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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

CRYSTAL COMPLEXITY OF
5-NITRO-2-AMINO-ANISOLE → NAS-D

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Final Report

CRYSTAL COMPLEXITY OF 5-NITRO-2-AMINO-ANISOLE ⟶ NAS-D

December 10, 1947 to June 14, 1948.

SUBMITTED BY: A. R. Hanke

APPROVED BY: A. A. Brizzolara

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INTRODUCTION:

This report attempts to point out that the subject pigment exists in more than one crystal modification and that because of this, anomalous physical behavior can be expected. It is not intended that this be considered a finished piece of work. More accurately it is designed to point to possibilities inherent in an heretofore neglected field of pigment research. Extending this work may well modify some of the ideas expressed here but that in no way detracts from the fundamental idea that much information of value to the pigment industry can be gained through a study of the crystal modifications of our pigments.

It has been casually observed, while working with "Naphthanil" pigments, particularly PCONA → NOL, that marked changes in color could occur during treatment with solvents such as chloroform or acetic acid. This suggested a major crystal change but nothing was done to substantiate this idea until certain rather large discrepancies were noted while attempting to determine the chloroform solubility of $5\text{-}NO_2\text{-}2NH_2$ anisole → NAS-D.

This information was to be used as an aid in studying the impurities present in typical "Naphthanil" pigments and also throw some light on the phenomenon of "reactivity" of $5\text{-}NO_2\text{-}2NH_2$ anisole → NAS-D in alkyd systems. When it became evident that the solubility was not a simple phenomenon, the attempt was made to find out why.

Although this report concerns itself only with $5\text{-}NO_2\text{-}2NH_2$ anisole → NAS-D, the attempt to determine the solubility of other "Naphthanil" pigments gave strong indication that a similar situation exists for the other pigments. This was particularly true of MNPT → NMX. It is entirely reasonable to suppose that considerable of our pigments are polymorphic and that a detailed study from this point of view could lead to the discovery of new products with useful pigment properties.

CONCLUSIONS:

1. $5\text{-}NO_2 2NH_2$ Anisole → NAS-D exists in at least two crystal phases. Crystallization from chloroform yields one phase and crystallization from acetic acid yields another phase.

2. The commercial pigment appears to exist in the same phase as that formed by crystallizing from acetic acid but there is strong evidence that a solid solution exists as well as a marked change in crystal habit.

3. The presence of impurities appears to act as a directing influence (solid solution?) while crystallizing from chloroform, causing the formation of a meta stable phase. This means that the two phases can co-exist in varying amounts. The conversion of this meta stable phase to the less soluble stable phase through recrystallization is very slow. It is the presence of this more soluble meta stable phase in varying amounts that accounts for the variation observed in the solubility determinations.

4. Seeding with crystals of the stable phase hastens the conversion of the meta stable phase to the stable (less soluble) phase but the rate of conversion is still slow.

EXPERIMENTAL TECHNIQUES

Purification

For the solubility measurements, a sample of K-2292, lot 55110, ($5\text{-}NO_2\text{-}2NH_2$ Anisole $\longrightarrow$ NAS-D) was purified by slurrying with hot dilute hydrochloric acid, washing free of acid, and drying. This was then crystallized twice from chloroform and had a melting point of 287°C. This was subsequently shown to still contain traces of impurities when compared to a sample of pigment prepared by coupling in alcoholic solution. This sample was prepared by Arline Mills and designated 1264-11B. After crystallising once from chloroform it had a melting point of 296°C. A comparison of the optical extinction coefficient of the two materials in chloroform showed only a slight difference between them. This fact served to indicate that the impure sample contained only traces of impurities or that the impurities also were strong light absorbers in the region of the spectrum where the optical density measurements were made. Since the curve shape of the two were in good agreement it is reasonable to conclude that the less pure sample did, in truth, contain only traces of impurities.

Solubility Determination

Solubility measurements were made by two alternative methods. A weighed amount of pigment was refluxed in a given amount of chloroform. This was then transferred to a flask and held at a constant temperature of 25°C in a thermostat for a definite length of time. This was usually several days, and on some occasions several weeks. Refluxing always put more into solution than could go in at 25°C so equilibrium was always approached from the supersaturated side. The solutions were filtered while in a desicator placed in the thermostat. The air in the desicator was saturated with respect to chloroform to minimize evaporation. A given volume of the clear solution was pipetted into a tared dish and the residue, after evaporation to dryness, was weighed. In the alternative method a given volume of the clear solution was pipetted into a volumetric flask instead of a tared dish and made to a given volume with chloroform. The spectrophotometric curve of this solution was obtained using 1 cm light path cells. The optical density was recorded at the wave-length of maximum light absorption. With a knowledge of the extinction coefficient of the pigment at that wave-length, the solubility could be calculated. The extinction coefficient was determined by completely dissolving 0.016 g. of the pure pigment in one liter of chloroform and obtaining the optical density of the solution at the wave-length of maximum light absorption. The extinction coefficient was conveniently expressed in units of reciprocal concentration for a light path of 1 cm. Concentration was expressed as grams per 100 ml and since a 1 cm light path cell was always used, the concentration of the solution could be calculated from the equation.

$$\text{Conc. (g./100 ml)} = \frac{\text{optical density (O.D.)}}{\text{extinction coefficient (k)}}$$

This method was always found to be in good agreement with the gravimetric method, hence because of its simplicity it was used exclusively in the latter part of this work. At the start, "as is" technical grade chloroform was used and later redistilled chloroform was used but no difference could be ascribed to any variation in the quality of the chloroform.

Crystal Study

Light micrographs were obtained using our standard equipment. No difficult or unusual techniques were involved because the crystals obtained from chloroform and acetic acid were quite large and did not require extremely high magnification.

X-ray diffraction curves were obtained from the Experimental Station's North American Philips X-ray diffraction unit which provides a graph plotting diffraction angle 2 θ against relative intensity of the diffracted beam. Filtered copper K alpha radiation was used in all cases.

EXPERIMENTAL RESULTS:

Evidence for Crystallographic Changes

That the original phase and the phase after crystallizing from chloroform were different was established by obtaining X-ray diffraction records of each material. The "as is" material was that specially prepared by coupling in alcoholic solution and designated as 1264-11B. It was considerably purer than commercial material but gave an X-ray diffraction curve sufficiently similar to commercial material so no phase change existed here. Some 1264-11B was crystallized from hot chloroform and this material was shown to exist as a different phase. Figures I and II show the X-ray diffraction records and clearly illustrate the change of phase. Figure III shows the X-ray record of 1264-11B material after crystallizing from hot glacial acetic acid. This curve bears a displaced peak for peak relationship with the "as is" material indicating a larger space lattice for the "as is" material. The region at the diffraction 2 θ angle of 25° is also modified with respect to relative intensity. A marked change in crystal habit along with solid solution effects will cause changes such as these observed.

That a marked change in crystal habit is possible is illustrated in Figures IV and V which are light photomicrographs of the crystals forming from hot glacial acetic acid and from hot chloroform.

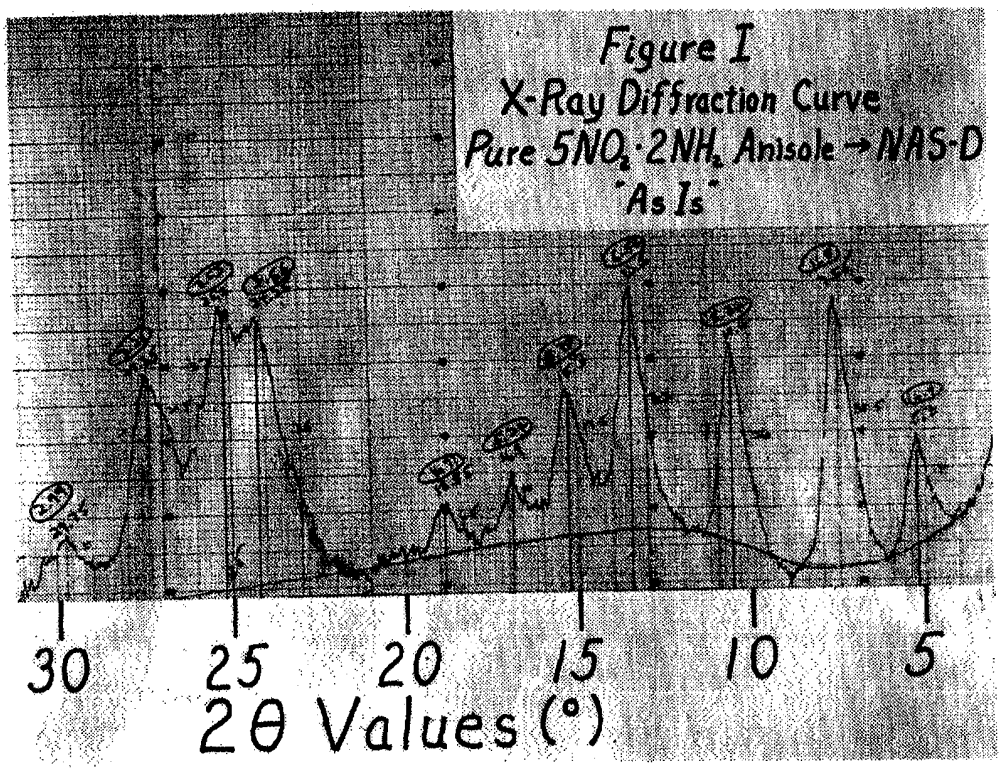

Figure I
X-Ray Diffraction Curve
Pure $5NO_2 \cdot 2NH_3$ Anisole → NAS-D
"As Is"

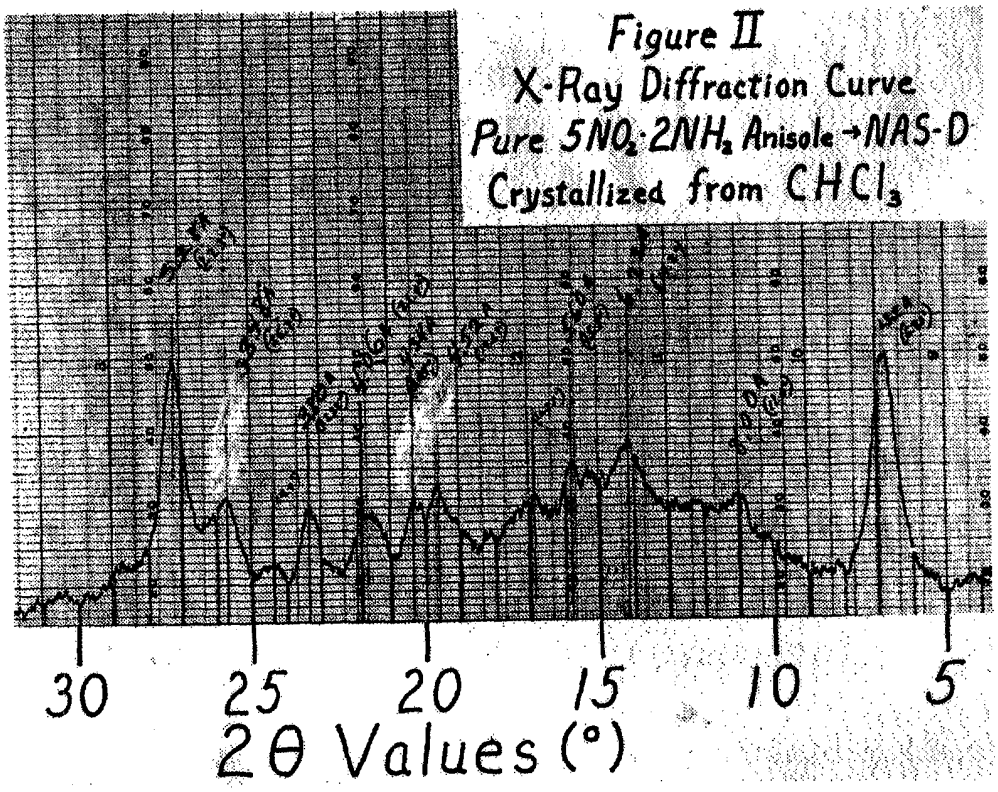

Figure II
X-Ray Diffraction Curve
Pure $5NO_2 \cdot 2NH_3$ Anisole → NAS-D
Crystallized from $CHCl_3$

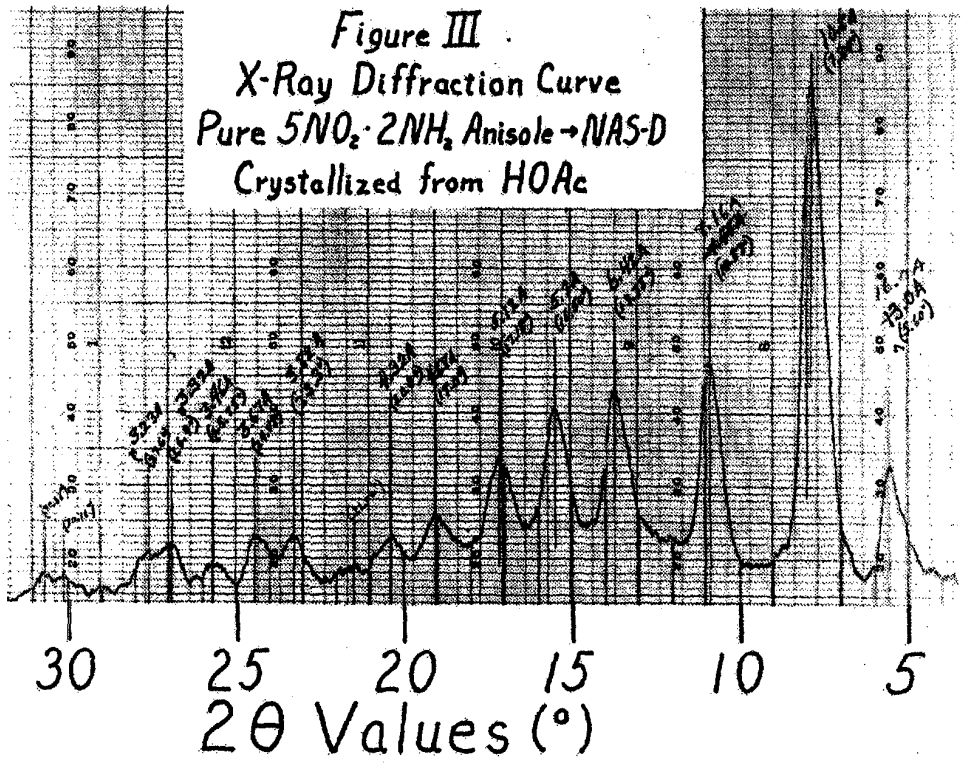

Figure III
X-Ray Diffraction Curve
Pure $5NO_2 \cdot 2NH_2$ Anisole → NAS-D
Crystallized from HOAc

Fig. IV
Pure 5 NO_2-2NH_2 Anisole → NAS-D
Crystallized from HOAc

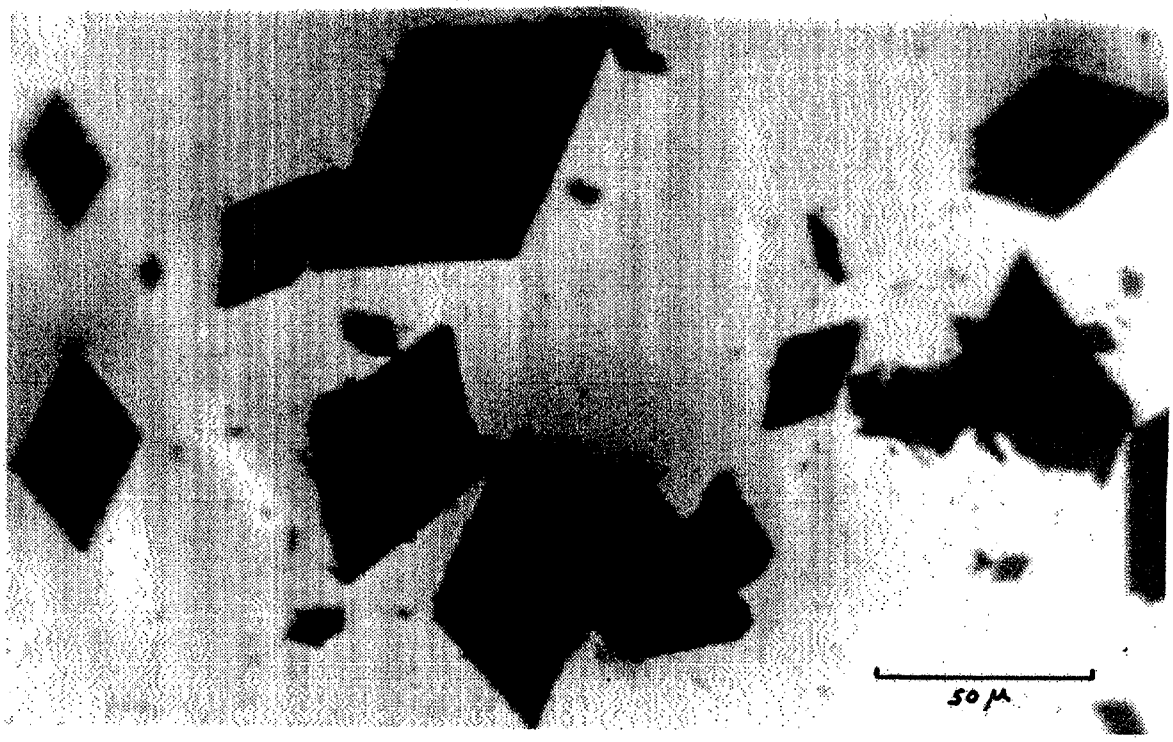

Fig. V
Pure 5 NO_2-2NH_2 Anisole → NAS-D
Crystallized from $CHCl_3$

The Effect of Crystal Type on Solubility

One of the ways in which the presence of small amounts of impurities can be detected is by noting the increase in amount of dissolved substance when the ratio of substance to solvent is increased. This measured solubility should be a linear function of the ratio of substance to solvent, and an abrupt change in slope should indicate the saturation point for one of the impurities, or the major constituent. A pure substance would show a plot of a 45° line for the region before saturation and zero slope after saturation. In other words, after sufficient pure substance has been added to a solvent to saturate it, adding more will not change the amount that goes into solution.

When such an experiment was performed on purified K-2292 ($5\text{-}NO_2\text{-}2NH_2$ Anisole → NAS-D) the amount in solution did increase with the ratio of substance to solvent suggesting impurities. This was not surprising because impurities were suspected in small amounts, but no simple linear relationship existed. Identical ratios gave solubilities further apart than could be attributed to experimental error. It was suspected that this discrepancy was in some way connected with the type of crystals produced during the experiments.

To test this point, the mother liquor from one of the trials giving an unusually high solubility, was divided into two portions. To a clear filtered portion was added some of the crystals separated from the mother liquor of a trial which had yielded a low solubility. To the other portion, which still contained the original crystals, was added some original purified K-2292 in an amount such that the ratio of solid to solution was the same for each of the two portions of mother liquor. The reasoning was that if there was something about the crystals that could alter the amount in solution, seeding a "high concentration" solution with "low concentration" crystals should cause a lowering of the high concentration. The original purified K-2292 was added to an identical portion of the high concentration mother liquor to act as a control, eliminating the possibility of the existance of a state of super-saturation as an explanation for the high concentration.

As a parallel experiment, some of the pure $5\text{-}NO_2\text{-}2NH_2$ Anisole → NAS-D (1264-11B) after crystallization from chloroform was also used as the seed crystals for a different "high concentration" solution. The concentration of all of these seeded solutions was examined as a function of time.

It was observed that the solubility did fall off with time for all but the control. The pure crystals caused the greatest decrease in solubility. The control, which was that seeded with original purified K-2292, showed a slight increase in solubility. This was expected since purified K-2292 still does contain some impurities. Table I shows the solubility figures obtained.

TABLE I

SOLUBILITY MEASUREMENTS AFTER CRYSTAL SEEDING

	$CHCl_3$ Solubility at 25°C (g./100 ml) Time after seeding (Hrs.)			
	0	48	70	382
Seed crystals A	0.069	-	0.066	0.060
" " B	0.072	0.055		
" " C (Control)	0.069		0.071	

Seed Crystals A

These were obtained from a solubility trial in which the ratio of solid to solvent was 0.100 g./100 ml. The solubility of the crystals for this trial was 0.064 g./100 ml. These crystals were added to a mother liquor derived from a ratio of solid to solvent of 0.080 g./100 ml.

Seed Crystals B

These were obtained by a $CHCl_3$ crystallization of pure 5-NO_2-2NH_2 Anisole → NAS-D (1264-1IB). They had a solubility before crystallization of 0.042 g./100 ml. These crystals were added to a mother liquor derived from a solid to solvent ratio of 0.100 g./100 ml.

Seed Crystals C

These were simply more purified K-2292. They were added to the same mother liquor used for seeding with crystals "A". They were added in such an amount that the ratio of solid to solvent was increased from 0.080 g./100 ml. to 0.100 g./100 ml. making it comparable to the ratio in the "A" experiment, after the addition of the seed crystals.

DISCUSSION:

These observations can be explained on the basis of a polymorphic existance for 5-$NO_2$2NH_2 Anisole → NAS-D. For the sake of simplicity, let it be assumed that we are concerned with only two phases. Under normal conditions, pure 5-NO_2-2NH_2 Anisole → NAS-D will crystallize from chloroform to give a phase that is stable for the set conditions of temperature and solvent. This phase can be designated alpha phase. In the presence of impurities, and these impurities need be present in only small amounts, the tendency for another phase to appear can become quite marked. The mechanism by which this tendency operates can be through the formation of a solid solution of the impurity and a new phase of the 5-NO_2-2NH_2 Anisole → NAS-D. It is also conceivable that a solid solution of an impurity with the original phase could constitute

the new phase. This phase which is really a meta stable phase, can be designated beta phase. It then becomes possible to have both phases co-exist and the amount of beta phase will be roughly determined by the amount of "phase directing" impurity in solution. This amount is in turn dependent on the ratio of pigment to solvent and on the temperature. It may be quite critical and be decided to some extent by the whim of the crystal that is forming. The type of nucleation provided for the crystal can play a very important role in the nature of the crystal that is produced. Since a meta stable phase is a more soluble phase, it is evident that the measured solubility of a system when the solid phase consists of two phases will be a variable depending on the ratio of these two phases. This will not be an equilibrium condition, but where the surface energy difference between the two phases is slight or where the stable phase is present in only small amounts, the conversion of meta stable to stable can be very slow. In the crystal seeding experiment previously described, increasing the amount of alpha phase by deliberately adding it, changed the rate of conversion to alpha phase by supplying a greater number of alpha phase nuclei. The measured solubility then fell off with time as would be required for the then new ratio of alpha to beta phase. It follows that no simple statement can be made regarding the solubility of this "Naphthanil" pigment in chloroform as long as poly-phase material exists in contact with the solution.

SUGGESTIONS FOR FURTHER RESEARCH

1. Prepare 5-$NO_2$2NH_2 Anisole $\rightarrow$ NAS-D in a phase different from that of the commercial pigment in large enough quantities to test its pigment properties. This may be accomplished by refluxing in a proper solvent and possibly seeding with the right type of crystal.

2. Examine other pigments for evidence of heretofore unknown polymorphism and evaluate for pigment properties the various polymorphic forms.

3. Study in greater detail the conditions of temperature, solvents, addition agents, etc., that control the phase and crystal habit of a pigment.

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