

ATTORNEY WORK PRODUCT
ATTORNEY-CLIENT PRIVILEGE

2,4-Dichlorophenoxyacetic Acid(2,4-D)

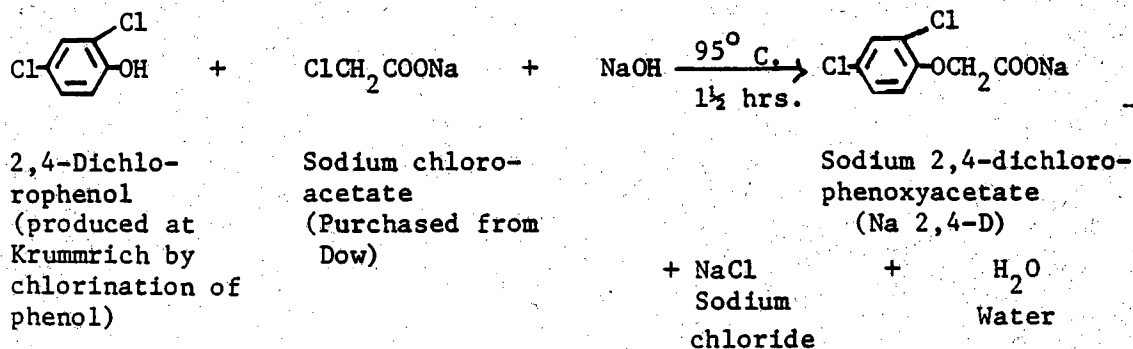
Ref: (1) Tent. Proc. for 2,4-D
Job No. 155-5018 4/4/46
(2) Description of Pro-
ducts-Nitro Plant 12/13/46

On December 6, 1948, the manufacture of 2,4-D was started in Building 79 of the Nitro plant at an estimated rate of 300,000 lbs. per month. This operation was of limited duration, since 2,4-D was regularly produced at the Krummrich and Queeny plants at that time. The process was essentially the same as that run at these plants.

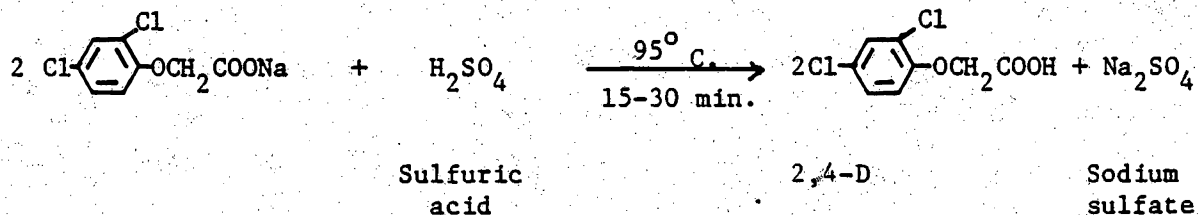
Chemical Reactions:

A. Basic Process

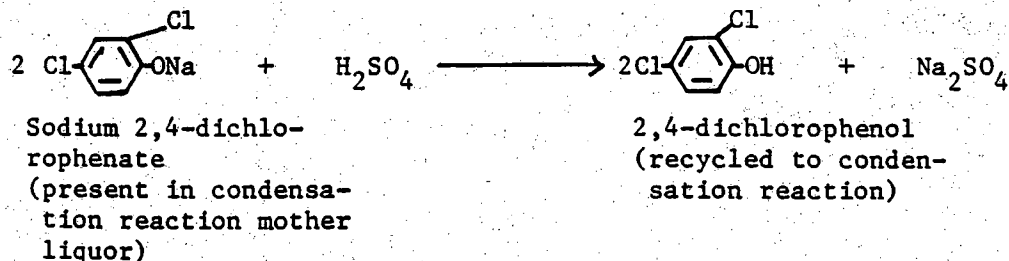
Step 1 - Condensation Reaction



Step 2 - Acidification



Step 3 - 2,4-Dichlorophenol Recovery

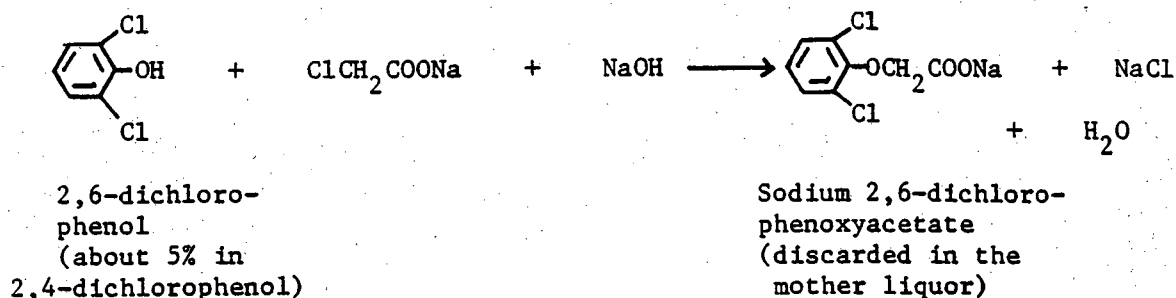


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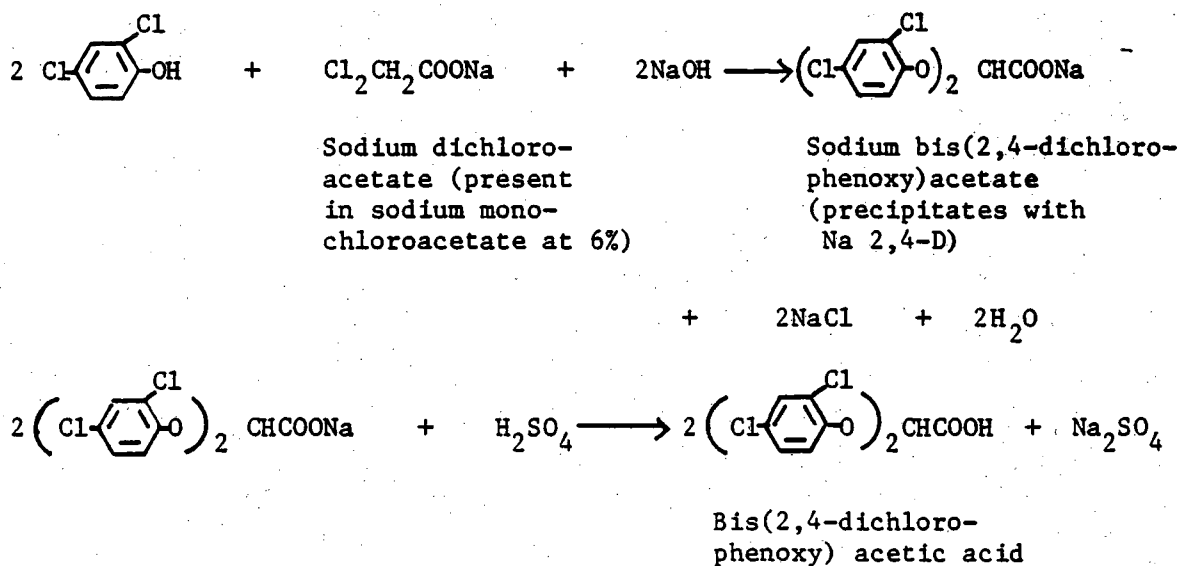
2,4-Dichlorophenoxyacetic Acid (2,4-D)

B. Impurity and By-product Formation

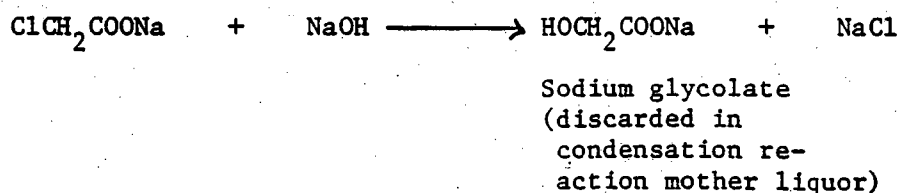
(1) Sodium 2,6-dichlorophenoxyacetate



(2) Bis(2,4-dichlorophenoxy)acetic acid and sodium salt



(3) Sodium glycolate



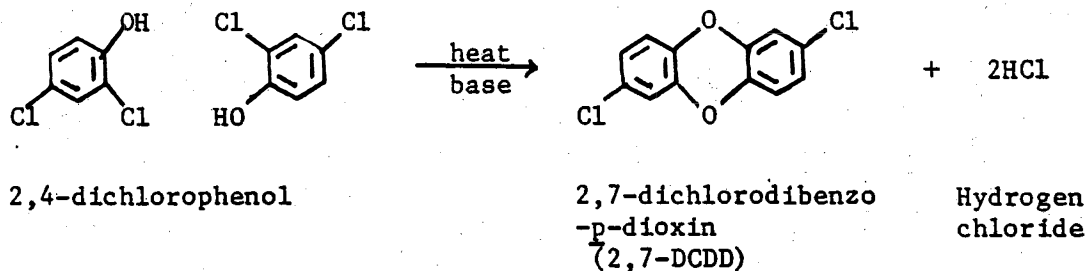
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2,4-Dichlorophenoxyacetic Acid(2,4-D)

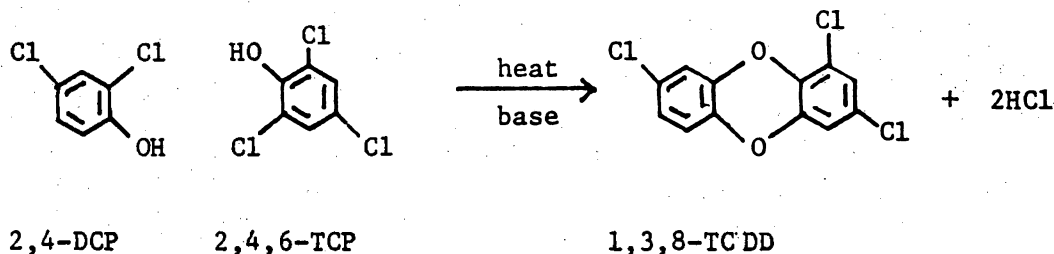
(4) Chlorinated dibenzo-p-dioxins formed as impurities*

The predominant chlorinated dioxins formed in the processes for 2,4-dichlorophenol and 2,4-D are as follows;

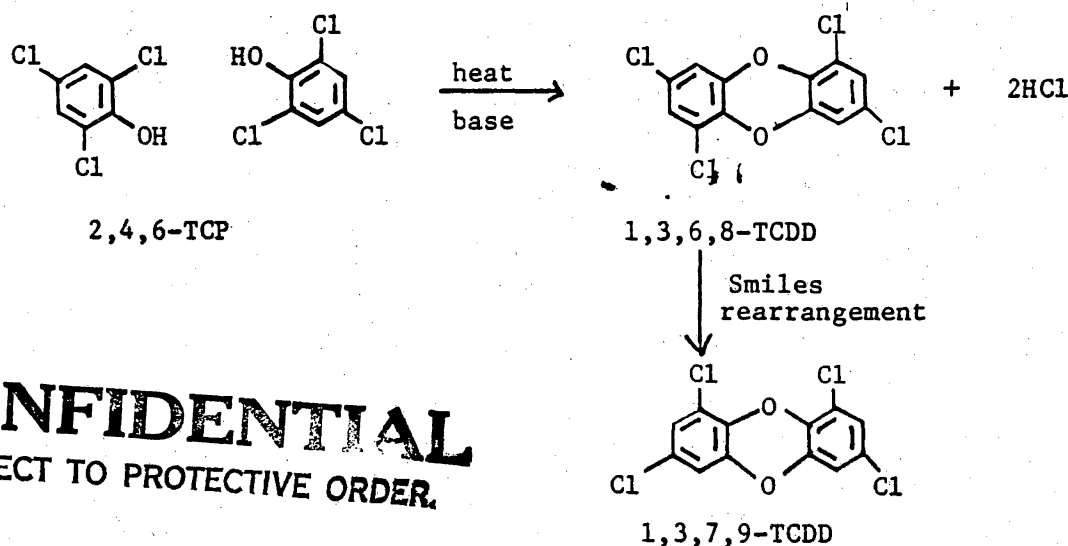
(a) 2,7-DCDD



(b) 1,3,8-TCDD



(c) 1,3,6,8-and 1,3,7,9-TCDD



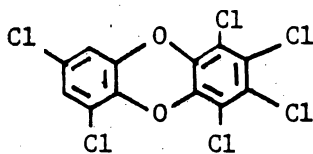
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* References: (1) Persamon Ser. Environ. Sci. (PSSID2) Vol. 5, p. 209-213) (1982)
(2) Journal of Chromatography, 217, 289-299 (1981)

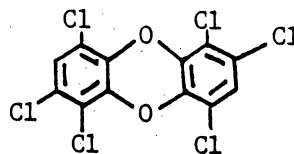
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2,4-Dichlorophenoxyacetic Acid(2,4-D)

(d) 1,2,3,4,6,8-and 1,2,4,6,7,9- HCDD (Chemistry not clear)



1,2,3,4,6,8-HCDD



1,2,4,6,7,9-HCDD

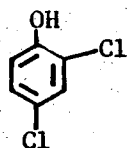
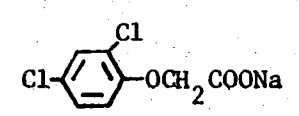
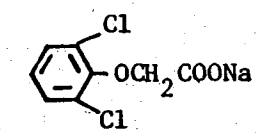
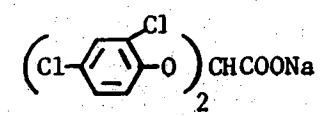
Others are formed in lesser degree, but no 2,3,7,8-TCDD
has been found.

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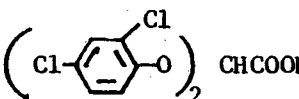
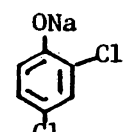
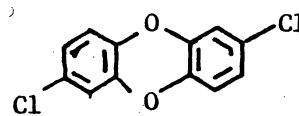
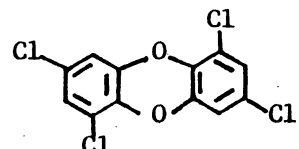
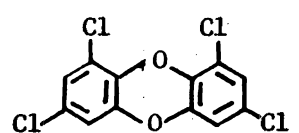
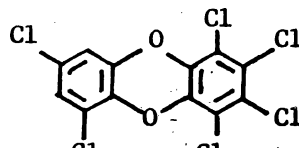
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2,4-Dichlorophenoxyacetic Acid(2,4-D)

<u>Chemicals</u>	<u>Structural Formula</u>	<u>Empirical Formual</u>	<u>CAS No.</u>
A. <u>Starting Materials</u>			
2,4-Dichlorophenol		$C_6H_4Cl_2O$	120-83-2
Sodium chloroacetate	$ClCH_2COONa$	$C_2H_2ClO_2Na$	3926-62-3
Sodium hydroxide	$NaOH$	$HNaO$	1310-73-2
Sulfuric acid	H_2SO_4	H_2O_4S	7664-93-9
Decolorizing carbon	C	C	7440-44-0
Sodium chloride (used in wash of Na 2,4-D)	$NaCl$	$NaCl$	7647-14-5
B. <u>Isolated Intermediates</u>			
Sodium 2,4-dichlorophenoxyacetate (Na 2,4-D)		$C_8H_5Cl_2O_3Na$	2702-72-9
C. <u>By-products and Impurities of Toxicological Significance</u>			
Sodium 2,6-dichlorophenoxyacetate		$C_8H_5Cl_2O_3Na$	No CAS No.
Sodium bis(2,4-dichlorophenoxy)acetate		$C_{14}H_7Cl_4O_4Na$	No CAS No.

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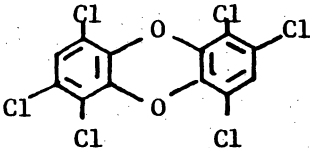
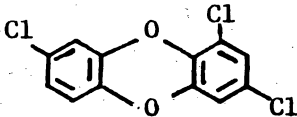
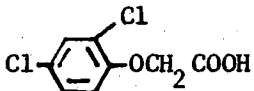
2,4-Dichlorophenoxyacetic Acid(2,4-D)

<u>Chemicals</u>	<u>Structural Formula</u>	<u>Empirical Formula</u>	<u>CAS No.</u>
Bis(2,4-dichlorophenoxy) acetic acid		$C_{14}H_8Cl_4O_4$	No CAS No.
Sodium glycolate	$HOCH_2COONa$	$C_2H_3O_3Na$	2836-32-0
Sodium 2,4-dichlorophenate (NaDCP)		$C_6H_3Cl_2ONa$	3757-76-4
<u>Known Chlorinated Dioxin Impurities</u>			
2,7-Dichlorodibenzo-p-dioxin (2,7-DCDD)		$C_{12}H_6Cl_2O_2$	33857-26-0
1,3,6,8-Tetrachlorodibenzo-p-dioxin (1,3,6,8-TCDD)		$C_{12}H_4Cl_4O_2$	33423-926
1,3,7,9-Tetrachlorodibenzo-p-dioxin (1,3,7,9-TCDD)		$C_{12}H_4Cl_4O_2$	62470-53-5
1,2,3,4,6,8-Hexachlorodibenzo-p-dioxin (1,2,3,4,6,8-HCDD)		$C_{12}H_2Cl_6O_2$	58200-67-2

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2,4-Dichlorophenoxyacetic Acid(2,4-D)

<u>Chemicals</u>	<u>Structural Formula</u>	<u>Empirical Formula</u>	<u>CAS No.</u>
1,2,4,6,7,9-Hexachlorodibenzo -p-dioxin (1,2,4,6,7,9-HCDD)		$C_{12}H_2Cl_6O_2$	39227-62-8
1,3,8-Trichlorodibenzo-p-dioxin (1,3,8-TCDD)		$C_{12}H_5Cl_3O_2$	82306-61-4
D. <u>Product</u>			
2,4-Dichlorophenoxyacetic acid (2,4-D)		$C_8H_6Cl_2O_3$	94-75-7

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All construction work was completed approximately on schedule, and, after start-up, the expanded MHA Acid plant appears to be producing MHA Acid at design rates.

SANTOQUIN

Three batches of Santoquin residue were vacuum distilled at the J. F. Queeny plant to determine if Santoquin and para-phenetidine could be recovered from Santoquin residue. The percent recovery varied from 12.4 to 15.2 with approximately 90 percent usable product. Based on 1971 Santoflex AW requirements of 13.3 million pounds and a usage of 140 pounds of Santoflex AW per cwt of Santoquin, a residue recovery unit savings would be \$124,000 per year.

Santoquin losses, from the lower bearing of a LUWA thin-film evaporator, were encountered since the units initial start-up. Humble Oil's Primol 355 mineral oil was successfully substituted for Santoquin as the lower bearing lubricant. Raw material usage savings of approximately \$8,000 per year are now being demonstrated on this \$500 expenditure.

TETRACHLOROPROPENE

By-products formed from overchlorination of trichloropropene are responsible for considerable yield losses in the tetrachloropropene process. To prevent this overchlorination, evaluations are being made to control the chlorine charge endpoint and also to insure that better assay trichloropropene is being supplied. Laboratory work was begun to find a solvent or catalyst to change the reaction mechanism. However, this was unsuccessful and work on development of an inline GLC is in progress. Inquiries have been sent out to determine the cost of better assay trichloropropene.

2, 4, 5-T

A \$1,070 capital project, to improve the color of 2,4,5-T, was installed during March, 1969. The project provided for a new Elmco cake wash system that would permit the sodium 2,4,5-T cake to be washed with caustic. A plant demonstration showed that a caustic wash improved the product color and decreased the percent TCP in the product. This quality improvement was necessary to maintain sales to certain customers.

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New autoclave charging conditions were initiated during February, 1969. These new charging conditions, recommended by Agricultural Research, were intended to reduce the TDD content from the 1968 average of 40-50 ppm to 5-7 ppm with an associated reduction in the TCA content from 1 percent to trace amounts. Results from a thirty-day extended trial run showed a concentration drop in TDD to an average of 4 ppm with an associated reduction in the percent TCA to approximately 0.17%.

A \$2,200 capital project to control the condensation reaction pH is awaiting installation. This project will permit the use of a 34% NaTCP solution instead of the present 25% NaOH solution. A four-day trial run was conducted during August, 1969, with no adverse effects on product quality or yield. Estimated caustic savings will be \$7,900 per year based on a product rate of 1.0 million pounds per year.

An experimental project permitting the recycle of the pan filter wash water to the Na 2,4,5-T reslurry tank and the pan filter filtrate to the primary settler was installed in November, 1969. Recycling wash water to the Na 2,4,5-T reslurry tank will permit the recovery of dissolved 2,4,5-T. Also, recycling the filtrate to the primary settler will reduce the amount of new 93% H_2SO_4 required to lower the settler pH. Estimated TCB and H_2SO_4 raw material savings are \$22,000 per year based on a product rate of 1.0 million pounds per year. The experimental project is due to be tested during the next 2,4,5-T production period.

Additional H_2SO_4 raw material savings may be realized by the installation of a \$7,500 capital project to reduce the H_2SO_4 usage in the primary TCP settler. The project provides for a ratio control loop to add H_2SO_4 to the Limco filtrate as it is transferred to the settler rather than depending on a variance of pH at the lower portion of the pH scale. Installation of this project will result in a H_2SO_4 raw material savings of \$8,100 per year based on a product rate of 1.0 million pounds per year.

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