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

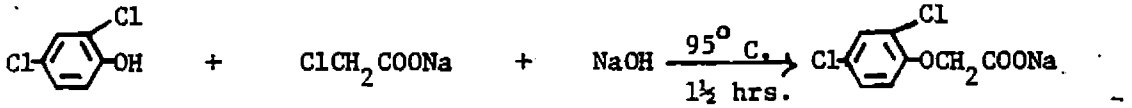
Ref: (1) Tent. Proc. for 2,4-D Job No. 155-5018 4/4/46
(2) Description of Products-Nitro Plant 12/13/4[illegible]

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



2,4-Dichlorophenol (produced at Krummrich by chlorination of phenol)

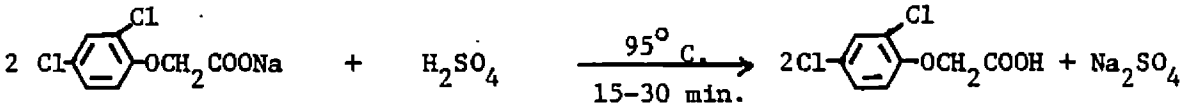
Sodium chloroacetate (Purchased from Dow)

Sodium 2,4-dichlorophenoxyacetate (Na 2,4-D)

+ NaCl Sodium chloride

+ H_2O Water

Step 2 - Acidification

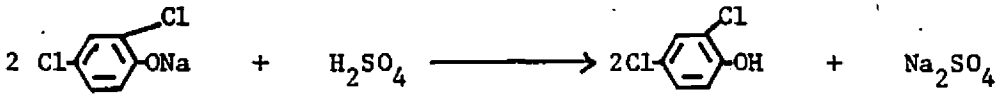


Sulfuric acid

2,4-D

Sodium sulfate

Step 3 - 2,4-Dichlorophenol Recovery



Sodium 2,4-dichlorophenate (present in condensation reaction mother liquor)

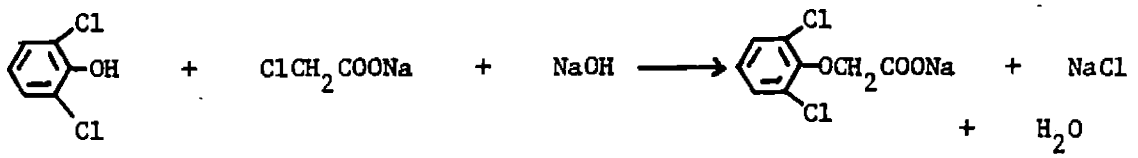
2,4-dichlorophenol (recycled to condensation reaction)

HCG 11/21/83

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

B. Impurity and By-product Formation

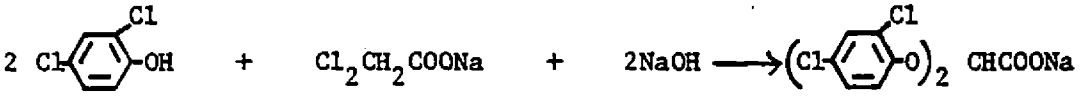
(1) Sodium 2,6-dichlorophenoxyacetate



2,6-dichlorophenol (about 5% in 2,4-dichlorophenol)

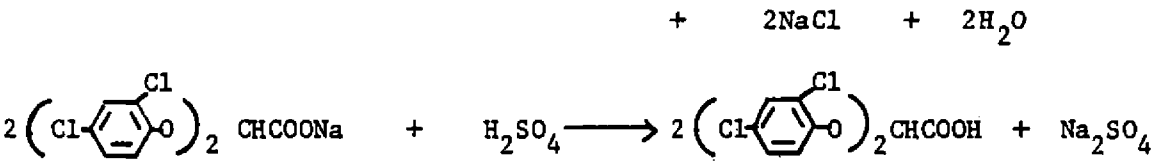
Sodium 2,6-dichlorophenoxyacetate (discarded in the mother liquor)

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



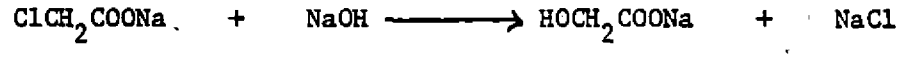
Sodium dichloroacetate (present in sodium monochloroacetate at 6%)

Sodium bis(2,4-dichlorophenoxy)acetate (precipitates with Na 2,4-D)



Bis(2,4-dichlorophenoxy) acetic acid

(3) Sodium glycolate



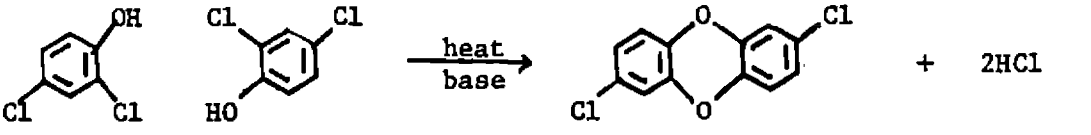
Sodium glycolate (discarded in condensation reaction mother liquor)

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

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

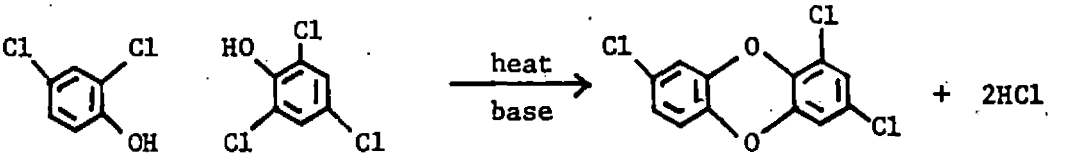
The predominant chlorinated dioxins formed in the processes for 2,4-dichlorophenol and 2,4-D are as follows;

(a) 2,7-DCDD



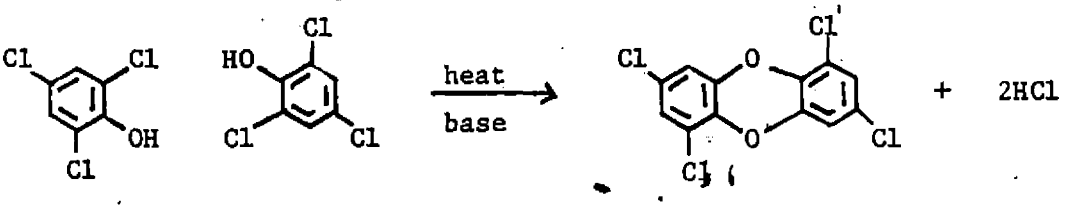
2,4-dichlorophenol — 2,7-dichlorodibenzo-p-dioxin (2,7-DCDD) — Hydrogen chloride

(b) 1,3,8-TCDD

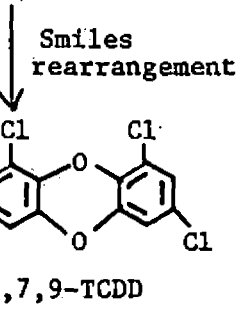


2,4-DCP 2,4,6-TCP 1,3,8-TCDD

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



2,4,6-TCP — 1,3,6,8-TCDD



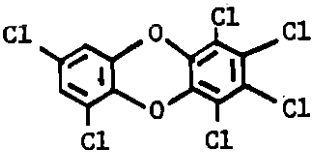
1,3,7,9-TCDD

* References: (1) Persamon Ser. Environ. Sci. (PSSID2) Vol. 5, p. 209-213) (1982)

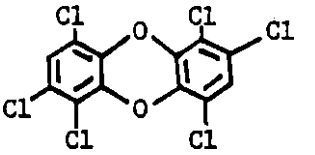
(2) Journal of Chromatography, 217, 289-299 (1981)

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)



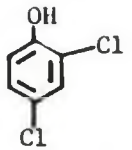
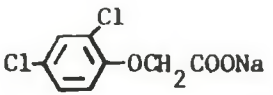
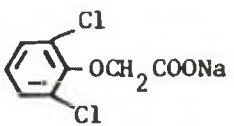
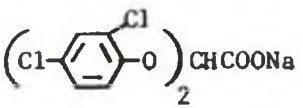
1,2,3,4,6,8-HCDD



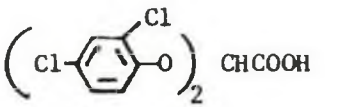
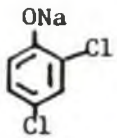
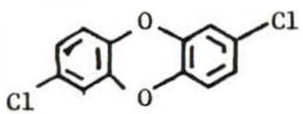
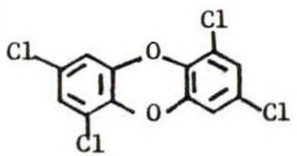
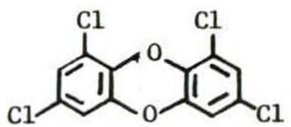
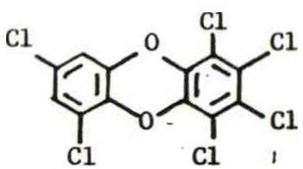
1,2,4,6,7,9-HCDD

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

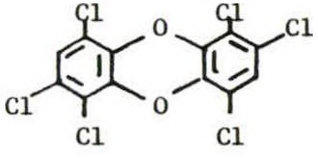
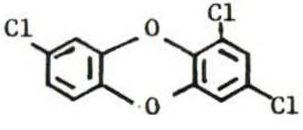
2,4-Dichlorophenoxyacetic Acid(2,4-D)

Chemicals	Structural Formula	Empirical Formual	CAS No.
A. Starting Materials			
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. Isolated Intermediates			
Sodium 2,4-dichlorophenoxyacetate (Na 2,4-D)		$C_8H_5Cl_2O_3Na$	2702-72-9
C. By-products and Impurities of Toxicological Significance			
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.

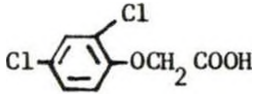
2,4-Dichlorophenoxyacetic Acid(2,4-D)

Chemicals	Structural Formula	Empirical Formula	CAS No.
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
Known Chlorinated Dioxin Impurities			
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

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

Chemicals	Structural Formula	Empirical Formula	CAS No.
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. Product

2,4-Dichlorophenoxyacetic acid (2,4-D)		$C_8H_6Cl_2O_3$	94-75-7