene research, and benzene research, at that time, one of their responsibilities was supporting the agricultural chemicals business at that time. The period of time of '69 to '75, I had no involvement at all in ag.

Q Go back to '65, from '65 to '69, then, did you have any involvement with polychlorinated phenols, I think they're called, those type of chemicals?

A The polychlorinated phenols, yes. In 1966, I began doing production research on dichlorophenol.

Q Any others?

A And, of course, by association, I was aware of what was going on in the other chlorinated phenol areas of research at that time.

Q To be more specific, did you produce any documentation from 1965 through 1969 with regard to any research on 2,4-D or 2,4,5-T or Silvex?

A No.

Q Did you work on any projects that involved 2,4-D,

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2,4,5-T or Silvex during that time period?

A No.

Q Did you produce any research during that time period, from '65 through '69, that had to do with any of the component parts that went either 2,4-D, 2,4,5-T or Silvex?

MR. WAGNER: I object as vague.

A I'm sorry, would you rephrase the first part of your question?

Q Between '65 and '69, did you produce any research at Dow Chemical Company on any of the component chemicals that went into making 2,4-D or 2,4,5-T or Silvex?

A Yes, I did.

Q And which chemicals are those, as you recall?

A 2,4-dichlorophenol.

Q And that is involved with the production of 2,4-D?

A Yes.

Q Did you have one or were there many projects involving 2,4-dichlorophenal?

A It was one major project.

Q And without getting too technical on me, can you tell me basically, in laymen's terms, what the

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project involved?

A The project involved trying to improve the isomer purity of the raw material, of the 2,4-dichlorophenol.

Q And did you produce a paper or papers regarding that?

A Yes.

Q Was the process that you were involved with ultimately implemented commercially?

A No.

Q And do you recall the reason why?

A Subsequently some additional work was done that found something better.

Q And who did that additional work, do you recall?

A Let's see, one of the gentlemen's names was W. David Watson. Dave Watson was the primary researcher. He would have been the primary researcher in that area.

Q Was there a fellow by the name of Brust or --

A Harry Brust, yes.

Q Was he also working in that area in the process for 2,4-dichlorophenol, or attempting to improve the isomer from which 2,4-D is made?

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A By the time I got to know -- well, I didn't actually get to know Harry until I came back into organic chemicals research in 1975. I'm aware of what he did in years before that, but only because I knew -- I got to know him when I came back into the department. And he was not involved in the dichlorophenol part, as best I can recall.

Q Between '65 and '69, though, he was not directly involved in the research and development for 2,4-D as far as you know --

A I don't know what Harry Brust did in that period of time.

Q Between '65 and '69, did you have occasion in your research to analyze or write about any potential contaminants of 2,4-dichlorophenol or 2,4-D, itself, such as any of the dioxins, TCDD or any of the dioxins, for example?

MR. WAGNER: I object as to the breadth.

A Are we specifically talking about polychlorinated dibenzo-para-dioxins when we use the term dioxin?

Q Yes.

A Not that I recall.

Q What about furans? I know that's a broad

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statement, but did you do any papers or analysis with regard to the presence of --

A Again, polychlorinated dibenzofurans?

Q Yes.

A Not that I recall.

MR. WAGNER: He sounds like a scientist.

THE DEPONENT: Well, I'm going to do that.

Q Did you do any toxicological research between '65 and '69?

A I have -- no.

Q Let me ask you a very general question here as well, do you consider yourself, I know you're an organic chemistry researcher, do you consider yourself to have expertise in toxicology?

A No, I have no training whatsoever in that area.

Q Again, a general question, which will save time later on, as far as the, when I'm going to ask you some questions about the report you did, I think in 1978, although the date is hard to make out here, but with regard to any contaminants that you ultimately may have dealt with in your research with 2,4-D or 2,4-dichlorophenol, you would not be

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an expert on the toxicological impact of those contaminants?

A That's correct.

Q That type of research would be carried on by others at Dow?

A Yes.

Q Between '65 and '69, did you do any research that was connected with any Dow involvement with any claims that either 2,4-D or 2,4,5-T or Silvex caused various injuries or diseases?

MR. WAGNER: I object, over broad and vague.

A Are you asking me did I consult with Dow attorneys?

Q Yes, that would be part of it, I assume.

A No, I never did.

Q Did you ever testify in any form regarding 2,4-D or 2,4,5-T or Silvex from, excuse me, from '65 to '69, again, I'm talking about?

A No.

Q Did you ever relate any communications to any governmental agencies regarding 2,4-D or 2,4,5-T or Silvex or their component parts?

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A No.

Q Did you, and I'm going to open this up to the entire time all the way to the present, did you ever give a deposition in any any case involving allegations of personal injury as a result of exposure to 2,4-D, 2,4,5-T or Silvex?

A This is my first deposition.

Q This is your first deposition, period, you've never given one before?

MR. WAGNER: You're it.

Q I have to get the answer from you, though. This is your first one?

A Yes, sir.

Q There has been testimony in this case that, I'm not sure as I look back at it, the exact date, but there was a meeting regarding contaminants found in 2,4,5-trichlorophenol of various manufacturers, I think either in '64 or 65. You wouldn't have attended that meeting, would you?

A Well, no, obviously not, because I didn't join the company until June of '65, and I had no involvement whatsoever in the area of halogenated phenols until after 1966.

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Q So you wouldn't have attended any meetings with regard to the presence or absence of TCDD in any of the Dow chemicals from 1965 to 1969?

A Correct. I'm sorry, would you ask that question again? I want to make sure --

(The requested material was read by the reporter.)

A The question should probably be, I attended no meetings, I was not involved in anything dealing with 2,4-D, 2,4,5-T or Silvex.

Q Nothing whatever during that time period?

A Correct.

Q Let's skip forward to your moving into the organic chemicals research in 1975. Were you assigned responsibilities when you went into that particular department back in 1975, any responsibilities with respect to 2,4-D or 2,4,5-T or Silvex or their component parts with respect to doing research?

A Yes, I was.

Q What responsibilities were you assigned initially when you first went into the department?

A When I first went to that department, I was

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assigned the responsibility of doing process research for the new 2,4-D plant that was scheduled for start up in approximately two years from the time that I joined the group.

Q And when you say process research for the new 2,4-D plant, 1975, when you went back to organic chemistry research or the organic chemicals research department, 2,4-D was being made by Dow Chemical Company at that time?

A Correct.

Q It was being made pursuant to a process that they had been using for a number of years, correct?

A That's also correct.

Q Do you know the history of the process of 2,4-D, in other words, the process that was being used in 1975? When you went to the organic chemicals research department, do you know, was there a name for the process they were using at that time?

A Well, it was just simply called the 2,4-D plant.

Q And what building was it located in?

A 489 building.

Q And there wasn't any specific name for the process, who put the process together or anything

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like that?

MR. WAGNER: I object, compound.

A Not to my knowledge. It was just known as the 2,4-D plant.

Q What was the purpose, if you recall, for attempting to put together a new process for the manufacture of 2,4-D?

A We developed some new technology that was much more efficient, produced much higher yield, and produced isomer purity in the final product.

Q When you say we developed?

A Our department.

Q I understand, but were there certain individuals that were responsible for developing that new process?

A Well, the scientists. David Watson, that I mentioned before, was the primary investigator in improving the quality of our 2,4-dichlorophenol from an isomer specific standpoint. Harry Brust is the chemist who developed the chemistry that was eventually implemented in the 2,4-D process.

Q Is Mr. Watson still with the company, by the way?

A Yes.

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Q Is he in your department?

A No. He's in another department. He's located at Midland.

Q Do you know what department he's located in?

A The department is called design thermoplastics research.

Q What about Mr. Brust, is he still with the company?

A No. Harry retired a number of years ago.

Q Is he still in Midland, or did he move away somewhere?

A I believe he's moved away, although I see him in town every once in a while.

Q Did you know whether or not, with the process that was being used in 1975, for the manufacture of 2,4-D, whether there were any problems, from an organic chemistry standpoint, with contaminants being found in the 2,4-D being manufactured, I'll call it by the old process that was in existence, 1975?

A No.

MR. WAGNER: I object, vague.

Q You don't know one way or the other?

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A No, I don't.

Q Do you know who might have, if anyone, done research on the 2,4-D that was manufactured in 1975, to determine its purity or to determine whether there were any contaminants in the 2,4-D?

MR. WAGNER: Calls for speculation.

A Could you be more specific?

Q Well, it's relatively specific. Let me see if I can make it more clear. Do you know who the individual was in the organic chemicals research department, if anyone, who might have done research on the 2,4-D being manufactured in 1975, to determine whether there were any contaminants in the 2,4-D?

MR. WAGNER: Same objection.

A No, I can't recall.

Q Let me ask the question this way, maybe this will make it more clear, was there anyone that you knew back in 1975, in the organic chemicals research department, that was responsible for doing the basic research on 2,4-D back then?

A Well, Dr. Brust was responsible for the research on the new developing process. I did some

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research in the, as it relates to the old process, not specifically targeted at trace impurities.

Q In other words, you weren't just looking for trace impurities; you were just doing research on it for other purposes?

A For other purposes, yes.

Q Did you produce tapes that outlined your research back in 1975?

A Yes, I would have.

Q Do you recall whether, in the course of doing your research, you found any impurities in the process for making 2,4-D in 1975?

A For me to answer that question properly, I guess I'd like to know what impurities you're specifically asking about.

Q TCDD, for example.

A No.

Q No, you did not find TCDD?

A No, nor did we analyze -- was I responsible for determining TCDD in that time frame?

Q You were not looking for that?

A Correct.

Q Do you know if there was anyone that was looking

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for TCDD, for example, in 2,4-D back in 1975?

A No.

Q You don't know, no, or --

A No, I don't know.

Q How big was the department back then in 1975?

MR. WAGNER: Organic chemistry research?

MR. SCHULER: Yes.

A More or less the same size. At this point I don't recall exactly how many people we had.

Q What I'm getting at, do you have an idea of who may have been involved in that type of research, or you're just not sure who it was?

A I just simply don't recall anyone doing any research at that time, and I would, if it were done, I'm sure.

Q Okay, to get back to my earlier question, I asked you about whether in your research I think you found any TCDD. I know you weren't looking for these things, but in the course of your research on the 1975 process, did you find any of the other polychlorinated dibenzo-p-dioxins, did I pronounce it properly?

A What you're specifically asking me about is did we

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look for these compounds in the old 2,4-D process, in the 1975 time frame?

Q Correct.

A No.

Q Let me change the question a little bit to, even though you weren't looking for them, did you find any of those?

A No.

Q Did you work with someone in doing your research on 2,4-D in 1975?

A Within our department?

Q Yes.

A No. I was doing the work. Excuse me, are you asking about the old process work?

Q The old process, that's right.

A Yes, that was done by me.

Q You didn't have someone that worked with you in the department, it was just you?

MR. WAGNER: Asked and answered.

A As best I can recall at this point.

Q In your work on the old process, can you just tell me what your research did involve back in 1975?

A At that time, again, we were just -- one of my

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roles as a process chemist is to make sure we're using the most modern, up-to-date technology and chemistry that we can do. And my research was essentially aimed at doing just that, making sure the plant was operating, that the chemistry in the lab was operating most efficiently within the boundaries in which we could operate in the plant, maximizing yield, maximizing product quality, that sort of thing.

Q Would you try different things in the laboratory to see if you could improve the quality to maximize yield and maximize purity?

A Correct.

Q And if they appeared to be, the things that you did were improvements and appeared to be things that could be incorporated into the process, then that suggestion would be made, is that how it worked?

A It would certainly be considered.

Q Who would make the ultimate decisions as to whether a particular change in the process would be incorporated? I know there's probably a number of people it went through, but just give me a

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general idea how it worked.

A At that time the, well, the ultimate -- the person ultimately responsible for the plant would be the plant superintendent.

Q Who was the --

A But the plant superintendent would work with people in the agricultural chemicals production department because we had some senior level experienced engineers that were located in that department, whose responsibility it was to maintain high standards of technology from the engineering perspective.

Q That was the agricultural chemical production department, you say?

A Yes.

Q Who was the plant superintendent for the 489 2,4-D process back in 1975?

A At the time I joined the group, the man's name was Bill Jones, William Jones.

Q Is he still with the company, to your knowledge?

A As far as I know he is.

Q Do you know where he is in the company, what department?

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A I haven't any idea at this point.

Q In the plant, would records be kept about the process, in other words, the yields that were being obtained, the quality of the product, would that periodically be tested and records be kept on that?

MR. WAGNER: 1975 time period?

MR. SCHULER: Right.

A During that time period, yes.

Q Do you know what other records that would be kept in the plant, primarily?

A Well, they would keep operational records of how the plant was running, product quality, the results of quality control testing, records on plant maintenance and et cetera, et cetera.

Q Would the plant superintendent be specifically responsible for the quality control testing?

A He's the person who is in charge of the people who do the work, yes.

Q Some of these questions, I'm sure, seem very basic to you, but I need to know, do these plants run continuously?

A Yes.

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Q 24 hours a day?

A Yes.

Q And besides operational records and records dealing with yield and purity and quality control testing, are there any other types of records kept in the plant back in 1975, I'm talking about?

A I think I covered the ones that certainly I'm aware of.

Q Was it ever your function to go and review the records in the plant to see how the plant was doing?

A Oh, yes, I would, on a regular basis, review records on how the plant was operating and how the product quality was holding up. I didn't have any reason to review records on maintenance or scheduling or things like that.

Q When you say product quality, and taking 2,4-D specifically in 1975, and again, as generically as you can, what would you look for to determine product quality?

MR. WAGNER: I object to the form of the question.

A We -- well, we had certain specific indications

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that we -- that the product was required to meet by our customers, and we would maintain a track of that and try to maintain an awareness of how the product quality was related to the specs that we were -- specifications that we were expected to meet. And if problems or issues came up with regards to meeting specs, then we would attempt to solve the problem or issue.

Q What type of specs are you talking about?

A Assays, A-S-S-A-Y, the tracking of normal isomer, isomeric impurities. We had several final product quality control tests that we would monitor on a regular basis.

Q When you talk about assays, what are you talking about, what type of assays? You mean concentration of the product?

A Well, the quality of the technical product, the assay at that time was expected to be 95 percent pure 2,4-D, so that's what I mean by assay. Now, what I'm talking about is the technical 2,4-D assay, which is 2,4-dichlorophenoxyacetic acid, A-C-E-T-I-C, acid.

Q And the spec at that time was 95 percent purity?

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A Yes.

Q And when you say 95 percent purity, was that in what form, was that in liquid or powder?

A Powder form.

Q Was the powder put in suspension before the product was shipped, or was it shipped both ways, how did that work, if you know?

MR. WAGNER: I object to the form of the question.

A It was -- we did supply, some of our materials were supplied to the customer as the acid form, but then it was supplied in a number of other physical forms.

Q Depending on the customers' requirements, more or less?

A Right.

Q Now, when you said they were tested for isomeric impurities, was there any test for the dioxins that we discussed earlier, for example, TCDD?

A I simply don't recall how that was handled in those days.

Q What about any of the other polychlorinated dibenzo-p-dioxins, were there tests for any of the

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others?

A Not that I specifically recall.

Q Same question with regard to the furans, were there any tests for those?

A Not that I specifically recall.

Q What type of impurities, when you say isomeric impurities, do you recall any that was tested for?

A We would, our quality control procedures at that time did not require that we analyze for other isomeric impurities.

Q I thought you told me earlier that there was testing for isomeric impurities. Did I misunderstand you?

A I'm trying to recall 18 years ago. If I said that, I guess I must have misspoken. At that time, the specs that we were required to meet in our quality control was 95 percent assay, a 95 percent assay. We had the ability to analyze for other isomeric impurities, but that was not an official specification. That may be where we got confused a little bit.

Q Does that mean that it wasn't done or it was done periodically or what, testing for isomeric

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impurities?

MR. WAGNER: I object to the form of the question.

A It was more likely to be done on an irregular basis, and most likely from a research standpoint.

Q As opposed to a quality control standpoint?

A As opposed to a quality control standpoint, yes.

Q You mentioned initially you did some research on the old process for manufacturing 2,4-D, and at some point you were given responsibilities to do process research for what was potentially going to be a new process, correct?

A Correct.

Q Was there any other research, before we get to that, that you did with regard to the old process? I know I've focused on impurities, and you've told me basically what you did, but was there any other aspect of your research that we haven't covered from the old process?

MR. WAGNER: This is 1975, before he started working on the new one?

A As it relates to the 2,4-D acid process in the 489 building?

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Q Right.

A As best I recall, I've told you essentially everything I did at this time.

Q From a chronological standpoint, how long were you involved in the research in the old process before you turned your attention or your responsibilities were directed to doing research on the new process?

A Only a few months.

Q And when your attention was directed to the new process, what was your initial assignment with regard to that?

A Essentially to provide chemistry support to the construction of the new plant, focusing on gaining a personal understanding of the way the new process was going to operate.

Q Let me get some time parameters in here, too, so perhaps this can save me some effort later on. Did the new process -- was it implemented?

A Yes.

Q Can you tell me at what point in time the new process was implemented?

A We started the new 2,4-D process in the spring of

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'77, I think. I see you've got my report. I think it talks about May of '77.

Q Okay, was it May of '77, is that when the process was began?

A That's when we started the production of 2,4-D.

Q And up until May of 1977, the old process was being used?

A Yes.

Q Was the new process, did the new process, was that put in the same building, 489?

A No. It was a new structure.

Q What was the new building?

A 948 building -- 948-949 building.

Q From your recollection, if you know, when the new process was started in the spring of '77, was the product, in May of '77, was the product sold right away or was there any delay in the sale of the product?

MR. WAGNER: I object to the form of the question, vague.

A I have no personal knowledge as to when we actually began -- the old process continued to operate for approximately 18 months after, as best

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