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CPC-AF: CHARACTERIZATION AND ASSAY

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

CPC-AF: CHARACTERIZATION AND ASSAY

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ABSTRACT

CPC-AF, as currently made, is ca. 80% or more CPC and only 20% or less of the actual crystal-stabilizing agent. This report includes evidence to aid in identifying the active ingredient(s), a proposed assay method, and suggestions for further study.

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CPC-AF: CHARACTERIZATION AND ASSAY

I. INTRODUCTION

The additive "CPC-AF" was developed several years ago primarily as an "anti-flocculation agent" for copper phthalocyanine (CPC) pigments. It was found to also impart crystal stability to the unstable α phase, chlorine-free CPC, preventing it from converting to large β phase crystals in solvent-containing systems. There has been a gradual deterioration in quality of the CPC-AF in BT-427-D (Blue R/CPC-AF/Ca Staybelite) and BT-425-D (Blue B/CPC-AF/CaSx), thus requiring undesirable higher levels of the agent for effective stabilization. A number of recent batches of CPC-AF were so poor that acceptable quality BT-427-D could not be made even with use of a considerably increased amount of CPC-AF.

Although CPC-AF has been made for a number of years, its actual composition is not known with certainty. It is, therefore, of considerable interest to characterize this additive and, if possible, to develop an assay method to determine its composition.

II. SUMMARY AND CONCLUSIONS

1. CPC-AF, as currently made in the plant (N-873-A), is primarily α phase, partially chlorinated CPC in the order of 80% or more. The active ingredient ("active AF"), which stabilizes the unstable α phase Cl-free CPC in BT-427-D, is in the order of 20% or less.

2. The CPC component can convert partially to β phase, indicating the presence of some α phase Cl-free CPC.

3. The "active AF" is a CPC-like material which is most likely one or more substituted CPC's. There is strong IR and elemental analysis evidence for it (or them) to be something like a carboxy-benzoyl and/or a carbamido-benzoyl substituted CPC.

4. "Active AF" can be isolated, at least in part, from as-made CPC-AF by dissolving in 96% H_2SO_4, diluting to 60 to 80%, filtering off the CPC-HSO_4, and hydrolyzing the filtrate. The material so obtained imparts stabilization to Blue R in solvent systems.

5. "Active AF" gives a poorly crystalline x-ray diffraction pattern with some resemblance to α phase CPC. This indicates very small or "mixed-up" crystals. Since the material dries out hard (except when freeze-dried) it could be small crystallites and/or quite hydrophilic.

6. Since "active AF" most likely is effective in stabilizing α phase Cl-free CPC in solvent systems through a solution-adsorption mechanism, it should be readily available at the time it is needed to be used efficiently. If, for example, it was inside hard aggregates, it would not be available until dispersed.

7. In many cases where samples of CPC-AF in BT-427-D were tested for crystal stability in a rapid hot solvent test, considerable growth and conversion to β phase resulted, whereas, the same samples were stable in the 30J paint test. If, however, the sample was ball-milled in solvent before heating, considerably less change was observed because of the greater availability of "active AF" when dispersed. It is, therefore, strongly recommended that the common hot solvent test no longer be used with BT-427-D type pigments.

8. It is fairly certain that a more efficient use of the "active AF" could be obtained if the BT-427-D process was changed to make this material more readily available. For example, since it is more soluble in, say, 70% H_2SO_4 than CPC, it would be interesting to try a co-acid swelling with sufficient acid of as-made CPC-AF with pre-milled Blue R. This should be then slowly hydrolyzed so that the "active AF" comes out of solution strongly attached to the surfaces of the unstable CPC.

9. A potential source of poor stability in BT-427-D, other than sub-standard CPC-AF, is that of Blue R of less than standard stability without the CPC-AF.

10. The 30J paint test for crystal stability of BT-427-D-type pigments is recommended in preference to any other test. It can be used to give reliable data by (1) ball milling for 2 or 3 days, (2) storing wet tints in oven at 140°F. for 2 or 3 days, and (3) using slurry-mixed or dry-mixed counterparts of BT-427-D. The dry mix test saves considerable time and results are essentially as valid as with the slurry mixed samples.

11. Differential thermal analyses confirm the differences in phthalonitrile behavior. The "old" yellow type quite definitely contains a catalyst-type impurity which causes it to react at a lower temperature than the new gray type.

12. An analytical method for assaying the percent "active AF" in CPC-AF-containing samples is under development and is to be proved out. It involves a fractionation of 70% H_2SO_4 and appears reliable.

III. PATENT SITUATION

Consideration should be given to the patent possibilities of the suggestion of making the "active AF" more readily available through the proposed procedures of co-acid swelling with pre-milled Blue R.

IV. SUGGESTIONS FOR FURTHER WORK

1. Determine solubility of "active AF" in 70% H_2SO_4 at 100°C. to establish a desirable pigment to 70% H_2SO_4 ratio in acid swelling.

2. Acid swell Blue R in a saturated solution of "active AF" and hydrolyze by adding water gradually. Determine minimum quantity of "active AF" to give desired stability.

3. Determine function of CaSx and whether, say, MgSx or ZnSx are more effective. Is CaSx really necessary if "active AF" is efficient?

4. Try HT drowning a 96% solution of as-made CPC-AF (no salt) or with crude CF/CPC or a co-pre-milled mixture, to, say, 80% to precipitate most of the CPC but leave the "active AF" in solution. Then HT drown at, say, 60% to hydrolyze the CPC and precipitate some of the "active AF". Then finally, HT drown at 50% H_2SO_4 to hydrolyze the "active AF" on the CPC. A continuous, refrigerated, pipeline process in which water is added at different lengths, may be applicable. The objective is to dilute the acid gradually so as to "coat" the CPC with available "active AF".

5. Determine adsorption isotherms of "active AF" on purified CPC in various % H_2SO_4 in range 50% to 80% to clarify what goes on in the acid swelling and in the preferred assay method.

6. Determine adsorption isotherms of "active AF" on purified CPC in solvents, such as xylene, to learn more about the crystal stabilization process.

7. Reflux "active AF" in a strong base, such as alcoholic KOH, to see if the proposed amide substituent hydrolyzes to carboxyl (suggested by H. Matrick). This could also happen in acid swelling of the crude CPC-AF (SF-83) and might be determined by IR before and after refluxing in a strong base. It would also be interesting to determine composition of "active AF" component of CPC-AF unextracted bake (without salt).

V. EXPERIMENTAL DETAILS NB 1849

A. Characterization of CPC-AF

CPC-AF, as currently made in the plant, i.e., N-873-A of standard quality, is a mixture of at least two principal components. The major component, in the order of 80% or more by weight, is a partially chlorinated CPC. The minor component, in the order of 20% or less, appears to be one or more substituted CPC's. This minor component is the "active AF" in the additive. Examination of CPC-AF by IR spectra, x-ray diffraction, near IR absorption of H_2SO_4 solutions and analyses for Cl, C,

H, N, and Cu, show definite evidence for only α phase, low chlorine CPC. The quantity of "active AF" is too low for unequivocal identification.

1. CPC Component

IR spectra of as-made CPC-AF samples show definite evidence for only α phase, chlorine-containing CPC. Near IR spectra of concentrated H_2SO_4 solutions show low chlorine CPC. X-ray diffraction patterns show α phase, low chlorine CPC. Sublimate and residue from a sublimation of plant CPC-AF contain some β phase in with α phase, indicating some chlorine-free α phase in the original sample which converts to β phase at high temperatures (>400°C.). The α phase which does not convert to β is most likely chlorinated, e.g., monochlor. Similar results are obtained when plant CPC-AF is refluxed in solvents such as xylene, i.e., some β phase is formed.

2. "Active AF" Component

The component of as-made CPC-AF which imparts crystal stabilization to the unstable, α phase, chlorine-free CPC in the presence of calcium Staybelite (BT-427-D) is a CPC-like material which is most likely one or more substituted CPC's.

Acid crystallization of lab-made CPC-AF (2.0 moles pyridine) by P. H. Griswold gave at least 10% of material soluble in 80% H_2SO_4, with a major portion of this being soluble in 60% acid. When his three fractions were incorporated with Blue R and CaSx (BT-427-D) and subjected to the 30J paint stability test, the 95-80% H_2SO_4 fraction (soluble in 95% H_2SO_4, precipitates on dilution to 80% H_2SO_4), which contained most of the CPC and relatively little "active AF", showed some but relatively little stability. His fractions at 80-60% and 60-25% H_2SO_4, which contained very little CPC and most of the "active AF", showed essentially perfect stability, indicating that the "active AF" is indeed the material which stabilizes the unstable CPC. It must be reiterated here that the CaSx is also a required component in BT-427-D, as shown in the past.

To further characterize "active AF", a relatively "large" sample (10 grams - 1849-24A) has been isolated from 500 grams of plant N-873-A, lot 139, by dissolving in 10,000 grams of 96% H_2SO_4, diluting with water to 70%, filtering, and hydrolyzing the filtrate to 30% H_2SO_4. Since the CPC component is practically insoluble in 70% acid, this sample should be essentially pure "active AF". It is not feasible at present to determine whether any "active AF" of a composition different from that which is soluble in 70% H_2SO_4 is insoluble in 70% acid and is not removed with the soluble portion.

A study of the "active AF" has shown the following:

a. Its IR spectrum is somewhat similar to that of α CPC, but it is definitely different in many respects. The spectrum is consistent with the several proposed structures involving substituted CPC's. IR and elemental analyses strongly indicate something like carboxy-benzoyl and/or carbamido-benzoyl substituted CPC.

b. Its x-ray diffraction pattern resembles that of a very poorly crystalline α phase CPC, indicating very small or "mixed-up" crystallites. Since this material dries out extremely hard (unless freeze-dried), very small crystallites are indicated. It is probably very hydrophilic which might also cause it to dry out hard.

c. It is more soluble than is CPC in H_2SO_4 down to 60%.

d. Its λmax in 96% H_2SO_4 solution is lower than that of CPC (ca. 4% Cl). λ_{max} of each varies with percent H_2SO_4 as follows:

% H_2SO_4	λmax "Active AF"	λmax CPC
96	785	798
70	755	765
65	750	762
60	735	-

e. Although not actually measured, it should have a slightly greater solubility than CPC in paint solvents such as xylene. This is necessary to permit it to dissolve and adsorb on the surfaces of the unstable CPC crystallites to inhibit their growth and phase conversion.

f. Analytical data on the following samples of CPC and "active AF" are tabulated below:

1. 1727-20 Purified Blue B/CPC from BT-304D Std.
2. 1849-21J Purified Blue B/CPC from N-623, X-149.
3. 1849-21G CPC component of CPC-AF, lot 139 (contaminated with some polychlor CPC and residual "active AF")
4. 1849-24A "active AF" isolated from lot 139 at 70% H_2SO_4.
5. 5116-70A_1 PHG's acid crystallization at 95-80% H_2SO_4 of 2.0 mole pyridine AF - contains mostly CPC with some "active AF" (ca. 90% of yield).
6. 5116-70B_1 as A, but 80-60% H_2SO_4 - contains mostly "active AF" with some CPC (ca. 3% of yield).
7. 5116-70C_1 as B, but 60-25% H_2SO_4 - mostly active AF with probably no CPC (ca. 7% of yield).

Sample	% By Weight CPC	Cl	Cu	C	N	H	Totals+
1. Purified BT-304-D	100.0*	4.9	10.1	63.7	15.9	2.3	96.9
2. Purified N-623	92.7	3.5	9.9	61.5	16.0	3.1	94.0
3. CPC from CPC-AF	99.1	(8.3)	10.2	65.1	11.8	2.3	97.7
4. "Active AF"	-	2.1	6.8	58.7	13.1	3.2	83.9
5. PHG's 95-80%	88.9	3.2	-	64.3	15.5	3.2	86.2
6. PHG's 80-60%	-	2.7	-	59.1	15.7	3.1	80.6
7. PHG's 60-25%	-	2.7	-	58.7	14.3	3.4	79.1

*Reference standard for the analysis of CPC content.
+Except % CPC

g. An indication that "active AF" is more than one compound is the observation that when 24A ("active AF") is dry mixed with CPC from N-623 and dissolved in 96 % H_2SO_4, diluted to 70% and filtered, the filtrate has a λ_{max} = 742 mμ as compared with 755 for 24A. The absorptivity is also low (ca. 30 vs. 110) indicating removal of something from the "active AF" solution. It is conceivable that something is adsorbed on the CPC from solution.

B. Availability of "Active AF"

It is fairly definite that the "active AF" in as-made CPC-AF stabilizes α phase chlorine-free CPC through a solution-adsorption mechanism in the end-use solvent system. To be most effective in this application (it also imparts flocculation resistance), the active component of the as-made product must be readily available to go into solution and adsorb on the surfaces of the CPC crystallites soon enough to prevent any crystal growth and phase conversion. For example, if the "active AF" was in very hard aggregates, in solid solution, or as very large crystals, it would be necessary to use considerably more per unit CPC than if it was, say, already coated on the CPC surface in the dry pigment.

In many cases where samples of plant and laboratory BT-427-D were evaluated for crystal stability, using a hot solvent test with dry pigment, apparently anomalous results were obtained which were opposite to results of a 30J paint test. In most of these cases, samples which were good in the 30J test showed considerable conversion to β phase in a hot xylene test (or with 30J solvent blend). This can be explained by assuming that the "active AF" was not available soon enough to stabilize the pigment when it was exposed to the hot solvent. We have demonstrated in the lab that if such a pigment is first ball-milled (dispersed well) in a solvent at room temperature and then heated it is much more stable than if put directly in the hot solvent.

Since the "active AF" is much more soluble than the CPC component of CPC-AF in, say 70% H_2SO_4, the acid swelling step (70% H_2SO_4 at 100°C.) should permit sufficient H_2SO_4 to give essentially complete solution of the "active AF". Under these conditions, when water is added, the CPC hydrosulfate would hydrolyze first, following by the "active AF" and it would most likely be at the surfaces of the CPC crystallites where it would be most readily available when mixed with Blue R/CaSx. Under current acid swelling conditions of 1 g. CPC-AF/2.8 ml. 70% H_2SO_4, it is likely that all of the"active AF" does not dissolve.

The most effective utilization of "active AF" should be attained when as-made CPC-AF is co-acid-swelled with pre-milled Blue R where sufficient 70% H_2SO_4 is used to give considerable solubility of the "active AF". Then, when water is added, the "active AF" is hydrolyzed at the surfaces of all the CPC crystallites. For reference, a saturated solution of 24A ("active AF") at room temperature is ca. 2 grams per liter of 70% H_2SO_4. In normal acid swelling at 100°C., a ratio of 1 gram/2.8 ml. 70% H_2SO_4 is used.

C. Stability of Blue R in BT-427-D

A potential source of poor stability of BT-427-D is Blue R (α phase Cl-free CPC) of less than standard stability without the CPC-AF. By exposing various lots to xylene at room temperature for 4 hours it was determined that standard quality Blue R would convert to 5-10% β phase. In BT-427-D, Lot 42208, which was $worse_{99}$ in crystal stability vs. standard, one of the four lots of Blue R used contained 5-10% β phase in the retained sample. On exposure of this lot to xylene as above, >50% conversion to β phase occurred. In lot 42186, which was $worse_{29}$, one of its two lots of Blue R gave considerably more conversion to β phase than normal lots. On the other hand, in lot 39171 which was vs better, its three lots of Blue R were normal.

D. Crystal Stability Testing Methods

In studies involving crystal stability and phase conversion of pigments in solvents, it is essential to have an accelerated testing method which reliably predicts behavior in end-use systems. In the laboratory, the simplest test in the past has been that of heating dry pigment in xylene in a test tube in a boiling water bath. As developed in this laboratory many years ago, this test served very well to distinguish poorly stable α phase, Cl-free CPC's from the more stable β phase or partially chlorinated CPC's. However, in cases where stabilization is due to a solution-adsorption mechanism with an additive, the simple solvent test can be very misleading. It is strongly recommended that hot solvent crystal stability

tests no longer be used in cases where stabilization is due to solution-adsorption. The use of solvent tests in other cases should be correlated with tests more nearly duplicating end-use systems.

Because of the frequent anomalies in the hot solvent test, attention was directed to simplifying the 30J paint test. In cooperation with B. J. Godfrey, it was established that the 30J paint test could be used reliably with BT-427-D samples as follows:

1. Ball milling 2 or 3 days.
2. Oven at 140°F. 2 or 3 days.
3. Dry mix (instead of slurry mix struck with CaSx) was practically as good as the slurry mix, especially for preliminary screening. It is not recommended for critical samples. This technique saves the several days required to make up slurry-mixed samples. It is also very desirable for running ladder series of components of BT-427-D.

The following short-cuts were not reliable:

1. Jiffy milling for 2 hours was satisfactory for very unstable samples but was not comparable to ball milling 2-3 days in near-standard pigments. It was also found to be less convenient than ball milling.
2. Heating the 30J tints at 80-100°C. overnight was not as reliable as 2-3 days at 140°F. (60°C.).
3. Ball milling overnight was not as reliable as 2-3 days.

Exploratory study of the applicability of a simple rubout test for crystal stability showed some promise of giving valid results. Using a non-drying vehicle, such as the vinyl plasticizer Aroplex G-62, and a rubout dispersion, tints can be diluted with solvent and heated as in the 30J test. Drawdown comparisons of initial and heated tints indicate stability of pigments used. This test requires further study to check its reliability vs. the 30J paint test.

E. Differential Thermal Analysis

Thermograms, on the DuPont DTA apparatus, of CPC-AF bakes have confirmed the differences in phthalonitrile behavior as follows:

1. "Old" PN (yellow) reacts at a lower temperature than the "new" PN (gray).
2. "New" PN reacts like the "old" PN if the catalyst ammonium molybdate is added.
3. "Old" PN, recrystallized from dilute HCl (by A. H. Oberle), which lost fluorescence in conc. H_2SO_4, reacts at a higher temperature than the original material. It is quite definite that the "old" PN

has its own catalyst as an impurity. PN of high purity is apparently not as desirable as the less pure "old" PN for making CPC-AF, where the required high temperatures are difficult to obtain, unless a catalyst can be used.

F. CPC-AF Assay

A reliable method for assaying the amount of "active AF" in as-made CPC-AF would be extremely useful in production control and especially in experimental studies of this valuable additive.

Since the currently-made CPC-AF is a mixture of predominately CPC with a relatively small amount of "active AF" all analytical approaches using the as is material show only CPC itself with little or no indication of anything else. Because of this, it is almost definite that a fractionation procedure is required.

Attempts to extract "active AF" with xylene, DMF, and acetic acid were unsuccessful. The most promising reagent for fractionating seen to date is sulfuric acid. It has been determined that "active AF", as in 1849-24A and PHG's 5116-70B_1 and C_1, is extractable from CPC-AF by dissolving in 96% H_2SO_4, diluting to 80 to 60% acid, filtering, and hydrolyzing the filtrate. The crystal stabilizing activity of PHG's 70B_1 and C_1 in BT-427-D was demonstrated in the 30J paint test so it is reasonably safe to say that the "active AF" is being obtained at <80% H_2SO_4. IR spectra and near IR λmax of H_2SO_4 solutions of 24A, 70B_1, and 70C_1, are all comparable.

It is, therfore, conceivable that an assay method making use of the differential solubilities in H_2SO_4 of "active AF" and CPC could be developed. So it is necessary to select a concentration of acid in which the "active AF" has a reasonable solubility and CPC is relatively insoluble. It is then necessary to separate the AF solution from the insoluble CPC hydrosulfate. At 60% H_2SO_4, CPC (up to 5% Cl) is essentially insoluble, whereas, "active AF" has a relatively low solubility. Since its solubility is quite low, the "active AF" can actually adsorb from solution in a fine sintered glass funnel. In a coarser funnel, some of the CPC hydrosulfate particles can actually pass through the sintered glass. In each of these situations, the quantitative nature of the filtration is destroyed.

At present, it appears that the most desirable procedure is to use 70% H_2SO_4. However, an early attempt to utilize an extraction procedure by adding the dry sample to 70% H_2SO_4 and then filtering off the soluble "active AF" resulted in relatively little extracted material and poor reproducibility due to inefficient contact.

The currently preferred procedure has been written up as the following "Tentative Analytical Method":

January 20, 1967

TENTATIVE ANALYTICAL METHOD

I. Subject: CPC-AF

II. Determination: "Active AF" Content by acid crystallization.

III. References: KN-67-3 and NB. 1849-27.

IV. Principle: "Active AF" content of CPC-AF, N-873-A, is determined spectrophotometrically in 70% solution after removing essentially all of the CPC component by precipitation from 96% H_2SO_4 on dilution to 70% H_2SO_4.

V

V. Status: This method is still under development but appears theoretically sound. There is a need for such a method to assay the % active ingredient in this CPC crystal stabilizing agent.

VI. Special Equipment: (1) A means of measuring absorbance of solutions in the near IR range of 700 to 800 mμ. (2) Fine porosity sintered glass funnels (60 ml.) with reasonable flow rates. (3) Syringes from 1 ml. to 50 ml. capacity for measuring H_2SO_4 solutions. Pipets are less desirable because of drainage problems. Concentrations in terms of weight would probably be more accurate but could take much longer than volumes measured with syringes.

VII. Procedure: The currently preferred procedure, which shows considerable promise, is as follows:

1. Weigh 0.1000 g. samples on tared weighing paper.
2. Transfer sample to 100 ml. beaker containing stirring rod (Note 1).
3. Add from syringe 5.0 ml. 96% H_2SO_4 at 22°C. (9.2 g.) (Note 2)
4. Stir with rod to complete solution over a 30 minute period at room temperature.
5. Cool in ice bath for 10 minutes. (Note 3)
6. Add from syringe, while stirring, 20.0 ml. 62.2% H_2SO_4 at 22°C. (30.8 g.) to give a total volume(at 22°C.) of 25.0 ml. of 70% H_2SO_4 (40.0 g.) containing 0.1000 g. sample.
7. Remove from ice bath and let stand 30 minutes at room temperature.
8. Filter on 60 ml. fine porosity sintered glass funnel into a test tube inside a vacuum flask. (Note 4) Collect the first 10 ml. (Note 5)(Note 6).

9. Dilute by volume with 70% H_2SO_4, using syringes, to give 10 to 50% transmittance at λmax in near IR on a spectrophotometer (Note 7).

10. Calculate % AF = $\frac{AVD}{10\ S\ k_{std}}$ where

A = absorbance at λ_{max} V = initial volume = 25 ml.

D = dilution (ml) S = sample weight = 0.1000 g.

k_{std} = absorptivity of "Active AF" = $\frac{AVD}{1000\ S}$ =

ca 110 (average for 1849-24A)

The value of k_{std} is determined by running a sample of "active AF", omitting the filtration step (Note 8). A desirable concentration is 0.1000 g. in 10.0 ml. 96% + 40.0 ml. 62.2% to give 50.0 ml. 70%.

It was determined that Beer's law is obeyed within the range of 0.0100 g. to 0.1000 g. "active AF" per 50.0 ml. 70% H_2SO_4.

This procedure has to be proved-in by a qualified analyst.

Notes:

1. All glassware should be free of sulfuric acid - soluble contamination. It is advisable to clean all glassware with sulfuric acid-dichromate cleaning solution, rinse well with water, rinse with alcohol, and dry with suction tube. Sample is much easier to work into sulfuric acid when it is finely divided. Do not use a brush in transferring the sample from the weighing scoop. A spatula is more desirable.

2. Since Sp.G. varies with temperature, the temperature should be controlled closely.

3. To counteract heat of solution during addition of 62% H_2SO_4.

4. Temperature should be ca. 22°C. to avoid differences in solubility at other temperatures.

5. It is assumed that the first 10 ml. of filtrate is representative of the "active AF" in the sample. This should be explored further.

6. It is assumed that the composition of the filtrate does not change while it is under vacuum in the flask. The time under vacuum should be kept to a minimum.

7. The most desirable range is 30-45% T where absorbance varies the least with % T.

8. The best sample of "active AF" currently available is 1849-24A which was obtained by dissolving plant N-873A, lot 139, in 96% H_2SO_4, adding H_2O to 70%, filtering, and hydrolyzing the filtrate to 30% H_2SO_4. This was filtered by gravity, washed $SO_4^{=}$ free and freeze-dried. If dried normally, it would aggregate severely.