

November 22, 1949

TO: Mr. L. A. Kolker

FROM: Joseph Smith

SUBJECT: Preparation of 2,4,5-Trichlorophenol

The following is a detailed resume and analysis of the work done to date on the preparation of 2,4,5-Trichlorophenol as a basis for plant production:

PROCEDURE:

The procedure below is for Run No. 2. Except for changes in quantities charged and times and temperatures of reaction, the same general procedure was followed in all subsequent runs.

The autoclave was charged with 432 grams (2 mols) of 1,2,4,5-tetrachlorobenzene, 160 grams (4 mols) of sodium hydroxide, and 1000 cc. of methanol. The autoclave was sealed except for the vent line which was open. The agitator was turned on and maximum heat applied. When the temperature of the batch was 68°C., the vent was closed. Heating was continued until a temperature of 180°C was reached. The batch was then held at 180°C, as closely as possible, for a period of six hours. At the end of the reaction period, the agitator was shut off and the batch allowed to cool by convection over night.

The following day the batch was heated to 100°C in the autoclave to distill off the methanol. Three liters of water were next added to the autoclave and the mix was agitated for 15 minutes. This mix was then siphoned out of the autoclave and filtered hot (80°C). A rinse of 555 cc. of water was put into the autoclave and stirred for fifteen minutes. This in turn was siphoned from the autoclave and used as a rinse for the cake collected on the filtration of the main batch. The two filtrates were combined and cooled to 20°C. They were then acidified with 50% sulfuric acid and filtered. The filter cake was transferred to a still, water stripped off, and the product distilled off under vacuum.

RESULTS

A complete tabulation of the runs made showing conditions, reactants, and results is given in Table I of this report. These data show that time of reaction, temperature of reaction, ratio of tetrachlorobenzene to caustic, and volume of methanol all affect the reaction. Since all of these factors are independent variables, there are limitless combinations of conditions that could be employed, only a few of which has been examined to date. In addition, the effects of such other factors as purity of raw materials, amount of water present during the reaction, and substitution of other reactants have not been investigated. Consequently it must be realized that conditions selected for plant operation on the basis of present knowledge are not necessarily optimum, although a good product in satisfactory yield can be expected.

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In addition, the feasibility of using the crude trichlorophenol from the autoclave without a distillation should be further investigated. Thus far, Mr. Barna has made one condensation using crude material directly from the autoclave. He obtained a 50% yield of off-color 2,4,5-trichlorophenoxyacetic acid. While this one result is poor, it is, of course, not conclusive and the possibility exists that by proper manipulation of the autoclave reaction, a crude phenol might be prepared that could be used directly in making 2,4,5-T.

PLANT PROCEDURE

1. Charge.

On the basis of the expanded volume at the reaction temperature, the laboratory charges are approximately 2/3 of the autoclave capacity. Operation at 75% of capacity in the plant should be feasible. Best results so far were obtained with tetrachlorobenzene, caustic soda, and methanol in molar ratios of 1.0: 2.5: 12.2. For a 500 gallon autoclave this would mean a charge of 535# of tetrachlorobenzene, 247# of caustic soda, and 980# of methanol. Yield would be approximately 415# per batch.

In the laboratory the sodium hydroxide and tetrachlorobenzene were charged as solids and the methanol added last. The heat of solution of caustic in methanol is sufficient to raise the temperatures to 60-65°C. The tetrachlorobenzene, however, is not appreciably soluble at this temperature and the mixture is a slurry from which the tetrachlorobenzene settles out rapidly. If it were desirable in the plant to make up this mixture outside of the autoclave, provisions would be necessary to prevent excessive methanol losses through vaporization and to keep all undissolved material in suspension.

In most, but not all, cases the charge was made into a water-wet autoclave. The small amount of water present had no discernable effect on the reaction.

2. Expulsion of air from the autoclave.

This procedure should be followed until such time as it has been shown on a pilot scale that the presence of air will not cause oxidation at the reaction temperature.

3. Reaction time.

The average time to heat a batch from room temperature to reaction temperature was 129 minutes in the laboratory. Since it is probable that the plant autoclave can be heated up in a shorter period, a compensating adjustment in holding time at the reaction temperature will be necessary.

Correspondingly, it would be desirable to cool the batch as rapidly as possible once the reaction is completed, which would also necessitate increasing the holding period. It is not possible to accurately predict the heating and cooling cycles in the plant or to compute the exact effect of these cycles being reduced. However, it is suggested that a 6 hr. hold period be used together with minimum heating and cooling periods.

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4. Reaction Temperature and pressure.

Best results obtained thus far were for reactions run at 170°C. Corresponding pressure was 380 to 395 pounds per square inch.

5. Removal of methanol.

It was found in the laboratory that very little methanol distilled off after a batch temperature of 100°C was obtained. This temperature should accordingly be used as the cut off point in the plant. For convenience the laboratory autoclave was also used to distill off methanol. It may be desirable in the plant to empty the autoclave as quickly as possible and use another vessel for recovery of the methanol. If this is to be done, it will be necessary to make the transfer while the batch is above 40°C, since it has been found that at temperatures of 35°C or lower the autoclave agitator may be frozen by solids. Best methanol recovery in the laboratory was 75%, but higher recoveries should be possible if leaks are completely eliminated.

6. Clarification.

The amount of water used to dissolve the sodium trichlorophenolate was designed to give a 10% solution based on a 100% yield. Since the sodium salt is very soluble the amount of water can be decreased to yield solutions up to 50% by weight of the sodium salt if desired.

It was found in the laboratory that, although the insolubles collected were only about 2% by weight of the tetrachlorobenzene charged, the filtration proceeded slowly unless filter aid was used. Using filter aid in an amount approximately 1/2% by weight of the total solution made it possible to filter at a rate of 0.83 gals. per square foot per minute on a Buchner filter. The cake should be washed with a small amount of water and the wash water added to the filtrate to minimize loss of product at this point.

7. Recovery of crude trichlorophenol.

It was determined that a pH of 4.0 was required to completely convert the sodium trichlorophenolate to the phenol. At temperatures above 30°C the phenol was obtained as an oil instead of a solid. In the laboratory separations were made either by filtering off the solid trichlorophenol at 20-25°C or by separating the oil layer at 50-60°C, either process giving the same end results. Trichlorophenol obtained by separation from water as an oil layer had the advantage of containing less water and acid than phenol obtained by filtration of a solid precipitate, thus facilitating the subsequent distillation. The interface between oil and water is distinct and should be easily seen in a sight glass in plant operation.

50% sulfuric acid was used for this step. However, there is no evidence that other strengths or other acids would not serve as well.

8. Distillation.

The entire distillation was performed under vacuum. Since the condenser was run warm to prevent solidification of trichlorophenol, the water vapor that came over first was not condensed. Consequently all material collected in the receiver was specification-grade product.

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The end of the distillation is indicated by two signs: first, the temperature begins to climb rapidly; and secondly, the distillate becomes yellow to brown instead of white. The distillation should be stopped as soon as these signs are apparent to prevent contamination of the product and to prevent baking the residue in the still.

Liquid residue should be dropped hot, immediately upon completion of the distillation. When solid residue builds up in the still, it can normally be removed by dissolving in caustic or 98% sulfuric.

Since the 1, 2, 4 trichlorophenol has a melting point of 59 to 65° C, it is necessary to carefully regulate the temperature at which the condenser is operated.

Chart No. 1 appended to this report shows the vacuums and corresponding temperatures at which satisfactory product was distilled in the laboratory. It should serve as a guide in determining whether distillations are proceeding normally in plant operation.

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TABLE 1
Preparation of 2,4,5-Trichlorophenol
Tabulation of Laboratory Results

Run No.	Reaction Conditions			Mol Ratio Caustic to Tetrachloro- Benzene	Methanol, cc.		Product	
	Temp. °C	Maximum Pressure	Holding Time, hrs		Charged	Recovered	Melting Range, C	Yield, %
1	170	325	6	2	1000	—	58-62	71.1
2	180	450	6	2	1000	40	59-65	83.8
3	160	275	6	2	1000	375	65-68	72.5
4	160	250	6	3	1000	121	59-62	82.5
5	160	230	6	4	1000	71	53-56	78.9
6	170	320	6	2.5	1000	244	59-62	83.2
7	160	250	6	2.1	1000	207	59-63	83.5
8*	170	400	—	2.5	1000	—	—	0
9	170	365	4-1/2	2.5	500	203	59-62	74.8
10	170	365	3	2.5	500	178	59-62	44.0
11	170	395	4-1/2	2.5	1000	666	59-63	91.3
12	170	380	4-1/2	2.5	1000	752	59-62	84.0

* Batch oxidized in autoclave during reaction and completely charred.

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