54-32 PREPARATION OF MONOCHLOR/CPC SALTS OF ACETIC ACID, PROPIONIC ACID, PHOSPHORIC ACID AND SULFURIC ACID
By: A. R. Hanks 1/54 - 9/54

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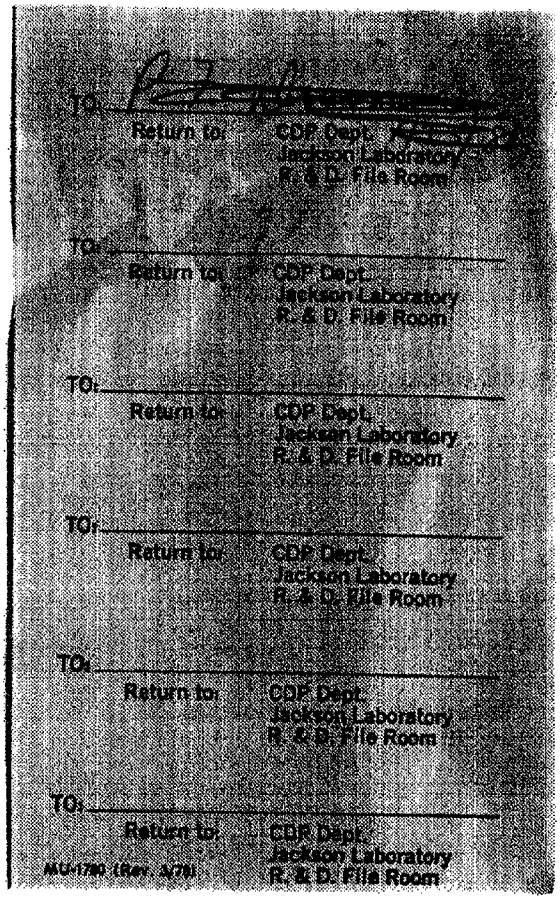

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Progress Report

PREPARATION OF MONOCHLOR/CPC SALTS OF ACETIC ACID, PROPIONIC ACID, PHOSPHORIC ACID AND SULFURIC ACID.

JANUARY - SEPTEMBER, 1954.

CHARGE: A-IC-20

SUBMITTED BY: A. R. Hanke

APPROVED BY: B. H. Perkins 10/11/54

DATE SUBMITTED: 10/4/54

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I - INTRODUCTION:

This work was started in connection with establishing the existence of a crystal modification of monochlor/CPC which we have called σ phase. It had been hoped that regenerating the solid phase Monochlor/CPC in different ways would lead to a means of converting α to σ phase CPC which conversion had never been accomplished. The way chosen for study was the formation of Monochlor/CPC salts other than the hydrosulfate and subsequent hydrolysis of these salts. This part of the experiment was only moderately successful, but the work done in preparing salts other than the hydrosulfate was of sufficient interest to record. This report summarizes that work.

II - SUMMARY AND CONCLUSIONS:

1. MonoCl/CPC salts of the following acids were prepared:

   a. Acetic Acid
   b. Propionic Acid
   c. Phospheric Acid

2. In the case of Acetic Acid, the dry salt analyzed to MonoCl/CPC.2HOAc.

3. All the salts were prepared by first dissolving the MonoChlor/CPC in H_2SO_4 and then precipitating a particular salt by slowly adding the acid to the sulfuric acid solution.

4. All of the salts are highly crystalline materials with characteristic X-ray records. The hydroacetate and hydropropionate are isomorphous.

5. The attempt to prepare salts of formic acid and benzoic acid failed. The reaction of formic acid with sulfuric acid prevented the utilization of this method. In the case of benzoic acid, no CPC salt precipitated.

6. The X-ray patterns of the heated hydro acetate shows that CPC can exist in a modified crystal structure, but this is not the σ phase configuration. No σ phase was produced by hydrolysis of any of the salts investigated.

7. The hydro sulfate, when precipitated slowly, forms crystals easily seen in the light microscope. During hydrolysis, the external form of these crystals remains the same, although the internal structure transforms from that of highly crystalline hydrosulfate, through an amorphous stage, and finally to α phase CPC.

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III - PATENT ACTION:

This work shows that treatment of CPC salts can result in a modified crystal lattice for CPC. More work would be necessary to establish whether or not these products containing a modified crystal lattice are patentable from the pigment point of view. No such additional work is planned.

IV - EXPERIMENTAL:

The following two samples were used for this work.

1467-13A - α phase monochlor/CPC
1479-3B - γ phase pigmentary crude monochlor/CPC

A - Preparation and Hydrolysis of MonoChlor/CPC Hydroacetate

1. Dissolve 10 g. sample in 158 g. conc. H_2SO_4.
2. Add glacial HOAc dropwise until the appearance of a solid phase (microscope). This requires about 15 ml. Let stand about 1/2 hour after which time the solid phase appears as a mass of acicular crystals. The actual appearance is very dependent on the rate of addition of the HOAc and on the aging conditions.
3. Continue adding HOAc at a more rapid rate until about 450 ml. has been added.
4. Filter. Reslurry in more HOAc and filter again. Continue this washing process until the hydro acetate is washed sulfate-free. Dry at 140°F.
5. Hydrolyze a portion of the dry hydro acetate by throwing it into water. Also hydrolyze a portion by throwing it into dilute NH_4OH solution.
6. Heat a portion of the hydro acetate in a vacuum to 280°C for 2 hours.
7. Follow all of these operations by means of X-ray diffraction records of the wet presscake and the dry pigment.

NOTE:
The hydroacetate (dry) was subjected to total acidity analysis by the analytical group with the result 17.3% HOAc. A result of 17.9% HOAc is theoretical for MonoCl/CPC.2HOAc.

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B - Preparation and Examination of MonoCl/CPC Hydropropionate

1. Dissolve 10 g. pigment in about 160 g. of H_2SO_4.

2. Add propionic acid dropwise until the appearance of crystals (microscope). About 30 ml. will be required.

3. Allow crystals to ripen for about 2 hrs. and then add propionic acid more rapidly to a total volume of approximately 600 ml.

4. Filter through sintered glass.

5. Wash by reslurrying and direct washing until sulfate-free.

6. Dry at 110° for 5 hours.

NOTE: Upon analysis of total acidity by the anayltical group, 24.7% propionic acid was found. The theory for 2 molecules associated with one CPC molecule is 19.5%. The high figure is probably due to some sulfuric acid not washed out of the sample or some remaining propionic acid. X-ray diffraction shows the hydroacetate and hydropropionate as isomorphous; hence, it is reasonable to assume that CPC is associated with two molecules of propionic acid.

7. Hydrolyze the salt by slurrying it in water and adding a slight excess of caustic solution followed by boiling.

8. Obtain an X-ray record of the hydropropionate as a wet presscake and as a dry powder; also, after aging as a dry powder for 8 months, obtain an X-ray record of the hydrolyzed product.

C - Preparation and Examination of MonoChlor/CPC Hydrophosphate.

Procedure:

1. Dissolve 10 g. pigment in 165 g. H_2SO_4.
2. Add H_3PO_4 dropwise to incipient precipitation (microscope). This takes around 37 ml. Continue the dropwise addition to a total addition of 100 ml. Filter through sintered glass.

NOTE: The filtration was very slow. Centrifuging was not much better. Diluting with n-propanol, dioxane, acetic acid or formic acid all caused destruction of the hydrophosphate.

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3. Since no good way of washing out the sulfuric acid or excess phosphoric acid is known, suck the presscake as dry as possible and store as a presscake.

4. Run an X-ray record on the wet presscake. Rerun the wet presscake after about 8 months.

D - Preparation and X-ray Examination of MonoCl/CPC Hydrosulfate

Trial I

1. To about 0.5 g. pigment add enough H_2SO_4 to make a fairly stiff paste.

2. Obtain X-ray diffraction record of this paste as soon as possible before the H_2SO_4 has a chance to pick up much moisture.

3. Obtain another X-ray record after moisture pick-up from the air is allowed.

4. Observe crystalline nature of solid phase with microscope.

Trial II

1. Repeat the above experiment but add enough H_2SO_4 to dissolve the CPC.

2. Add water dropwise to incipient crystallization. Observe under the microscope.

3. Let crystals digest for about an hour.

4. Add more water to complete hydrolysis.

5. Obtain X-ray record and observe appearance under the microscope.

E - Attempt to Prepare the Salt of Benzoic Acid

Benzoic acid was dissolved in H_2SO_4 and this solution added to a solution of MonoCl/CPC in H_2SO_4. Nothing happened. Adding solid benzoic acid eventually produced a saturated solution of benzoic acid and the microscope showed benzoic acid crystals but nothing else.

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F - Attempt to Prepare the Formic Acid Salt

Formic acid was added dropwise to a solution of 10 g. pigment in 150 g. H_2SO_4. Gas evolution was observed. After the addition of about 25 ml. of formic acid, crystals were observed. The formic acid addition was continued to a final volume of about 600 ml.

It was observed that it was practically impossible to wash these crystals sulfate-free. An X-ray record of the wet crystal mass taken early in the washing cycle showed much amorphous material with some evidence of MonoCl/CPC hydrosulfate. No CPC or hydroformate salt was present. Later in the washing cycle, the X-ray pattern was that of poorly formed α phase CPC.

V - DISCUSSION:

One of the outstanding observations of this work is that these CPC salts are highly crystalline materials, yielding well defined X-ray diffraction records. They are not materials in which a variable amount of acid enters the CPC lattice, swelling it in varying amounts, causing a disorder in the crystal structure resulting in an amorphous pattern.

Such a range of disorder has been observed in the case of MonoCl/CPC hydrosulfate, but this is not because of the effect of the sulfuric acid, but because of the effect of the water. MonoCl/CPC hydrosulfate is highly crystalline, but this fact must be observed rapidly because as water is rapidly taken up by the sulfuric acid, hydrolysis begins and the crystal structure of the hydrosulfate is destroyed. The new structure of α phase CPC does not immediately manifest itself until more water is added. Then, there is a reorganization from an amorphous state to the crystalline state of poorly formed α phase MonoCl/CPC. This transition is not a simple one and does deserve more study than was given here.

Another observation is that if the hydrosulfate is allowed to form slowly, it forms yellowish green crystals easily seen in a light microscope. This fact is well known but an interesting additional observation is that these crystals do not change in their external form as hydrolysis proceeds. The only apparent change is from green to blue, and yet internally they have undergone a change from crystalline hydrosulfate to an amorphous stage, to poorly crystalline α phase CPC. It is impossible then, that the external form of the final crystal reflects the internal structure of this crystal. It must be a pseudo crystal that has the external form of the initially precipitated MonoCl/CPC hydrosulfate, but the internal structure of α phase CPC.

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The preparation of the hydroacetate presented no difficulties. The resulting crystalline form is far more resistant to hydrolysis than the hydrosulfate. It can be dried at 110°C and keeps indefinitely as a dry powder with only superficial evidence of hydrolysis. Analysis shows it to exist as MonoCl/CPC.2HOAc. It is a dull green in color. The acetic acid can be driven off by heating to around 250°C. for several hours in a vacuum. When this is done the resulting CPC exhibits a modified α phase lattice. The peaks at 6.4°, 6.9°, 9.5°, and the group around 15.5°, represent a displacement to lower 2θ values than typical α phase monochlor CPC. This is shown by Figure 1. When the hydroacetate is hydrolyzed, it also yields α phase CPC, but with less change in the crystal lattice. This is also shown in Figure 1. It can be seen that the shift is so slight that it approaches the experimental error. However, in view of the shift observed in the patterns derived from the heated hydroacetate product, it is reasonable to conclude that this type of change in the lattice occurred upon hydrolysis, as well as upon heating, but to a lesser degree. Such a shift can be interpreted as meaning an increase in the interplane spacing distance for those planes responsible for the diffraction peaks that shifted. Figure 1 also shows, for reference, a typical α phase curve, showing an unusually high degree of crystallinity. Its high degree of crystallinity was obtained by refluxing an acid-pasted MonoCl/CPC in dichlorbenzene for 4 hours, followed by heating in a vacuum for two hours, at 300°C. This is the most crystalline appearing X-ray pattern of α phase CPC on record.

The hydropropionate was prepared as easily as the hydroacetate. In outward appearance it is the same as the hydroacetate. Its hydrolysis appears to be even more sluggish than the hydroacetate. No heating experiment was attempted because propionic acid has a higher boiling point than acetic acid and it was difficult to drive off the acetic acid from the hydroacetate. Chemical analyses showed 2.5 moles of propionic acid for one mole of monoCl/CPC but this figure is thought to be too high either because of failure to wash out all of the sulfuric acid or because of some residual propionic acid. Since the X-ray records show the hydroacetate and hydropropionate as isomorphous crystals, it is reasonable to suppose that the MonoCl/CPC crystallizes with 2 moles of propionic acid. The hydrolyzed salt gave an X-ray record very much like that of the hydroacetate. The change in position of some of the diffraction peaks from normal α phase CPC was about the same.

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The preparation of the hydrophosphate presented some difficulties. No good way was found to remove the small amount of sulfuric acid present and no good way was found for removing the excess phosphoric acid. That a hydrophosphate was actually formed can be seen from Figure 2 which shows an X-ray record of the presscake. Hydrolysis appeared to take place more readily than in the case of the hydroacetate or hydropropionate, but less rapidly than in the case of the hydrosulfate. Upon aging in the presence of moisture-containing air, the crystalline X-ray pattern was replaced by one that was practically amorphous. In this respect it is like the hydrosulfate, but not like the hydroacetate. It appears that the higher the ionization constant of the acid, the more prone to hydrolysis is the CPC salt. This is contrary to the usual rule of almost complete hydrolysis of the salts of weak acids and bases. Figure 2 shows X-ray records of all of the CPC salts discussed. It clearly illustrates the isomorphism of the hydroacetate and hydropropionate. The hydrophosphate and hydrosulfate are seen to be different.

No doubt it is possible to prepare still other salts of CPC using this method. No attempt was made to prepare salts of butyric or pentanoic acid. No success was had in preparing the salts of benzoic acid. It may be possible that such salts can be prepared by some other method but the time was not taken to explore other methods. One such method may be ball milling the CPC in the particular acid whose salt is desired. This method failed in the case of chlorine-free CPC ball milled in HOAc (KN-54-25), but it might work for H_3PO_4.

VI - NOTEBOOK REFERENCES:

This work is recorded in Notebooks:

1463-13-17-26.

1476-16-17-18-27-35.

MPH

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FIG. 1

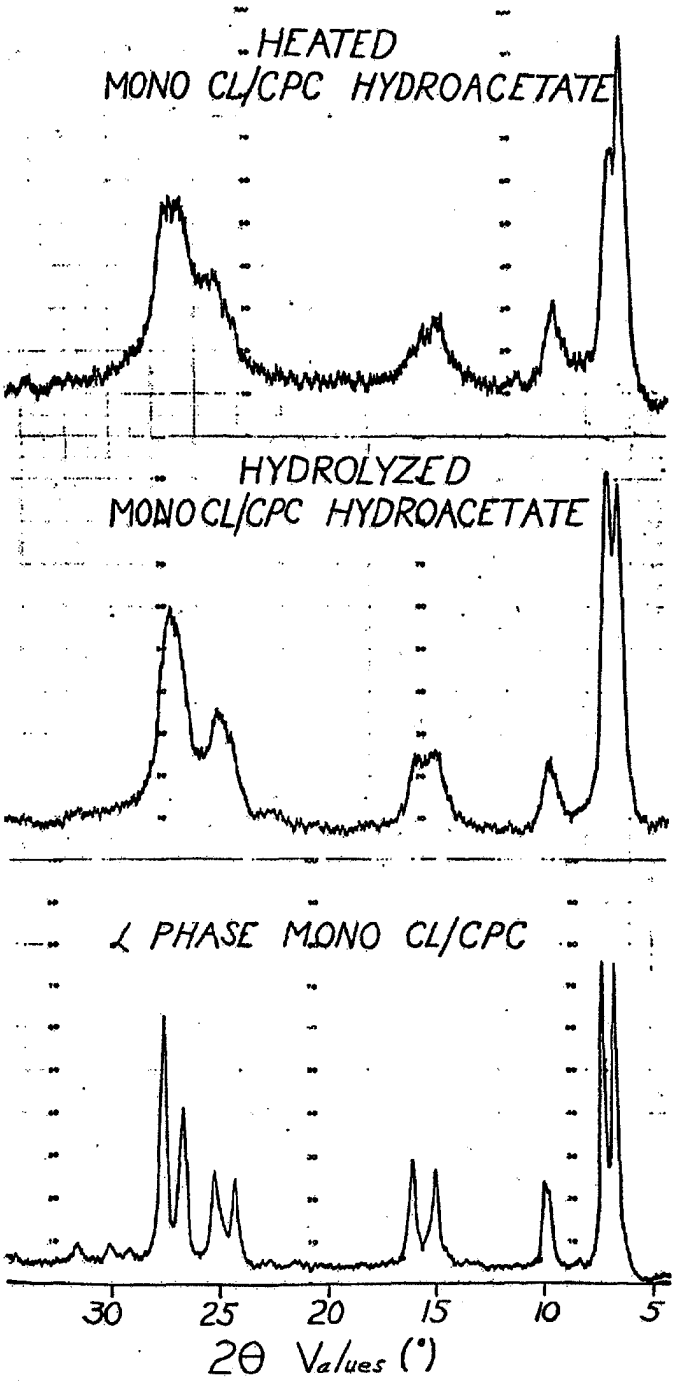

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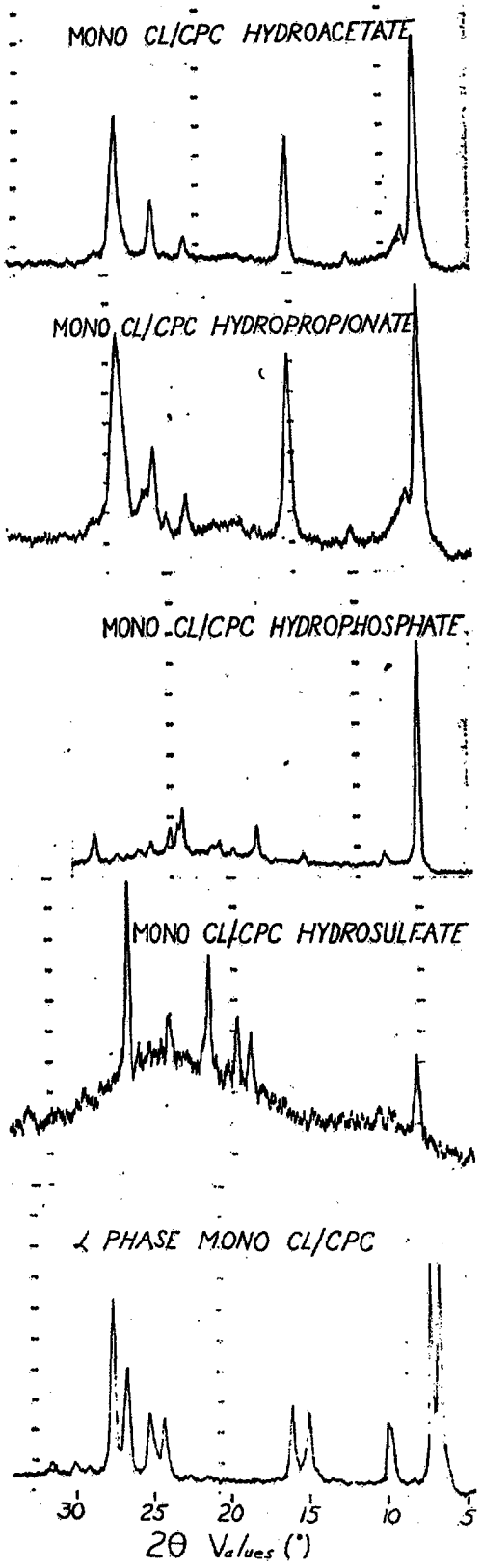
FIG. 2



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