Spectral properties of the UV absorbing and near-IR reflecting blue pigment, $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$

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Graphical Abstract

Abstract

Materials in the full miscibility range of YInO_3 - YMnO_3 were prepared and compared to CI Pigment Blue 28 (CoAl_2O_4 spinel) industrial pigments. The materials were analyzed by XRD, UV-Vis-NIR spectroscopy, SEM, Laser particle size analysis, and accelerated/outdoor weathering. The optimal composition, $\text{YIn}_{0.8}\text{Mn}_{0.2}\text{O}_3$, is comparable to standard CoAl_2O_4 pigments, for example, having similar CIE color L^* (~ 34) and b^* (~ -39) values, and increased a^* (~ 10) values in an acrylic coating. The potential utility of $\text{YIn}_{0.8}\text{Mn}_{0.2}\text{O}_3$ as an industrial pigment was demonstrated by 5000 hours of accelerated QUV weathering ($\Delta E^* = 0.5$) and 48 months of Cincinnati, Ohio outdoor exposure ($\Delta E^* = 1.1$) in which the performance was comparable or improved compared to CoAl_2O_4 . The increased UV absorbance measured by thin film absorptivity, and decreased heat buildup determined from PVC spectral properties demonstrate that the YInO_3 - YMnO_3 materials offer a robust and 'cool' cobalt-free alternative to CoAl_2O_4 pigments.

1. Introduction

Among complex inorganic colored pigments (CICPs), the primary chromophores resulting in blue color are Co^{2+} and Cu^{2+} . While several other chromophores also yield blue color, $\text{Fe}^{2+}/\text{Fe}^{3+}$, S^{3-} , V^{4+} , Mn^{5+} , Mn^{6+} , and Ni^{2+} , the most stable are the cobalt based pigments having the spinel type structure [1-12]. These include Co_2SiO_4 (olivine – spinel like; CI Pigment Blue 73), Co_2SnO_4 (inverse spinel; CI Pigment Blue 35), CoAl_2O_4 (spinel; CI Pigment Blue 28), and $\text{Co}(\text{Cr},\text{Al})_2\text{O}_4$ (spinel; CI Pigment Blue 36) of which the latter two are preferred due to the intense blue hue, acid/base stability, and lower cost. Despite the superb properties of spinel structured blue pigments, the toxicity of cobalt metal is of concern in the preparation and use of pigments. Current regulations on cobalt metal exposure limits inhalation of dust and particulates to 0.1 mg/m^3 (as Co) 29 - 34% metal PEL (OSHA) [13]; however, modern precautionary equipment and strict monitoring have made working with cobalt and cobalt oxides safe. Several cobalt based spinel blue pigments have received FDA approval for specific applications suggesting the material is quite robust. Notwithstanding, concerns related to safe handling have prompted a search for alternative cobalt-free blue colorants.

The solar irradiance incident on the surface of the Earth can be divided into three weighted regions; 5% ultraviolet (UV, 290-380nm), 43% visible (VIS, 380-720nm), and 52% infrared (IR, 720-2500nm), Figure 1 [14]. The way that pigmented coatings interact with this energy can affect long term performance. Pigments that absorb in the UV may help limit or delay binder degradation. Absorption of solar energy can lead to heat buildup that can result in premature weathering and warping. In general, light-colored pigmented coatings tend to have lower heat buildup than dark-colored coatings as a result of higher solar reflectance. Some dark-colored

pigmented systems are highly absorbing in the visible region, yet weakly absorbing and highly scattering in the near infrared region. A system of this sort can provide dark shades with low heat buildup compared to pigment systems that absorb across a broader wavelength range.

Roofing and exterior architectural applications require materials with high durability, weatherability, and temperature stability. White opaque surfaces, generally rutile TiO_2 based, are often preferred for flat or low slope roofing systems as they reflect the most visible and IR radiation which results in reduced heat buildup (HBU). The reduction in HBU, while slowing binder degradation, can also improve energy efficiency by means of reduced convection and conduction about the roof. This results in reduced air conditioning energy costs during peak energy consumption months such as in the summer and fall [15]. Advances in the fundamental knowledge of pigment technology have allowed for the use of a variety of colors to be used as cost effective means to reduce energy consumption and improve product life. CoAl_2O_4 and $\text{Co}(\text{Al,Cr})_2\text{O}_4$ spinel blues exhibit reasonably high UV opacity which contributes to their effective weathering in exterior coatings and plastics. Nevertheless, a relatively large Co^{2+} absorption band in the near-IR limits the solar reflectance and thus contributes to overall heat build-up. Suitable alternatives, with similar color and performance as CoAl_2O_4 , do not exist, or have not been reported at this point.

Recently, Mn^{3+} was shown to be a blue chromophore when occupying the trigonal bipyramidal site of In^{3+} in the hexagonal oxide YInO_3 [16]. The unique structure allows for metal specific apical bond distances of Mn and In which results in a systematic progression of color upon

increasing Mn^{3+} concentration. An intense blue color is observed over much of the miscibility range. Interestingly, few reports have addressed the material properties in terms of industrial pigment utility [17, 18], and such reports are based on solution methods. In this paper, we evaluate the hitherto unknown industrial performance of the full miscibility range of $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ pigments by comparing the color coordinates, UV and IR reflectance, and accelerated and outdoor weathering with that of existing spinel structured (CI Pigment Blue 28) industrial blue pigments prepared using traditional syntheses.

2. Experimental

2.1 Synthesis

Fourteen compositions within the YInO_3 - YMnO_3 solid solution were prepared by conventional solid state ceramic methods: a stoichiometric mixture of Y_2O_3 (H.C. Starck Grade A-99.9%+), In_2O_3 (Indium Corp. Grade B Fine-99.99%), and Mn_3O_4 (Chemalloy) was intimately blended and calcined in ceramic crucibles at temperatures from 1150 °C to 1300 °C for 6 hours in a muffle furnace. The resulting product was screened and milled as an aqueous slurry on a paint shaker for 300 minutes using deionized water, and 0.4-0.7 mm Ytria stabilized ZrO_2 media in a water/pigment/media ratio of 2 : 1 : 4.

2.2 Method of pigmentation

Acrylic-based coatings were prepared utilizing milled pigment compositions. An acrylic enamel blend (called a grind) was prepared by blending 50%/weight acrylic enamel (PPG Delstar DMR 499) and 50 %/weight xylene. The blend was then added to a cup with glass beads and pigment

in a ratio of 1.4 : 3.2 : 1 respectively, and ground in a Speed Mixer™ at 3500rpm for 5 minutes. The masstone mixture was then prepared by combining an aliquot of the grind and acrylic enamel (DMR 499) in a 2.165:1 ratio and mixing on a Speed Mixer™ at 3500rpm for 1 minute. The tint was prepared by combining an aliquot of the grind and white base (PPG Delstar DMR 400) in a ratio of 1 : 3.7 mixing on a Speed Mixer™ at 3500 rpm for 1 minute. The resulting masstone and tint mixtures were drawn on a Leneta card using a 15-mil precision wet film applicator. The wet coating was then dried in air for 30 minutes and placed in an oven at 60 - 70 °C for 1 hour.

PVDF (polyvinylidene difluoride) thin films were prepared using a mixture of isophorone, Solvay Plastics Hylar® 5000 PVDF resin, and pigment in a ratio of 35 : 19 : 1 respectively. After homogenization, the mixture was then drawn on a glass plate using a precision wet film applicator. A 4-mil, 6-mil, and 8-mil gage was used to prepare films of each composition and two different standards. The films were dried in an oven at 232 °C, allowed to cool to room temperature, and then cut into 2 inch x 2 inch squares. The thickness of each film was measured using a micrometer. Approximate film thicknesses of ~12 µm, ~20 µm, and ~28 µm were observed.

PVC (Polyvinyl Chloride) press outs were prepared by homogenizing a mixture of pigment and Natural PVC compound in a ratio of 1 : 21 respectively. The mixture is then preheated and further homogenized in a 2-roll milled heated to 205 °C. The final sheet is cooled to room temperature. Sections of the sheet are then cut and placed onto a Carver press preheated to

177 °C, and pressed under 6500 psi for 3 minutes. The resulting pressed panels had a thickness of ~1.5 - 1.75 mm and were cut to 76mm x 76mm squares according to ASTM D4803-97 [19].

2.3 Characterization techniques

Phase purity of the synthesized materials was characterized by X-ray powder diffraction (XRD) patterns collected on a Rigaku DMax 2100T using CuK α radiation. The applied tube energy was 40 kV and 40 mA and the optics used a traditional para-focusing beam configuration. All samples were analyzed with step scans from 10-90° 2 θ at 1°/min and 0.01 °/step. Jade software (Rigaku) was used to index the powder patterns to phases within the ICSD/JCPDS database.

The particle size distribution of milled material was analyzed using a Horiba LA900 Laser Particle Size Analyzer on the basis of Mie scattering theory. The suspension was stabilized by the addition of two drops of Dow Tamol SG-1 dispersant and then homogenized for three minutes by ultra-sonication.

SEM (scanning electron microscopy) images were obtained using a FEI/Philips Field Emission SEM model XL 30 . Prior to the SEM characterization, the powder samples were coated with a Au-Pd layer (thickness ca. 30 nm). The SEM images were collected using the following settings: High tension of 30 kV and a working distance of 10 mm. Images were obtained of samples before and after media milling.

Optical measurements were performed on a PerkinElmer Lambda 900 spectrophotometer utilizing a 150 mm integrating sphere with a Spectralon® reference. Samples were analyzed from 230 - 2500 nm at 0.08 sec/nm yielding an integration speed of 750 nm/min. Spectra were collected in %R (reflectance) mode for both 15-mil Acrylic coatings on Leneta cards and pressed PVC panels. Transmission spectra were obtained for thin films placed in the internal transmission port of the reflectance sphere. Transmittance was then converted to Absorbance.

Color coordinates were determined from reflectance spectra using PerkinElmer Color Module ver. 3.00. Solar reflectance values were calculated as described in ASTM method E903-12 using a weighted ordinate method [20]. In the CIE color coordinate system, L^* or lightness, refers to a numerical scale from 0 – 100 where 0 is black and 100 is white. Red and green colors are defined as a (+) and (-) a^* value respectively, and blue and yellow colors are defined as (+) and (-) b^* value respectively. Chroma, C^* , represents the saturation of a color and is quantified as $C^* = [(a^*)^2 + (b^*)^2]^{1/2}$. The hue angle, h° , represents the angle on a circular axis where the color ranges from 0° (red) through 90° (yellow), 180° (green), 270° (blue) and back to 0°. A common measurement for the 'distance' between two color parameters is the delta parameter, ΔL^* , Δa^* , and Δb^* . The ΔE^* parameter is a measurement of the distance between two colors which is calculated as $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$.

Gloss measurements were performed using a Byk – Gardner Co. Micro-TRI-gloss instrument. The instrument is calibrated using a black glass standard with an index of refraction of 1.567.

Depending on the gloss value at 60°, the proper angle of incidence may be 20°, 60°, or 85°. Semi-gloss surfaces generally range from 10 – 70 units at 60°. Highly reflective surfaces are measured at 20°, and matte surfaces are measured at 85°.

3. Results and Discussion

3.1. Phase and morphology

Precursor oxides for several compositions within the YInO_3 - YMnO_3 miscibility range were initially fired at temperatures from 1150 °C to 1300 °C for 6 hours to establish the optimal firing conditions to prepare phase pure materials. All compositions were found to form the hexagonal type structure after a single calcination at 1288 °C for 6 hours. Figure 2 depicts the X-ray powder diffraction patterns for the full miscibility range investigated. All of the diffraction peaks can be indexed to the hexagonal structure of YMnO_3 (JCPDS NO: 25-1079) having the $P6_3cm$ space group, or YInO_3 (JCPDS NO: 70-0133) having the $P6_3cm$ space group. No impurity peaks were evident. The inset of Figure 2 shows a magnified view of the (002) and (102) reflections showing the intensity increase and 2θ shift with Mn substitution. Lattice parameters and unit cell volumes of the solid solution decreased with increasing Mn concentration, and are consistent with values reported previously where $X = 0.2$ in $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ is previously reported to be $a = 6.24 \text{ \AA}$ and $c = 12.05 \text{ \AA}$, and is found to be $a = 6.26 \text{ \AA}$ and $c = 12.07 \text{ \AA}$ in this work [16]. The a -parameter decreases slightly while the c parameter decreases significantly upon Mn^{3+} addition to the lattice. This is consistent with the size variation between ionic radii of Mn^{3+} and In^{3+} , and the corresponding effect on the apical bond distances [16, 21].

As-fired samples across the solid solution exhibited mean particle size diameters in the range of 9.45 – 10.69 μm . Standard pigment applications in coatings and plastics generally require the mean particle size diameter of $\sim 1.0 \mu\text{m}$ for ease of dispersion. Therefore, each sample was media-milled to a mean diameter of $0.88 \pm 0.03 \mu\text{m}$. Figure 3 illustrates the particle size distribution curves based on intensity for the full range of materials after media milling. These values are consistent with current commercial CoAl_2O_4 blue pigments which range from 0.6 - 1.1 μm mean diameter and have a mono-modal distribution.

Figure 4 shows the morphology of pre-milled and post-milled materials for select compositions by SEM. Previously, it was shown that a spherical morphology could be obtained through pyrolysis of aerosols [17], and irregular and granular morphology could be obtained through sol-gel combustion techniques [18]; however, no details have been reported on particle morphology for traditional solid state syntheses. Interestingly, each composition appears to form large hexagon and plate-like, fused agglomerates. The fused agglomerates for all compositions appear similar in size distributions. After media milling, the particles are irregular in morphology and are again similar in size as confirmed by laser particle size analysis.

3.2. Spectral behavior

3.2.1 Visible (VIS)

Figure 5 shows the approximate orbital splitting for both tetrahedral (T_d) and trigonal bipyramidal (TBP) coordination environments with reference to the free ion, and O_h . In the spinel-type structure, $\text{Co}^{2+} (3d^7)$ may occupy a T_d coordination for which there are three spin

allowed transitions, or an octahedral (O_h) coordination environment for which there are three spin-forbidden transitions. In the ideal $CoAl_2O_4$ spinel pigment, however, Co^{2+} is found to occupy the T_d coordination environment. For Co^{2+} the quartet 4F ground state is split into two spin-orbit levels increasing in energy from e (doubly degenerate) to t_2 (triply degenerate) in a tetrahedral field. In the hexagonal $YIn_{1-x}Mn_xO_3$ structure, Mn^{3+} ($3d^4$) occupies a TBP coordination environment for which there are two spin-allowed transitions. For Mn^{3+} , the quintet ground state term 5D is split into three spin-orbit levels increasing in energy from e'' (doubly degenerate) $< e'$ (doubly degenerate) $< a$ in a trigonal bipyramidal field. In Figure 6 the approximated absorbance spectra calculated from diffuse reflectance values by the Kubelka-Munk remission function, $f(R) = (1-R)^2/2R$, are presented [22]. As described, the spin-allowed transitions are observed in the visible spectrum as three distinct absorption bands for T_d Co^{2+} in $CoAl_2O_4$ (Figure 6 bottom) and two distinct absorption bands for TBP Mn^{3+} in $YMn_{0.2}In_{0.8}O_3$ (Figure 5 top). In both cases, the absorptions in the visible spectrum occur over the entire red, orange, yellow, and green regions between 500 and 700 nm. Absence of strong absorption bands between 400 – 500 nm results in a pure blue color being reflected. It should be noted that the spectra provided for commercial $CoAl_2O_4$ do exhibit weak absorption peaks at ~405 nm, 450 nm, and 480 nm. These absorptions have been attributed to spin-forbidden transitions of O_h Co^{2+} , or spin-allowed transitions of O_h Co^{3+} [23].

The impact of weak absorption shifts on the color can be significant when considering variation in the a^* (red) value for blue shade materials. Table 1 provides the CIE LabCh color values and VIS absorption band minima for the full $YIn_{1-x}Mn_xO_3$ solid solution and $CoAl_2O_4$ commercial

pigments. Compositions with low Mn concentration result in a distinct and sharp absorption band in the 300 – 400 nm region and 500 – 800 nm region, Figure 6. The absence of absorption from 400 – 500 nm (absorption minima) for lower Mn concentration results in bright blue hues. This is observed for compositions of $0.05 < x < 0.5$ in $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$. However, as the Mn concentration increases, the doublet absorption band centered at ~ 600 nm broadens and intensifies which yields overlap with the absorption band at ~ 350 nm subsequently absorbing intermediately in the 400 – 500 nm range. The result of this overlap is a progressive decrease in the blue color as well as a decrease in lightness, Table 1. The materials with highest manganese content appear blue-black. This progression in both color and the absorption band center seems to be due to the structural effects caused by size differences between Mn^{3+} and In^{3+} in TBP coordination as well as the concentration effects on the orbital splitting energies, Figure 5 and Table 1 [16, 21]. Representative CIE color coordinates for traditional CoAl_2O_4 spinel pigments are $L^* = 33$, $a^* = 7$, $b^* = -35$. The blue color of the $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ system varies widely depending on Mn concentration and shows its versatility in color formulation as compositional tuning allows for color control. For $\text{YIn}_{0.8}\text{Mn}_{0.2}\text{O}_3$, CIE color coordinates are $L^* = 35$, $a^* = 10$, $b^* = -39$ which is red-toned, blue, and about as dark as CoAl_2O_4 , Table 1. These two pigments having different structures, chromophores, and optical transitions are remarkably similar in color.

3.2.2 Ultraviolet (UV)

Absorption of UV energy can cleave chemical bonds and cause polymer degradation. UV stabilizers are commonly added to plastic resin systems to suppress photo-degradation, but pigments that absorb in the UV region can function effectively in the same manner [24]. The UV

absorption spectra for $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ and CoAl_2O_4 pigments were obtained by dispersion in thin films of PVDF (polyvinylidene difluoride). The relative thin-film absorptivity of the $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ pigments is higher than that for CoAl_2O_4 across the UV region, Figure 7. The improved UV absorptivity of $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ suggests that these materials will likely provide greater protection than CoAl_2O_4 pigments against UV-induced photo-degradation. This inference was tested, in part, through natural and accelerated weathering trials.

In addition to testing the potential photo-stabilization effects of a pigment, natural outdoor weathering and accelerated UV weathering also evaluates the effects of other variables such as humidity, heat, and temperature in cycles. Weathering results are presented in Table 2. After 5000 hours of continuous accelerated UV exposure the $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ pigmented panels changed by less than $\Delta E^* = 0.5$ units. After 48 months of outdoor weathering the $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ pigmented panels changed color by less than $\Delta E^* = 1.4$ units. These weathering results compare well with those for standard CoAl_2O_4 pigmented panels shown in the Table 2 for comparison. The small changes in ΔE^* indicate minimal color shifts which we attribute to a lowering of the gloss value due to exposure. $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ pigments are durable, light-fast, and stable to changing conditions and appear to be a potential replacement for CoAl_2O_4 based pigments.

3.2.3 Near-Infrared (NIR)

The near infrared (NIR) region of the solar spectrum accounts for ~52% of incident solar energy, Figure 1. This energy, if absorbed in addition to UV and Vis energy, can result in heat build-up which can have negative effects on both the resin system and the immediate surrounding

environment. In architectural coatings, lighter colors are frequently used to reduce the total solar energy absorbed. By nature, darker materials tend to absorb more energy than lighter materials. For instance, carbon black absorbs ~95% of solar energy, whereas TiO_2 absorbs less than ~25%. Optimizing the NIR spectral character of pigments can improve heat build-up issues with dark colors leading to improved resin performance, reduced warping, and reduced cooling costs in some cases.

Figures 8 and 9 depict the full reflectance spectra of two CoAl_2O_4 pigments and the full $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ solid solution in acrylic resin. Cobalt based pigments are readily identified in the NIR spectral region by a large absorption band between 1200 nm and 1600 nm, Figure 9. In contrast, $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ materials do not exhibit any strong absorptions in the near infrared, and instead, scatter light with high reflectance (small distinct absorptions in the NIR that occur at 1400 nm, 1700 nm, 1900 nm, 2100 nm, and 2300-2500 nm are due to the acrylic resin), Figure 8 and 9. Total Solar Reflectance (TSR) is a measure of the incident solar energy reflected by a surface.¹⁰ More accurately, it is the solar-irradiance weighted average of a reflectance spectrum. It can also be useful to calculate related energy-weighted reflectance values in the specific UV, Vis, and NIR regions. Table 3 lists the TSR and the percent reflectance in the different spectral regions for the $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ materials alongside those for CoAl_2O_4 . The $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ materials have higher TSR values than the CoAl_2O_4 products listed, in large part because they reflect more of the incident NIR energy.

Theoretical heat buildup values, as described by Peake and Sullivan, were calculated from Reflectance spectra obtained on pigmented PVC panels as an alternative to ASTM D4803-97 [19, 25]. Table 4 lists the calculated HBU temperatures of the $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ materials as well as carbon black and other materials reported by Peake and Sullivan. The HBU temperatures for the $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ materials range from 27 to 30°C as compared to temperatures near 37°C for CoAl_2O_4 pigments and 42°C for carbon black. PVC pigmented with $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ materials will not experience the higher HBU temperatures calculated for cobalt based blues and other NIR absorbing materials. The difference of 7-10°C cooler indicates that over the lifetime of a pigmented PVC panel, $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ materials will result in the panel being exposed to lower temperature variation and thus have reduced potential to warp and degrade.

4. Conclusion

Samples across the full composition range $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$, $x = 0.05$ to 1, were prepared and compared to established industrial pigments. In some markets and applications, the Cr, Co, and Ni-free nature of this system is an attractive alternative to current blue pigments. A diverse blue color range is observed across the solid solution. The $x = 0.2$ composition, $\text{YIn}_{0.8}\text{Mn}_{0.2}\text{O}_3$, is similar to standard CoAl_2O_4 pigments, having similar L^* and b^* values, and increased a^* (red) values. To optimize the color, compositions of $0.17 < x < 0.23$ should be investigated further. The increased UV absorbance, stability in QUV and outdoor weathering tests, and low HBU temperature values demonstrate that the $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ materials offer a robust alternative to CoAl_2O_4 pigments. In addition, with high TSR and low HBU, this system provides a ‘cool pigment’ for use in a variety of exterior applications, reducing surface temperatures, compared

to similarly colored CoAl_2O_4 pigments, which could have beneficial impact on cooling costs and energy consumption.

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Figure 1. Solar spectral irradiance based on combined direct and circumsolar effects from ASTM G173-03 reference spectra derived from the Simple Model of the Atmospheric Radiative Transfer of Sunshine, SMARTS [14]. Shading of spectral regions has been added.

Figure 2. Normalized powder x-ray diffraction patterns of the YInO₃-YMnO₃ miscibility range. The inset shows the (002) and (102) peaks magnified.

Figure 3. Normalized particle size distribution of $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$, $x = 0.05 - 1.0$, and commercial CoAl_2O_4 pigments.

Figure 4. SEM images of $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$, before (a-c) and after (d-f) milling where $x = 0.2, 0.5$, and 1.0 , respectively.

Figure 5. Relative MO splitting levels for octahedral (O_h), trigonal bipyramidal (TBP), and tetrahedral (T_d) coordination environments. * Co_2SnO_4 is an inverse spinel in which Co^{2+} occupies both the T_d and O_h coordination environments.

Figure 6. Optical evolution of Kubelka-Munk absorption of pigmented acrylic resin. (Top) Full $YIn_{1-x}Mn_xO_3$ solid solution. (Bottom) Select $YIn_{1-x}Mn_xO_3$ compositions compared to two industrial $CoAl_2O_4$ pigments.

Table 1. Color coordinates calculated using spectral analysis of pigmented acrylic as a masstone.

Pigment composition	CIE Color Coordinates					Absorption Minima (nm)
	L*	a*	b*	C*	h°	
^a CoAl ₂ O ₄	32.6	12.8	-40.3	42.2	-72.4	435
^b CoAl ₂ O ₄	32.8	6.9	-35.0	35.7	-78.8	441
YIn _{0.95} Mn _{0.05} O ₃	45.4	10.9	-51.0	52.2	-77.9	449
YIn _{0.90} Mn _{0.10} O ₃	40.0	11.9	-47.9	49.4	-76.1	451
YIn _{0.85} Mn _{0.15} O ₃	36.3	12.0	-44.2	45.8	-74.8	453
YIn _{0.80} Mn _{0.20} O ₃	34.6	9.6	-38.9	40.1	-76.1	455
YIn _{0.75} Mn _{0.25} O ₃	33.4	7.7	-34.5	35.4	-77.4	455
YIn _{0.70} Mn _{0.30} O ₃	32.5	5.8	-30.1	30.6	-79.1	458
YIn _{0.65} Mn _{0.35} O ₃	31.3	4.2	-25.9	26.3	-80.8	459
YIn _{0.60} Mn _{0.40} O ₃	30.8	2.9	-22.3	22.5	-82.7	459
YIn _{0.50} Mn _{0.50} O ₃	29.8	0.6	-16.3	16.3	-87.8	462
YIn _{0.40} Mn _{0.60} O ₃	28.9	-0.9	-10.1	10.2	84.9	465
YIn _{0.30} Mn _{0.70} O ₃	28.4	-1.4	-6.1	6.3	77.0	468
YIn _{0.20} Mn _{0.80} O ₃	28.3	-1.5	-3.9	4.2	69.7	469
YIn _{0.10} Mn _{0.90} O ₃	28.2	-1.6	-4.4	4.7	70.0	470
YMnO ₃	28.4	-1.5	-4.4	4.7	71.3	468

*Representation of two different CoAl₂O₄ samples is denoted by superscripts **a** and **b**.*

Figure 7. Thin film absorption coefficient of pigmented PVDF resin for the full $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ solid solution and industrial pigment CoAl_2O_4 .

Figure 8. Reflectance spectra for cobalt blue pigments and $\text{YIn}_{0.8}\text{Mn}_{0.2}\text{O}_3$ pigmented acrylic resin.

Figure 9. Reflectance spectra for $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ pigmented acrylic resin.

Table 2. QUV and outdoor weathering of materials in PVDF/Acrylic resin as full masstone and 4:1 tint.

Pigment	Initial CIE Lab Color Values				QUV 5000hr Exposure Final CIE Color Value Changes					48 Months Cincinnati Exposure Final CIE Color Value Changes				
Masstone	L*	a*	b*	60° gloss	ΔL*	Δa*	Δb*	ΔE*	Δ60° gloss	ΔL*	Δa*	Δb*	ΔE*	Δ60° gloss
^a CoAl ₂ O ₄	36.1	11.2	-48.8	25	-0.2	0.9	-0.7	1.1	0	-1.2	1.2	2.0	2.7	-1
^a CoAl ₂ O ₄	36.1	10.9	-48.6	23	-0.2	1.2	-0.8	1.4	2	-0.9	1.8	2.8	3.5	-1
^b CoAl ₂ O ₄	35.8	6.7	-44.3	27	0.0	0.8	-0.4	0.9	0	-0.5	0.0	0.6	0.8	3
^b CoAl ₂ O ₄	36.0	6.4	-44.2	26	-0.1	1.0	-0.6	1.2	4	-0.5	0.0	0.6	0.8	1
YIn _{0.8} Mn _{0.2} O ₃	34.8	11.7	-45.2	55	0.0	0.3	-0.4	0.5	-1	0.1	-0.5	1.1	1.2	2
YIn _{0.8} Mn _{0.2} O ₃	34.7	11.6	-45.1	55	0.1	0.4	-0.4	0.5	-1	0.2	-0.5	1.2	1.3	2
4:1 Tint	L*	a*	b*	60° gloss	ΔL*	Δa*	Δb*	ΔE*	Δ60° gloss	ΔL*	Δa*	Δb*	ΔE*	Δ60° gloss
^a CoAl ₂ O ₄	77.7	-7.3	-25.3	64	-0.2	0.6	-0.9	1.1	4	-0.5	0.1	-0.3	0.5	-1
^a CoAl ₂ O ₄	77.7	-7.4	-24.9	64	-0.3	0.7	-1.2	1.4	3	-0.4	0.1	-0.3	0.5	-1
^b CoAl ₂ O ₄	77.6	-7.6	-24.4	63	-0.3	0.4	-0.7	0.8	2	-0.9	0.3	0.3	1.0	3
^b CoAl ₂ O ₄	77.6	-7.7	-24.2	63	-0.3	0.5	-0.8	1.0	2	-0.7	0.2	0.4	0.8	2
YIn _{0.8} Mn _{0.2} O ₃	77.6	-2.7	-21.4	69	0.0	0.1	-0.2	0.2	0	-0.5	0.1	0.9	1.0	3
YIn _{0.8} Mn _{0.2} O ₃	77.6	-2.6	-21.5	66	0.0	0.1	-0.1	0.2	4	-0.6	0.0	1.0	1.2	1

*Representation of two different CoAl₂O₄ samples is denoted by superscripts **a** and **b**. A replicate of each sample was analyzed to show variation due to sample preparation.*

Table 3. Solar reflectance percentages calculated from spectral analysis of pigmented acrylic resin as a masstone

Pigment composition	Solar reflectance (%R)			
	TSR	UV	VIS	NIR
^a CoAl ₂ O ₄	34.1	15.7	27.3	42.3
^b CoAl ₂ O ₄	31.8	12.3	25.1	39.9
YIn _{0.95} Mn _{0.05} O ₃	50.3	17.5	23.0	81.0
YIn _{0.90} Mn _{0.10} O ₃	45.4	13.0	17.1	77.2
YIn _{0.85} Mn _{0.15} O ₃	43.1	10.2	13.4	76.3
YIn _{0.80} Mn _{0.20} O ₃	40.9	9.1	11.4	73.8
YIn _{0.75} Mn _{0.25} O ₃	39.6	8.3	10.0	72.6
YIn _{0.70} Mn _{0.30} O ₃	37.9	7.9	9.0	70.0
YIn _{0.65} Mn _{0.35} O ₃	36.7	7.2	8.0	68.6
YIn _{0.60} Mn _{0.40} O ₃	35.5	6.9	7.5	66.7
YIn _{0.50} Mn _{0.50} O ₃	33.1	6.4	6.6	62.5
YIn _{0.40} Mn _{0.60} O ₃	30.2	6.0	6.0	57.2
YIn _{0.30} Mn _{0.70} O ₃	26.5	5.8	5.6	49.8
YIn _{0.20} Mn _{0.80} O ₃	23.2	5.8	5.5	42.9
YIn _{0.10} Mn _{0.90} O ₃	23.2	5.8	5.5	42.9
YMnO ₃	26.5	5.8	5.5	49.8

*Representation of two different CoAl₂O₄ samples is denoted by superscripts **a** and **b**.*

Table 4. Solar reflectance percentages calculated from spectral analysis of pigmented Polyvinyl Chloride (PVC) resin as a masstone at a 5% pigment loading.

Pigment composition	CIE Lab Color Values (PVC)			Solar reflectance (%R) (PVC)				Heat Build Up
	L*	a*	b*	TSR	UV	VIS	NIR	HBU (°C)
Carbon Black	25.3	-0.1	-0.9	4.6	5.0	4.5	4.6	42.0
^a CoAl ₂ O ₄	36.1	7.7	-39.8	27.2	19.7	17.4	34.9	37.5
^b CoAl ₂ O ₄	37.1	5.2	-38.0	28.4	18.4	18.3	36.5	37.0
YIn _{0.95} Mn _{0.05} O ₃	47.0	8.6	-49.7	44.3	22.7	21.5	62.5	26.9
YIn _{0.90} Mn _{0.10} O ₃	41.8	10.8	-48.8	41.0	17.4	16.8	60.4	26.9
YIn _{0.85} Mn _{0.15} O ₃	38.4	11.6	-46.0	38.6	14.2	13.8	58.4	27.1
YIn _{0.80} Mn _{0.20} O ₃	36.1	10.2	-42.4	36.4	11.9	11.9	56.0	27.4
YIn _{0.75} Mn _{0.25} O ₃	35.2	8.4	-37.8	35.4	10.9	10.8	55.1	27.3
YIn _{0.70} Mn _{0.30} O ₃	33.6	6.1	-32.9	33.6	9.6	9.5	52.8	27.7
YIn _{0.65} Mn _{0.35} O ₃	32.7	4.7	-29.9	33.5	8.9	8.8	53.2	27.3
YIn _{0.60} Mn _{0.40} O ₃	31.9	3.1	-25.5	32.4	8.2	8.1	51.8	27.5
YIn _{0.50} Mn _{0.50} O ₃	31.2	0.5	-19.7	31.2	7.5	7.4	50.3	27.5
YIn _{0.40} Mn _{0.60} O ₃	29.5	-1.2	-12.5	29.1	6.4	6.3	47.3	27.8
YIn _{0.30} Mn _{0.70} O ₃	30.0	-1.7	-7.1	26.1	6.6	6.4	41.8	29.0
YIn _{0.20} Mn _{0.80} O ₃	30.3	-2.0	-5.0	24.5	6.3	6.4	38.9	29.6
YIn _{0.10} Mn _{0.90} O ₃	27.9	-1.9	-4.7	23.1	5.7	5.4	37.1	29.9
YMnO ₃	28.7	-1.9	-5.6	27.4	5.9	5.7	44.7	27.6

*Representation of two different CoAl₂O₄ samples is denoted by superscripts **a** and **b**.*

Figure 1. Solar spectral irradiance based on combined direct and circumsolar effects from ASTM G173-03 reference spectra derived from the Simple Model of the Atmospheric Radiative Transfer of Sunshine, SMARTS [14]. Shading of spectral regions has been added.

Figure 2. Normalized powder x-ray diffraction patterns of the YInO_3 - YMnO_3 miscibility range. The inset shows the (002) and (102) peaks magnified.

Figure 3. Normalized particle size distribution of $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$, $x = 0.05 - 1.0$, and commercial CoAl_2O_4 pigments.

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Figure 7. Thin film absorption coefficient of pigmented PVDF resin for the full $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ solid solution and industrial pigment CoAl_2O_4 .

Figure 8. Reflectance spectra for cobalt blue pigments and $\text{YIn}_{0.8}\text{Mn}_{0.2}\text{O}_3$ pigmented acrylic resin.

Figure 9. Reflectance spectra for $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$ pigmented acrylic resin.

Table 1. Color coordinates calculated using spectral analysis of pigmented acrylic as a masstone. Representation of two different CoAl_2O_4 samples is denoted by superscripts **a** and **b**.

Table 2. QUV and outdoor weathering of materials in PVDF/Acrylic resin as full masstone and 4:1 tint. Representation of two different CoAl_2O_4 samples is denoted by superscripts **a** and **b**. A replicate of each sample was analyzed to show variation due to sample preparation.

Table 3. Solar reflectance percentages calculated from spectral analysis of pigmented acrylic resin as a masstone. Representation of two different CoAl_2O_4 samples is denoted by superscripts **a** and **b**.

Table 4. Solar reflectance percentages calculated from spectral analysis of pigmented Polyvinyl Chloride (PVC) resin as a masstone at a 5% pigment loading. Representation of two different CoAl_2O_4 samples is denoted by superscripts **a** and **b**.