

A) Chem,
2,4-D + 2,4,5-

DATE: November 2, 1954

TO: Mr. J. Burton

FROM: Mr. M. Schoffman

SUBJECT: 2,4,5-TRICHLOROPHENOL

cc: Mr. J. Browne - Newark
Dr. D. J. Porter - Painesville
Mr. J. R. Trocki - Newark
CF File
Lab File

PURPOSE OF INVESTIGATION:

The purpose of this investigation is, in general, to improve the yield and quality of 2,4,5-trichlorophenol as made in this plant. In particular, these are the problems which are being examined.

- I. Finding optimum conditions for the hydrolysis of tetrachlorobenzene to the 2,4,5-trichlorophenol.
- II. Improving the color of the phenol for possible sale.
- III. Use of the sodium salt of the phenol directly in the production of 2,4,5-trichlorophenoxy acetic acid, after purification by steam stripping.
- IV. Making tetrachlorobenzene in the plant.

STATUS OF THE PROBLEMS:

I. Hydrolysis of Tetrachlorobenzene

A. Operating Temperatures

- 1. Temperatures above 180°C. make dark batches (sodium phenate solution has purple overtones) but show uniformly good conversion to the phenol.
- 2. 2,4,5-trichlorophenol made from dark batches contains a very small quantity of dark, fluffy material which is insoluble in water, benzene and acid water.
- 3. Temperatures below 170°C. make lighter colored batches (sodium phenate solution shades of amber) but the conversion to the phenol may not be as good as at higher temperatures.

B. Use of More Sodium Hydroxide in the Reaction

Decreasing the weight ratio of tetrachlorobenzene to sodium hydroxide from 2.25/1 to 2/1 does not seem to increase the conversion substantially.

DS00011234

C. Premixing Methanol and Sodium Hydroxide

The premixing of the methanol and sodium hydroxide makes for a reaction which "takes off" to a higher initial temperature. Since most of the batches made in this were run at a higher temperature the influence of this operation on the yield is not clear. So that although two batches operated at ca 190°C. gave yields of over 98%, one batch which was cooled down and run at 168 degrees gave a 94.6% conversion.

D. Generally, reactions run at 170° or above give conversion of ca 95% or better. This does not gibe with previous plant standard yield data which report a conversion in the neighborhood of 87.5%. Current data are not available at this writing to indicate whether the standard has been improved.

E. The batch size has been increased from 2250 lbs. tetrachlorobenzene to 2400 lbs. without taxing the equipment.

II. Improving the Color of the Phenol for Sale Purposes

A. No practical way has been found to lighten the color of the very dark batches directly. Oxidizing, reducing and bleaching agents were tried as chemical treatments and activated carbon and alumina were tried as adsorbents without success.

B. A modified steam distillation operating at temperatures above 180°C. gave a white phenol, which when vacuum dried yielded a phenol having a setting point of ca 60°C.

C. Benzene solutions of the dark phenols when washed with water and the insoluble interface filtered off will result in lighter colored trichlorophenols after the benzene is removed.

D. Sodium salt solution of light (cream or buff) colored 2,4,5-trichlorophenol may still show up dark (with purple overtones).

III. Use of Na 2,4,5-TCP Solution, After Steam Stripping, Directly in Making the Derivative Phenoxy Acetic Acid.

Plant runs confirm laboratory experiments in the feasibility of this procedure. Insufficient runs have made (only two) to state whether yields are different than heretofore. The color of the TCP did not seem to affect the color of the T-acid.

IV. Tetrachlorobenzene from the chlorination of mixed dichlorobenzenes is being worked on in the plant at this time in an effort to reduce the cost of basic raw material for trichlorophenol.

RECOMMENDATIONS FOR FUTURE WORK:

I. Hydrolysis Step

A. Cutting reaction time for better color, and faster batch turnover.

DS00011235

- B. Eliminating methanol.
- C. Increasing the tetrachlorobenzene sodium hydroxide ratio preferably by holding the caustic constant and adding more tetrachlorobenzene.
- D. Determining the maximum allowable quantity of lower chlorinated benzenes in the TCB used, in view of our method of making tetrachlorobenzene.

DATA AND DISCUSSION:

I. Hydrolysis of Tetrachlorobenzene

A. Operating Temperatures: The graph of heating cycle in the autoclave is something like Fig. 1. The time between peak temperature

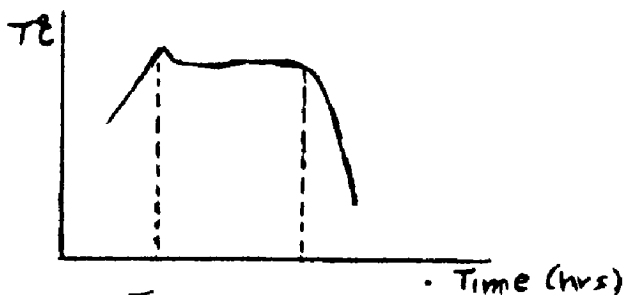


Fig. 1

and the moment when cooling water is put on will be for the purpose of this discussion the reaction time.

1. The relation of temperature to conversion: The following data are given without regard to what other operations may have been made to the batches considered. Three such series are given, each series having had one condition changed.

<u>Batch #</u>	<u>Time Reaction</u>	<u>t° at peak</u>	<u>t° Reaction</u>	<u>% Conversion</u>
L83	4.5	182	170-180	96.6
L84	Missing	Missing	Missing	99.5
L78	Missing	Missing	Missing	97.8
104	4.5	Missing	Missing	97.5
105	4.5	178	170-172	97.6
107	4.5	182	168-170	97.3
118	5.0	198	190	98.2
124	4.5	195	168	95.0
125	4.2	196	188-190	98.7

The "percent conversion" is derived in the following manner (See Appendix I for analytical procedure). The sodium trichlorophenol solution is extracted with benzene to remove caustic insolubles such as tetrachlorobenzene and trichloroanisole and the benzene evaporated. The water solution is acidified and the phenol

extracted with benzene and benzene evaporated. The "percent conversion" is (wt. of phenol/wt. caustic insolubles plus wt. phenol)100. In reality, this percentage is that of the phenol in the organic part of the solution. Since the residues are not analyzed for the components and since the molecular weights of all the components are not too far apart (TCB 216, TCP 197.5, TCAnisole 211.5) this value is fairly close to the actual yield based on tetrachlorobenzene.

From the chart it can be seen that operating at 170° or above gives yields of 95% or better with a strong indication that the higher the temperature the better the conversion.

2. The relation of temperature to color: Color in all cases is the color of a 2% solution of the sodium salt in water as seen through test tube of one inch diameter. Light color indicates shades of yellow to light amber. Dark color indicates brown with purple overtones.

<u>Batch #</u>	<u>t °C.</u>	<u>Color</u>	<u>Interface Residue</u>
104	-	Light	Slight
105	170-172	Light	Slight
106	168-170	Light	Slight
118	190	Dark	Bulky
124	168	Light	Slight
125	188-190	Dark	Bulky

It can be seen that when the temperature is kept in the neighborhood of 170°C. the material is light while in the 190°C. range it quite dark. Furthermore, during the analysis when the benzene solution is washed with water a precipitate forms at the interface. In those batches made at high temperatures, this interface is purple-brown in color and bulky, whereas, in the lower temperature batches the interface is very small in volume and orange in color. (NOTE: This interfacial material may be one of the components precipitating out of the T-ester formulations).

3. Relation of temperature to steam stripping time: The amount of material to be removed by steam will, of course, vary inversely with the percent conversion. Although the records are not too informative on this operation some indication may be had from them.

<u>Batch #</u>	<u>t °C.</u>	<u>S.S. time (hrs.)</u>
118	190	7.5
124	168	15.0
125	188-190	10.5

- B. The effect of using more sodium hydroxide in the reaction

<u>Batch #</u>	<u>TCB/NaOH</u>	<u>% Conversion</u>
L83	2.25/1	96.6
L84	"	99.5
L78	"	97.8
104	2/1	97.5
105	"	97.6
107	"	97.3

There is no evidence from the data that using more caustic in the hydrolysis has increased the yield. It is now proposed to cut back on the NaOH use by increasing the TCB charge while keeping the caustic charge constant.

- C. Effect of premixing methanol and sodium hydroxide: The effect of using this solution is better mixing and a faster time to reach peak temperature. The peak temperature is also higher. Batches 118, 124, 125 representative of this procedure show no yield differences which could not be explained by operating temperature.

II. Improving the Color of 2,4,5-Trichlorophenol

2,4,5-trichlorophenol precipitated by the acidification of plant sodium salt varies in color from light buff to purplish black. Three approaches were investigated to lighten the color of the dark batches:

- A. Chemical destruction of the color bodies
- B. Adsorption of the color bodies
- C. Distillation.

A. Chemical Destruction of the Color Bodies:

Unless otherwise indicated 1% by weight of the decolorizing agent based on the phenol was used at 65-75° while stirring for 30-40 minutes.

1. Bleaching agents:

- a. Sodium chlorite: No effect on the sodium salt solution (35%).
However, the precipitated phenol was reddish rather than purple.
- b. Sodium thiosulfate: Negative on both salt solution and the phenol.
- c. Ammonia: Negative on both salt solution and the phenol.

D200011238

2. Oxidizing Agents:

- a. Nitric acid: Phenol washed with equal volume of 50% concentrated HNO_3 , then water washed. No improvement.
- b. Sulfuric acid: Phenol washed with 50% concentrated sulfuric, then water washed. Phenol appears very slightly lighter.

c. Reducing Agents:

Hydrazine (85%). Negative results on both sodium salt and phenol.

B. Adsorption of color bodies:

1. Darco G60 3% by weight, Super-Cel 1%. Negative results at 65°C. and 30 minutes stirring of sodium salt solution. Precipitated phenol appears slightly lighter.
2. Activated alumina. Same treatment as with Darco. No improvement in sodium salt or phenol.

C. Distillation

1. Vacuum distillation: Vacuum distillation is frowned upon as being too taxing on steam supply and long in duration.
2. Steam distillation: Two methods of steam distillation were tried. In the first instance the sodium salt solution (previously steam stripped) was acidified in the still pot and steam started. The pot temperature did not go above 105° and the phenol/water ratio of the distillate was about 1/20 by volume. This method was discarded because of excessive time and steam requirements.

At the suggestion of Mr. Trocki, most of the water was removed from the phenol before the steam was put on, in order to operate at higher temperatures. Thus, the average pot temperature was ca 190° and the average vapor temperature was 145-165°.

Towards the end of the distillation, the pot temperature began to rise and the phenol came over yellow. Distillation was stopped when the color of the phenol was amber.

Av. pot temperature 189°C.
Highest pot temperature ... 210°C. (17 minutes).
Vapor temperature ... 138-165°C.
Time ... 2 hours.
Yield of 2,4,5-TCP ... 815 gms ... 43.5°C. set point.
Yield of 2,4,5-TCP after vacuum drying... 775 gms set point 59.9°C.
Volume steam condensate ... 1445 cc.
Residue: Black, but caustic soluble ... 56 gms (56/775 = 7.2%).
Color ... Slightly creamish white.
Color of sodium salt ... Light yellow.

DS00011239

3. Direct Use of Steam Stripped Na-TCP in Making the T-Acid: The standard method has been to acidify the NaTCP from the autoclave or steam stripping vessel, wash and resaponify. These steps were eliminated successfully in a laboratory run, (77% yield of good quality T-Acid).

Two runs have been made in the plant. Single autoclave runs (Ba 118 ff) were used in charging these special batches. The resulting T-acids were of normal quality. The batches were weighed off in the plant as well as yield assayed in the control laboratory.

<u>Batch #</u>	<u>Plant Weighed Yield</u>	<u>Yield Laboratory Assayed</u>	<u>Color</u>
19	79.5% dry basis	87%	Light
20	54% " "	71%	Light

The vast difference in yields between two runs cannot be explained by any reported operational errors. More runs will have to be made to determine the advisability of this method. These points can be made, however:

- a. The NaTCP from Ba 118 on were generally dark colored (due to high operating temperature) but the resulting T-acid was very light showing that for T-acid use the high operating temperature is acceptable.
- b. The huge discrepancy between plant and control laboratory yields put the yield determination system in doubt. Some credence may be lent to the plant yield in Ba 19 of 79.5% since it approximates that obtained in the laboratory utilizing a similar method.

4. Tetrachlorobenzene from Chlorination of Mixed Dichlorobenzene:

One run was made in the plant. Because of operational difficulties complete data could not be gained from this run as to yields, set points, etc.

The dichlorobenzene analyzed on the basis of chlorine determination is 99+%.

DS 00011240

APPENDIX A

ANALYSIS OF 2,4,5-TRICHLOROPHENOL AUTOCLAVE BATCHES FOR CAUSTIC INSOLUBLES

1. Na-TCP solution from autoclave diluted with enough water so that the batch is liquid at room temperature.
2. Ca 100 gms of sample are weighed out.
3. The NaTCP is extracted with 75, 50 and 50 ml of benzene to remove trichloroanisole and unreacted tetrachlorobenzene.
4. The benzene solution is washed once with 50 cc H₂O and the water added to the mother liquor.
5. The benzene solution is dried with anhydrous sodium sulfate in a beaker and filled into a tared 4" glass evaporating dish (weighed to .001 gms). The beaker and filter cake are washed with 2 x 25 cc benzene. The benzene is evaporated over a steam bath and the residue weighed (caustic insolubles).
6. The NaTCP solution is acidified to congo red with H₂SO₄. The water layer is decanted into a separatory funnel, extracted with 75 cc benzene and discarded. The same benzene is used for taking up the TCP from the beaker. The beaker is washed with 2 x 25 ml benzene and the washings added to the separatory funnel.
7. The benzene-TCP solution is washed with 2 x 75 cc water at 30°. Any suum at the interface is kept with the benzene.
8. The drying with sodium sulfate and filtration as in step 5 ff.

$$\% \text{ conversion} = \frac{\text{weight TCP}}{\text{weight TCP} + \text{wt. caustic insolubles}} \times 100$$

M. Schoffman

MS:jp

2800011241