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PIGMENT COLOR RESEARCH REPORT

THE EFFECT OF CHLORINE IN GPC ON THE SPECTROPHOTOMETRIC
CURVE OF SULFURIC ACID SOLUTIONS

1953

Period Covered

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NEWARK PLANT

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Final Report

Title: THE EFFECT OF CHLORINE IN CFC ON THE SPECTROPHOTOMETRIC
CURVE OF SULFURIC ACID SOLUTIONS

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SUBMITTED BY: C. W. MANGER

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INTRODUCTION

Copper phthalocyanine blue and polychlor copper phthalocyanine green in sulfuric acid solution give characteristic spectrophotometric light transmission curves in the near infrared. The curve for the polychlor CPC is markedly different from that of CPC Blue containing less than 6% Cl.

During the course of a study involving the comparative differences of polychlor CPC made by different processes, the presence of lower chlorinated species of CPC was suspected. Since the infrared curve of the polychlor CPC has three minima it is possible that there is a mixture of two or more species present. The most likely candidates would be CPC's containing somewhat less than 16 chlorine atoms, e.g. dodecachlor, octachlor, and tetrachlor CPC's. Although a sample of the dodecachlor CPC was not available, curves have been run on samples of octachlor, tetrachlor, and dichlor CPC's which can be compared with those of polychlor and Cl-free CPC's. Curves were also run on polychlor metal-free PC, polychlor ALPC, and several samples of "pigmentary crude" polychlor CPC.

II. Summary and Conclusions

1. The two transmission minima associated with Cl-free CPC shift to progressively higher wavelengths as the chlorine content of the CPC is increased up to the octachlor. The polychlor species, however, shows three minima, the strongest of which is at $860 \text{ m}\mu$ (See figure 1.)
2. Lower chlorinated species of CPC were not found in uncontaminated polychlor CPC. The three minima in the curve of a normal polychlor CPC are found only in that species.
3. The solubility of CPC in H_2SO_4 decreases as the Cl content increases.
4. The color of the H_2SO_4 solution of CPC changes from a greenish hue for the Cl-free, through amber for the octachlor, to a reddish hue for the polychlor.
5. A sensitive method for the separation of low chlorinated CPC from polychlor CPC was developed. It is possible to detect the presence of CPC Blue (6% Cl) in a sample of polychlor CPC by making use of the widely different solubilities in H_2SO_4 . A small amount of CPC Blue was found in GT-674-D SD-121, using this method. (See figure 2.) This is undoubtedly due to contamination in the plant, as a sample of lab extracted crude green showed no evidence of CPC Blue.
6. Polychlor ALPC and polychlor metal-free PC were found to be somewhat unstable in H_2SO_4 solution. Their spectrophotometric curves are similar in shape to those of polychlor CPC but the minima are at slightly higher wavelengths. (See figure 3.)
7. All samples of polychlor CPC tested gave essentially the same spectrophotometric curve.

III. Experimental

A. Samples Studied

The following samples were used in this study.

- 1) Chlorine-free CPC - acid-pasted 1226-7A (AJS)
- 2) Dichlor CPC - solvent-milled 1425-68A (FFE)
- 3) Tetrachlor CPC - acid-pasted 1425-36DP (FFE)
- 4) Octachlor CPC - acid-pasted 1425-25P (FFE)
- 5) Polychlor CPC - solvent-milled GT-674-D SD-121
- 6) Polychlor CPC - Orchem Green GX Lot 1 and Lot 2
- 7) Polychlor CPC - "Green 25" (1454-29A, FFE)
- 8) Polychlor CPC - Gottlieb 313-69B
- 9) Polychlor ALPC - 1348-SOC (FFE)
- 10) Polychlor Metal-free PC - Orchem J-59 - F-122

B. Procedure for Spectrophotometric Curves

A few milligrams of each pigment was completely dissolved in C.P. concentrated H_2SO_4 at room temperature. The concentration was adjusted by adding sufficient H_2SO_4 to give a transmission curve in the infrared having a minimum of about 10 to 20% transmittance. Transmission curves were run on the Beckman Model DU spectrophotometer, using H_2SO_4 as the blank, from 680 $m\mu$ to 1000 $m\mu$. Readings were taken every 10 $m\mu$ except in the vicinity of a minimum where they were taken every 5 $m\mu$. In the case of the polychlor ALPC and polychlor metal-free PC, which were not very stable in H_2SO_4 solution, fewer readings were taken.

C. Procedure for the Separation of CPC Blue from CPC Green

Two grams of pigment was placed in a clean beaker and 10 ml concentrated H_2SO_4 added gradually. After the mixture was thoroughly pasted, it was poured into a clean, fine porosity, sintered glass crucible and suction applied. The first few drops were collected in a test tube and removed from the filter flask. Sufficient H_2SO_4 was added to give a spectrophotometric transmission curve having a minimum of about 10 to 20% transmittance. If any CPC Blue is present in the CPC Green it will give a transmission curve in the infrared similar to that of CPC Blue. For comparison purposes, a curve may also be run on the bulk of the sample by using the paste in the crucible.

IV. Results

The following table shows the location of transmission minima of the samples studied.

<u>Sample</u>	<u>Wavelengths at Minima (mμ)</u>
1) Cl-free CPC	700, 785
2) Dichlor CPC	710, 800
3) Tetrachlor CPC	720, 805
4) Octachlor CPC	820
5) Polychlor CPC GT-674-D SD-121	730, 815, 860
6) Polychlor CPC-Oraham Green GK Lot 1, Lot 2	730, 810, 860
7) Polychlor CPC-"Green 25" (1454-29A, FFE)	730, 820, 860
8) Polychlor CPC-Gottlieb 313-69-B	ca 720, 820, 860
9) Polychlor AlPC	ca 840, 890*
10) Polychlor Metal-free PC	ca 820, 880*

* These samples are not very stable in concentrated H_2SO_4 solution, consequently, only approximate curves could be obtained. All other samples seemed to be stable in H_2SO_4 solution.

V. References

1462-7, 8
1268-12

VI. Patent Situation

Competitive Patents

None

Patent Protection

De Pont Patents and Applications

None

Filing Action

None. This work has been fact finding in character.





