Cocrystalline Mixtures of Titanyl Fluorophthalocyanine and Unsubstituted Titanyl Phthalocyanine:

The Mechanical Amorphization Process, Its Characterization, and Conditions for Cocrystallization

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Abstract

Cocrystalline mixtures of titanyl fluorophthalocyanine (TiOFPc) and unsubstituted titanyl phthalocyanine (TiOPc) have been reported.[1,2] Their preparation method involves a mechanical amorphization step (dry milling), followed by "re-crystallization" with an organic solvent, having a hydrogen bonding parameter γ_c lower than 9.0.

In this presentation, we will discuss the importance of the purity of the TiOPc for control of the mechanical amorphization process, as well as facilitation of co-crystallization. A novel two-step milling procedure, thermal characterization methods of amorphicity, and mixture composition will be introduced.

Introduction

We first reported the preparation of cocrystalline mixtures of titanyl fluorophthalocyanine (TiOFPc) and unsubstituted titanyl phthalocyanine (TiOPc) at the IS&T's NIP13 in Seattle, Washington.[1] Their preparation method involved a mechanical amorphization step (dry milling), followed by treatment with an organic solvent having a hydrogen bonding parameter γ_c lower than 9.0.

It is very important that the amorphization of the pigments be complete to ensure the proper formation of the subsequently formed cocrystal. In particular, complete amorphization of the pigment mixture breaks down the large particle size of the crude pigments and yields a cocrystal of desirably small particle. The original crystalline forms of the crude pigments frequently exhibit inherent dark decay characteristics. Since these forms are resistant to solvent treatment following milling, their residual presence in the final cocrystal will likely exert an undesirable effect on its dark decay performance.

In this paper we will discuss the importance of the purity of the TiOPc for control of the mechanical amorphization process, as well as facilitation of cocrystallization. A novel two-stage milling procedure, thermal characterization methods of amorphicity, and mixture composition will be introduced.

Results and Discussion

1. Effect of TiOPc Crystallinity

In our early work, we used a titanyl phthalocyanine pigment made from titanium tetrachloride in 1-chlroronaphthalene (Fig. 1). We were able to "amorphize" 100/0, 95/5, 90/10, 85/15, 75/25Wt% TiOPc/TiOFPc mixtures by the dry milling process. The x-ray diffraction patterns for all these compositions were similar to Fig. 2 below.

More recently, we have attempted to use a TiOPc pigment made from benzamide in xylene (Fig. 3). This reaction is more attractive for cost and ease of workup. We had no problem "amorphizing" a 75/25 TiOPc/TiOFPc mixture; however the TiOPc made from benzamide cannot be amorphized by the dry milling process in the absence of less than about 15Wt% of TiOFPc. The x-ray diffraction shown below (Fig. 4) captures the incomplete amorphization of a 90/10 TiOPc/TiOFPc using the benzamide-made TiOPc.

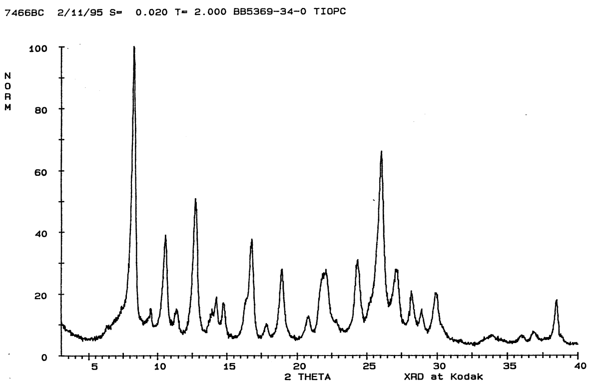


Figure 1. Cl-TiOPc made from titanium chloride

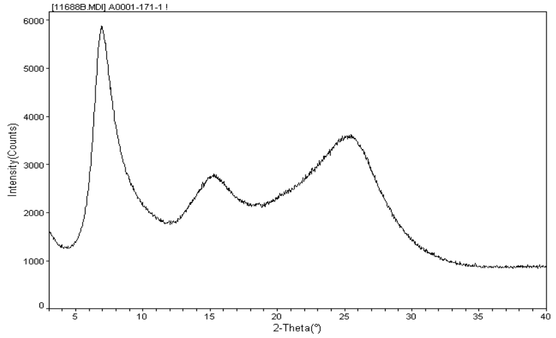


Figure 2. Amorphous Mixtures

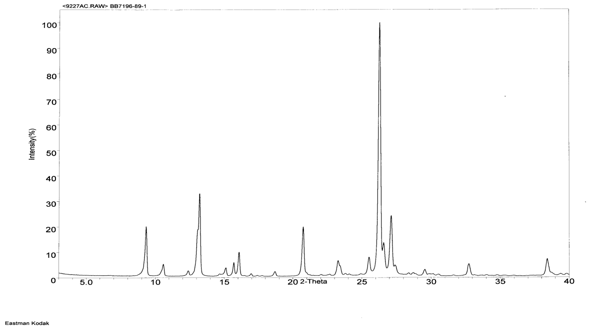


Figure 3. TiOPc made from benzamide

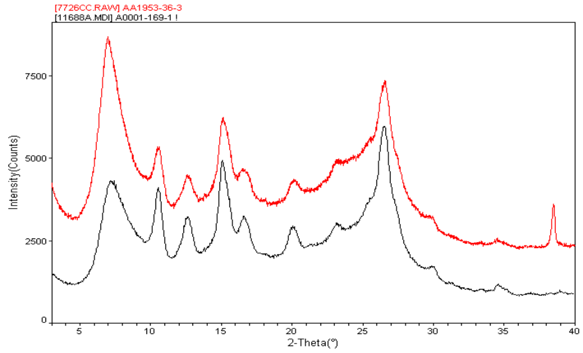


Figure 4. Incomplete amorphization

Comparing Fig. 1 and Fig. 3, it is easy to see from the difference in peak sharpness that the benzamide-made TiOPc is more crystalline than the titanium chloride-made TiOPc. Analytical data show presence of high level of chlorine in the latter, thus we designate it as Cl-TiOPc. We believe the chlorine substitution contributes to soften the crystallinity of the TiOPc.

2. A Two-Stage Dry Milling Solution

For digital application, it is very important to match the speed of the photoconductor to the rendering process in use. The ability to modify the photo speed of the cocrystalline mixture of TiOPc/TiOFPc is very valuable. Thus our ability to dry mill the various compositions is essential. We have previously seen that mixtures containing higher than 15Wt% TiOFPc can be dry-milled easily. TiOFPc is basically a mixture of isomeric fluorophthalocyanine pigment molecules. The degree of crystallinity of that isomeric mixture is rather low, thus contributing to the ease of dry milling.

We have thus developed a two-stage process that allows us to dry mill the lower-cost benzamide-made TiOPc, containing low levels of TiOFPc. In a first stage, we dry milled a highly-TiOFPc loaded mixture (60/40TiOPc/ TiOFPc) and isolated it in its amorphous state by using water in the solvent treatment step. In a second step, more TiOPc is added to bring the final mixture to the desired low concentration of TiOFPc. In both stages the concentration of the "lowly crystalline" portion of the milling mixture is high enough to ensure complete amorphization.

3. Thermal Characterization of Amorphicity

Thus far, we have characterized the milled mixture using x-ray diffraction analysis. While this technique has been very helpful, it does not provide a quantitative measure of amorphicity. A crystallizable material in its amorphous state should crystallize thermally under the right conditions. Further one should be able to measure that transition by thermal analysis. Figure 5 below shows differential scanning calorimetry traces for a dry milled and amorphized TiOPc/TiOFPc mixture. A clear crystallization peak is recorded. A temperature of spontaneous crystallization T_{sch} as well as a heat of crystallization can be measured. On the other hand the thermogram of the solvent treated mixture shows no transition, confirming its crystalline nature. No melting point is measured, the sample decomposed and or sublimed before reaching a melt.

It turned out that the temperature of spontaneous crystallization, T_{sch}, is a function of the mixture composition. Figure 7 illustrates that finding.

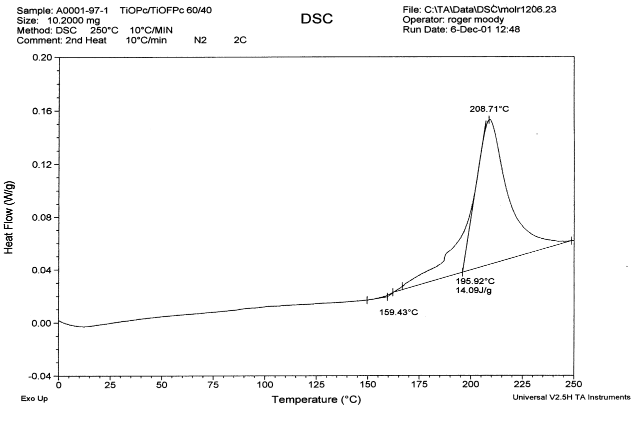


Figure 5. DSC thermogram for amorphous mixture

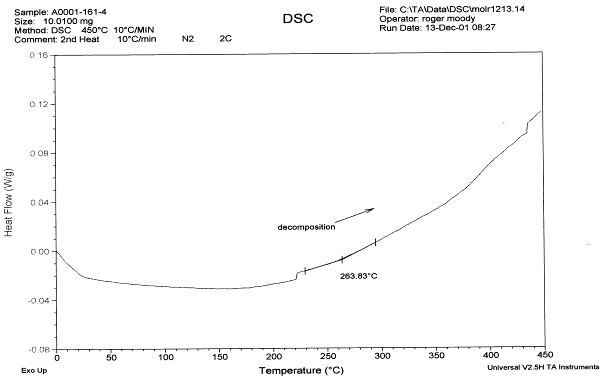


Figure 6. DSC thermogram for cocrystalline mixture

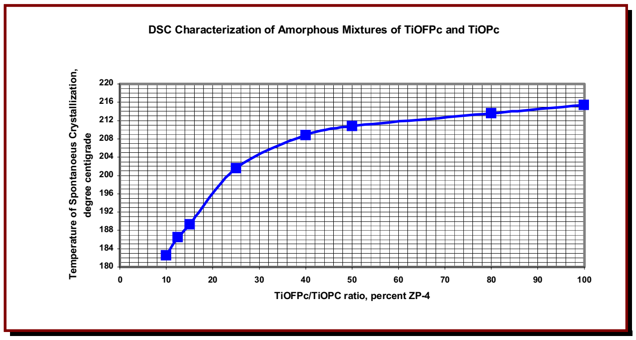


Figure 7. Tsch Vs TiOPc/TiOFPc Mixture.

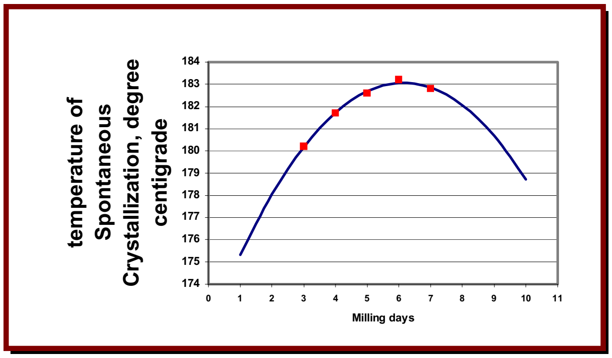


Figure 8. T_{sch} Vs milling time for 90/10 TiOPc/TiOFPc Mixture.

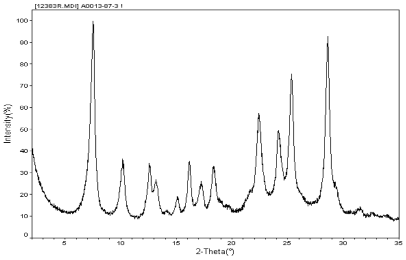
The dry milling process is not spontaneous. It takes several days to fully amorphize the mixture. Thus at any given time before complete amorphization, we have a mixture of crystalline and amorphous material. Consequently, the heat of crystallization and/or the temperature of spontaneous crystallization, T_{sch}, should reflect the degree of amorphicity of the mixture. Fig. 8 captures the change in T_{sch} for a 90/10 TiOPc/TiOFPc mixture as a function of milling time. The data seems to suggest an optimum milling time of about six days.

4. Conditions for Cocrystallization

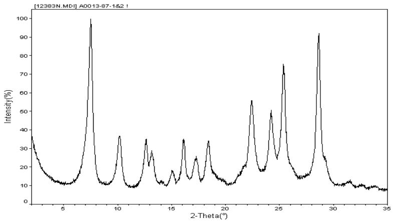
When the amorphized mixture of TiOPc and TiOFPc comes in contact with an organic solvent, "re-crystallization" is induced. The crystal form obtained for the mixture is identical to that obtained for a pure Cl-TiOPc amorphized and treated with the same solvent. As shown in the figure below, the crystal form is identical for mixtures containing from 2Wt% TiOFPc to mixture containing 50Wt% TiOFPc.

The TiOPc made from benzamide is very crystalline and difficult to amorphize in the absence of less than 15Wt% of TiOFPc unless the two-stage process is used.

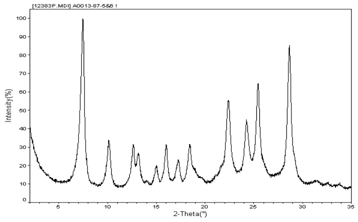
However even when full amorphization is obtained, cocrystallization is not guaranteed. Fig 9 above shows the crystal forms for 90/10, 87.5/12.5, 85/15, 75/25 TiOPc/TiOFPc (Chlorine-free TiOPc). Consistently, the cocrystal form is obtained for the mixtures at or above 15Wt% TiOFPc. Consistently a mixture of the cocrystal form and the crystal form of the starting chlorine-free TiOPc is obtained for the amorphized mixtures at below 12Wt% TiOFPc. For mixtures at 12.5W% TiOFPc, as shown in Fig. 10, the cocrystal form or a mixture of cocrystal form and that of the starting chlorine-free TiOPc is obtained without any consistent pattern.



98/2 Cl-TiOPc/TiOFPc Cocrystal

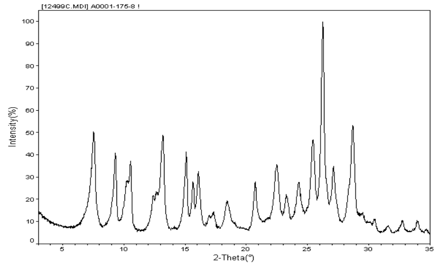


90/10 Cl-TiOPc/TiOFPc Cocrystal

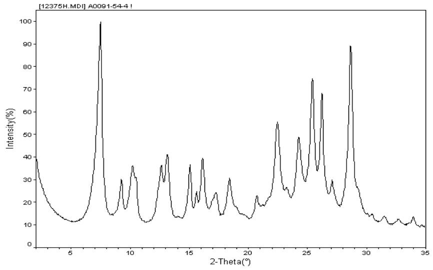


75/25 Cl-TiOPc/TiOFPc Cocrystal

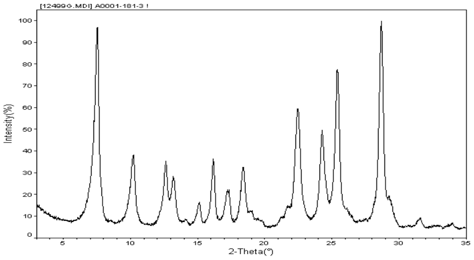
Figure 9. Crystal forms of Cl-TiOPc/TiOFPc Mixtures



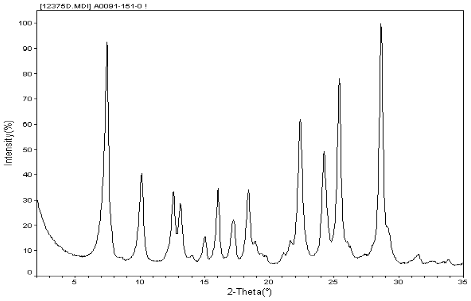
90/10 TiOPc/TiOFPc Cocrystal



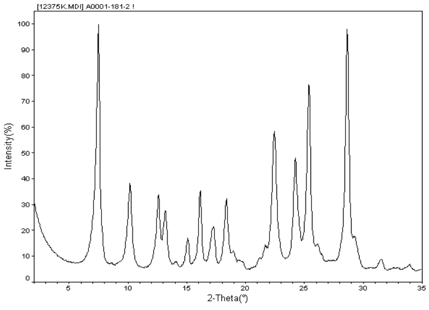
87.5/12.5 TiOPc/TiOFPc Cocrystal



87.5/12.5 TiOPc/TiOFPc Cocrystal



85/15 TiOPc/TiOFPc Cocrystal



75/25 TiOPc/TiOFPc Cocrystal

Figure 10. Crystal Forms of Cocrystalline Mixture From Chlorine-Free TiOPc

The same reason why it is difficult to amorphize mixtures of chlorine-free TiOPc/TiOFPc containing less than 15Wt% TiOFPc can explain the difficulty of making cocrystalline mixtures of those same compositions. The chlorine-free TiOPc crystal is thermodynamically more stable. The thermodynamic forces cannot be overcome by entropic mixing forces at concentration below 15Wt%. It appears that 12.5Wt% is a borderline composition where crystallization can drive to either form depending on certain conditions yet to be identified.

Conclusion

We have explored the various aspects of the mechanical amorphization process. The importance of crystallinty of starting TiOPc on the amorphization and the 're-crystallization' processes has been described. A novel two-stage amorphization method made possible amorphous mixtures containing less than 15Wt% TiOPc However, the thermodynamic forces of crystallization toward the crystal form of the chlorine-free TiOPc, were not overcome by the entropic mixing forces for mixtures below 15Wt% TiOFPc. We have developed a thermal characterization of mixture amorphicity and used it to follow the amorphization process.

Experimental

Crude Chlorine-Free Titanyl Phthalocyanine.

Phthalonitrile (1280 g), benzamide (1512.5 g), xylene (1250 ml), and pentanol (52 g) were added in that order into a 12-liter 3-necked round-bottomed flask equipped with a temperature probe, temperature controller, a condenser, and a paddle stirrer. After the stirrer was started, titanium (IV) butoxide (838 g) and xylene (1000 ml) were added. The reaction mixture was heated to reflux (144.degreeºC) for six hours, then cooled to 85ºC, and filtered through a medium frit sintered glass funnel. The pigment was rinsed first with 4.times.500 ml portions of toluene and then with 4.times.500 ml portions of hot dimethyl formamide. After an overnight soak in dimethyl formamide, the mixture was heated at reflux in that solvent for one hour. The product was collected and washed with methanol and acetone then dried at 70-80 ºC overnight. Neutron activation indicated 8.6. +/- 0.02Wt % titanium and less than 0.01Wt % chlorine.

Crude Lightly-Chlorine Substituted Titanyl Phthalocyanine (Cl--TiOPc)

Phthalonitrile (2302 g, 17.99 mole) and titanium tetrachloride (940.5 g, 4.95 mole) were suspended in 1-chloronaphthalene (12.2 l), heated to 218ºC, and maintained at that temperature for 2 hours. The reaction mixture was then cooled over 3 hr to 95ºC before filtering through a medium frit sintered glass funnel. The collected solid was rinsed with 500 g of 1-chloronaphthalene, then with 6 liters of acetone, and finally with 6 liters of methanol. The washed solid was placed into a 22-l flask and water was added. The following day, the mixture was boiled for 5-5.5 hr to hydrolyze the solid, which was collected by filtration and rinsed with water. The solid was treated with boiling water and collected by filtration three more times until the filtrate tested pH neutral. The product was then dried in an air oven at 50ºC, for several days. Neutron activation indicated 7.7 +/- .0.02Wt % titanium and 0.8Wt % chlorine.

When the same preparation was repeated and 0.5 equivalent of titanium tetrachloride was used, neutron activation indicated 7.9 +/- .0.02Wt % titanium and 1.2Wt % chlorine.

When the same preparation was repeated and the reaction temperature was 190ºC, neutron activation indicated 9.7 +/- .0.02wt % titanium and 1.5Wt % chlorine.

Preparation of Amorphous 60/40 TiOPc/TiOFPc

A 1-gallon-wide-mouth glass jar was filled with 9 kg of 3-mm diameter stainless steel balls, 45 g of crude TiOPc of Preparation 1, and 30 g of TiOFPc of Preparation 2 then put on a roller mill at 85 rpm. After milling of the mixture for 120 hours, 1.5 liters of water was added, and the mixture was milled for another 24 hours. After removal of the steel balls, the pigment was separated and dried at 110ºC for about 4 hours. A sample of the pigment was sent for x-ray crystallographic analysis for assessment of amorphicity. In the plot of intensity vs. Bragg angle 2.THETA shown in Fig.. 2, the three broad peaks are characteristic of an amorphized TiOPc/TiOFPc mixture.

Preparation of Cocrystalline Mixture of 90/10 TiOPc/TiOFPc

A 1-gallon-wide-mouth glass jar was filled with 9 kg of 3-mm diameter stainless steel balls, 56.25 g of crude TiOPc, and 18.75 g of the amorphous 60/40 TiOPc/TiOFPc (11.25 g TiOPc, 7.5 g TiOFPc), then put on a roller mill at 85 rpm. After milling the mixture for 120 hours, a small sample was removed and treated with water, and the resulting mixture was milled for another 24 hours. The sample was separated, dried, and subjected to x-ray analysis. The resulting plot, shown in Fig. 2, demonstrates that the mixture is fully amorphized. 1500 ml of dichloromethane were added to the bulk of the sample in the jar. The resulting mixture was further milled for 24 hours, after which the steel balls were separated from the pigment-dichloromethane slurry. The pigment was collected using a sintered glass filter, dried, and analyzed. The x-ray diffraction plot of Fig.10 shows a typical pattern for a cocrystalline TiOPc/TiOFPc mixture.

Reference

1. M. F. Molaire, J.T. Henry, J. E. Kaeding, IS&T's NIP13, p 799-804, November 1997.
2. M. F. Molaire, J.E. Kaeding, U.S. Patents 5,614,342, 5,766,810.
3. M. F. Molaire & al, US Published Patents Applications, 20040110075, 20040106055, 20040106053, 20040106052.

Biography

Michel (Mike) Frantz Molaire is currently a senior associate scientist at Nexpress Solutions LLC, a Kodak Company. He received his B.S. in chemistry, M.S. in chemical engineering, and MBA from the University of Rochester. His research experience includes polymer synthesis, photo-polymerization, organic monomeric glasses, optical recording materials, photo-electrophotographic masters, organic photoconductor formulation, infrared sensitive pigments, and dip coating technology. Mr. Molaire is the recipient of 38 US patents, more than 70 foreign patents, and author of several scientific publications. In 1984, he received the Eastman Kodak Research Laboratories C.E.K. Mees Award for excellence in scientific research and reporting. In 1994, he was inducted into the Eastman Kodak Distinguished Inventor's Gallery (Inventor Hall of Fame) for reaching the milestone of 20 or more patents. He is a member of the American Chemical Society and the Image Science & Technology Society. He presently serves on the council of the Rochester IS&T local chapter.