Spring 2020

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Recommended Citation

Laughorn, Tyler, "Design of Pigments for use in “Cool” Coatings" (2020). *Williams Honors College, Honors Research Projects*. 1111.
https://ideaexchange.uakron.edu/honors_research_projects/1111

Design of Pigments for use in "Cool" Coatings

4250:497 Honors Project in Corrosion Engineering

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Sponsored by Dr. Qixin Zhou

24 April 2020

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Abstract

This project was focused on the development and testing of several novel pigments that exhibit high NIR-reflectance and therefore show potential for use in “cool” coatings. A “cool” coating will reflect more solar radiation than other standard coatings, and so a coated structure would require less energy to keep cool. Four sets of pigments were synthesized: $Co_{1-x}Mg_xCr_2O_4$ (teal), $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue), $Ti_{1-x-y}Ni_xSb_yO_2$ (yellow), and $Cr_{2-x}Fe_xO_3$ (black). NIR and TSR values were then measured for these pigments at a Sherwin-Williams research and development facility. Results from the testing provided information regarding the optimal compositions for the different sets of pigments and indicated that the blue and black pigments seemed to show the most promise for use in “cool” coatings. The black pigments were then used to mix up simple epoxy coating systems that were used to testing the effectiveness of “cool” coatings at the small-scale when compared to coatings made using a control pigment. This coating testing was the focus of a second project done in conjunction with this one, by Ashleigh Carpenter, and results can be found in the corresponding paper published for that project.

Executive Summary

Problem Statement

Energy consumption for the purpose of keeping buildings and structures cool continues to rise, and one of the most promising ways to combat this problem is through the use of novel “cool” coatings. These coatings would utilize pigments that reflect a much higher portion of near-infrared radiation (the part of sunlight that generates the most heat) than other currently available pigments. This means less energy (and money) would be required to cool a structure coated in these “cool” coatings. In this project, several pigments were synthesized and tested to determine their potential for use in “cool” coatings.

Summary of Results

Four sets of pigments – $Co_{1-x}Mg_xCr_2O_4$ (teal), $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue), $Ti_{1-x-y}Ni_xSb_yO_2$ (yellow), and $Cr_{2-x}Fe_xO_3$ (black) – were synthesized and then tested at a Sherwin-Williams research and development facility. Results from the first two sets of pigments (teal and blue) indicated that higher magnesium content, and especially, higher aluminum content, improved solar reflectance. Results from the third set of pigments (yellow) indicated that higher titanium content improved solar reflectance. Results from the fourth set of pigments (black) indicated that higher iron content improved solar reflectance. The fourth set of pigments (black) was then used to make several sample coatings that were used for testing to determine the effectiveness of “cool” coatings made with these pigments. This testing was the focus of a second project, done in conjunction with this one, and full results can be found in the paper published for that project.

Conclusions

Visually, all the sets of pigments were impressive, and demonstrated the potential for future “cool” coatings to exist in a wide range of colors. The most promising test results came from the fourth set of pigments (black), which exhibited surprisingly high levels of solar reflectance compared to other darkly colored pigments. The first two sets of pigments (teal and blue) also had somewhat promising results, as the testing indicated that similar pigments formulated with high aluminum and magnesium contents could possibly be used in “cool” coatings. The third set of pigments (yellow) exhibited high levels of solar reflectance but were still outperformed by currently available yellow pigments. The testing of the coatings made from the fourth set of pigments (black) seemed to indicate that structures coated with these “cool” pigments were heated by solar radiation less than structures coated with control pigments.

Implications

This project could very likely serve as a starting point for future developments in the area of “cool” coatings, either by utilizing the pigments studied in this project, or other similar pigments. Down the road, widespread use of “cool” coatings could make a major impact in energy consumption by both residential and commercial buildings and structures, which could benefit numerous business sectors and people. More personally, this project has contributed to the development of various skills and knowledge including scientific research, laboratory experience, pigment design and synthesis, coating formulation, the business side of research, project collaboration, time management, and technical writing.

Recommendations

It is recommended that further work and testing be done on the $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue) and $Cr_{2-x}Fe_xO_3$ (black) pigments as these showed the most promise for future use in “cool” coatings. Specifically, efforts should be made to improve the coating formulation work that was done in this project. Subsequent coatings made from these pigments could then be subjected to more extensive testing to determine the impact of these new pigments on various coating properties when compared to current commercially available coatings.

Introduction

In the world today, energy, and its associated costs, are major concerns to many nations and their citizens around the globe. These are not concerning that will disappear anytime soon. Energy demands are expected to increase globally over the next few decades due to population increases, climate change, and infrastructure expansion in developing countries.[1, 2] One of the major sources of energy consumption is the building sector. In 2010, the building sector accounted for 32% of the global energy demand and was responsible for 30% of energy-related CO_2 emissions. Depending on the building and its location, heating and cooling can contribute to up to 73% of a building's total energy consumption.[1] This results in a massive amount of money being spent to heat and cool buildings worldwide. In 2010 it was estimated that the energy demand for cooling both residential and commercial buildings would increase by 750% and 275% respectively by the year 2050.[2] These concerns have led to a lot of time and money being invested in researching new ways to decrease the energy consumption of buildings, and specifically the energy spent on heating and cooling them. One of the most promising techniques for doing this, and the one that was investigated in this project, was the use of "cool" coatings.

Many buildings, both residential and commercial, are painted with some kind of coating, often to protect the underlying substrate, for aesthetic reasons, or for other miscellaneous purposes.[3-8] Most organic coatings, and the pigments they use, do a relatively poor job at reducing energy consumption. Instead, these coatings (especially dark ones) absorb solar radiation which leads to increased heating of the surface and interior of the structure. In urban areas with many buildings in close proximity to each other, this can result in an effect known as urban heat islands (UHI's) which end up requiring huge amounts of energy to cool.[9, 10]

One way to alleviate this problem is using coatings that exhibit high levels of solar reflectance. Doing this has been shown to significantly reducing cooling loads, with only a slight heating penalty, so that the net result is a drop in energy consumption by the building.[11] In the past, most of the organic coatings used for this purpose were a relatively light color (white or off-white). These light-colored coatings and their pigments typically absorb much less solar radiation than other, darker, coatings. This was demonstrated by field experiments that took place in Florida in 1997 that found the residential buildings studied saw average air conditioning energy savings of 19% by switching from dark-colored to white roof coatings.[12] However, this adoption of more reflective coatings for buildings has been limited in large part due to aesthetic influences. More recently, research has expanded around a variety of colored pigments that exhibit much higher levels of solar reflectance than traditional colored pigments. The use of coatings containing these pigments could reduce the UHI effect and lead to major energy savings worldwide.[13]

Pigments that reflect a relatively large amount of solar radiation are often referred to as "cool" pigments, and coatings with these pigments are referred to as "cool" coatings. This is due to the idea that buildings coated with these "cool" coatings will experience less sunlight-induced heating.[14, 15] About 52% of sunlight is made up of near-infrared radiation (NIR), which has a wavelength between 780-2500 nm; heat production from NIR is especially high in the 700-1100 nm range. By increasing the reflectance of solar radiation in this range, the overall heating effect from the solar radiation can be reduced.

This project focused on several "cool" pigments, which were investigated due to the high NIR reflectance that they exhibit, and the coatings that could be made using these pigments. The goal of this project was to synthesize these pigments, measure their NIR reflectance, use them to design simple coatings, and then to test these coatings to examine their impact on building heating caused by NIR.

Background

Two papers were used to help develop the methods of synthesis, coating development, and testing that would be used in this project. The first was published in 2010 by Giable George, V.S. Vishnu, and M.L.P. Reddy, and it focused on the inorganic pigments $Y_{6-x}Si_xMoO_{12-\delta}$ and $Y_{6-x}Pr_xMoO_{12-\delta}$.[15] The second paper was published in 2016 by Weiwei Bao et al., and it focused on the inorganic pigment $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$.[14] Two of the pigments synthesized in this project, $Co_{1-x}Mg_xCr_2O_4$ and $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$, were partly inspired by the paper from Weiwei Bao et al., and by previous work done by Dr. Qixin Zhou and her group at the University of Akron in conjunction with Sherwin-Williams. Some of the processes outlined in these two papers for the pigment synthesis and testing were mimicked in this project. The results from these two papers also demonstrated that there is potential for pigments made from certain combinations of metal oxides to be used in “cool” coatings.

Experimental Methods

Pigment Synthesis

The first steps in this project were concerned with synthesizing the pigments. The first set of pigments synthesized was $Co_{1-x}Mg_xCr_2O_4$ (x = 0.00, 0.25, 0.50, 0.75, and 1.00). This set of pigments was designed to be teal in color. To make these pigments, a Pechini-type sol-gel method was used, as described in the paper by Weiwei Bao et al.[14] Citric acid, cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), and magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) were dissolved in a round-bottom flask filled with 150 mL of deionized water. Specific amounts for the reagents can be seen in Table 1.

Table 1: Reagent amounts used for the synthesis of $Co_{1-x}Mg_xCr_2O_4$.

x-value	Citric Acid (g)	$Co(NO_3)_2 \bullet 6H_2O$ (g)	$Cr(NO_3)_3 \bullet 9H_2O$ (g)	$Mg(NO_3)_2 \bullet 6H_2O$ (g)	Ethylene Glycol (mL)
0.00	56.738	8.731	24.009	0.000	10
0.25	56.738	6.545	24.009	1.921	10
0.50	56.738	4.366	24.009	3.846	10
0.75	56.738	2.183	24.009	5.769	10
1.00	56.738	0.000	24.009	7.692	10

The solids were dissolved using a magnetic stir bar and plate at 300 rpm, and then the flask was submerged in an oil bath at 80°C for 1 hour, while still being stirred. After the hour, ethylene glycol was added to the flask and stirring/heating continued for another hour. The solution was then transferred to a beaker, which was placed inside a furnace at 120°C for 12 hours, followed by 350°C for 2 hours. The result was a hard and brittle puck, mostly homogenous, that was then hand-ground to a fine powder by using a mortar and pestle. The powder was then placed inside a high-temperature furnace at 900°C for 6 hours with a heating rate of 10°C/min.

The second set of pigments synthesized was $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (y = 0.5, 1.0, 1.5, and 2.0). This set of pigments was designed to be blue in color. The same process was followed as with the $Co_{1-x}Mg_xCr_2O_4$ pigments, with the main difference being the addition of aluminum nitrate ($Al(NO_3)_3 \bullet 9H_2O$). Specific amounts for the reagents can be seen in Table 2.

Table 2: Reagent amounts used for the synthesis of $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$.

y-value	Citric Acid (g)	$Co(NO_3)_2 \cdot 6H_2O$ (g)	$Cr(NO_3)_3 \cdot 9H_2O$ (g)	$Mg(NO_3)_2 \cdot 6H_2O$ (g)	$Al(NO_3)_3 \cdot 9H_2O$ (g)	Ethylene Glycol (mL)
0.5	56.738	2.183	18.007	5.769	5.627	10
1.0	56.738	2.183	12.005	5.769	11.254	10
1.5	56.738	2.183	6.002	5.769	16.881	10
2.0	56.738	2.183	0.000	5.769	22.508	10

The third set of pigments to be synthesized was $Ti_{1-x-y}Ni_xSb_yO_2$ ($x = 0.03$ and $y = 0.02$, $x = 0.06$ and $y = 0.04$, $x = 0.09$ and $y = 0.06$, and $x = 0.12$ and $y = 0.08$). This set of pigments was designed to be yellow in color. Due to the different reagents being used, and for the sake of time, a different process was followed for this set of pigments. The reagents used were titanium dioxide (TiO_2), antimony trioxide (Sb_2O_3), ammonium chloride (NH_4Cl), boric acid (H_3BO_3), and a basic nickel carbonate ($Ni_2CO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$), all of which were used as powders. The reagents were weighed out and then mixed until homogenous by using a repurposed coffee grinder. Specific amounts for the reagents can be seen in Table 3. As with the previous pigments, the powders were then placed inside a high-temperature furnace at 900°C for 6 hours with a heating rate of 10°C/min.

Table 3: Reagent amounts used for the synthesis of $Ti_{1-x-y}Ni_xSb_yO_2$.

x-value	y-value	TiO_2 (g)	Sb_2O_3 (g)	NH_4Cl (g)	H_3BO_3 (g)	$Ni_2CO_3 \bullet 2Ni(OH)_2 \bullet 4H_2O$ (g)
0.03	0.02	23.030	0.885	0.125	0.125	1.140
0.06	0.04	21.175	1.720	0.125	0.125	2.215
0.09	0.06	18.890	2.410	0.120	0.120	3.135
0.12	0.08	17.780	3.245	0.125	0.125	4.180

The fourth and final set of pigments to be synthesized was $Cr_{2-x}Fe_xO_3$ (x = 0.3, 0.6, 0.9, 1.2, 1.5, and 1.8). This set of pigments was designed to be black in color. The reagents used were chromium (III) oxide (Cr_2O_3), iron(III) oxide (Fe_2O_3), titanium dioxide (TiO_2), and boric acid (H_3BO_3). As with the $Ti_{1-x-y}Ni_xSb_yO_2$ pigments, the reagents were weighed out and then mixed until homogenous by using a repurposed coffee grinder. Specific amounts for the reagents can be seen in Table 4.

Table 4: Reagent amounts used for the synthesis of $Cr_{2-x}Fe_xO_3$.

x-value	Cr_2O_3 (g)	Fe_2O_3 (g)	TiO_2 (g)	H_3BO_3 (g)
0.3	20.839	3.871	0.124	0.124
0.6	17.162	7.742	0.125	0.125
0.9	13.063	11.250	0.125	0.125
1.2	9.500	15.000	0.123	0.123
1.5	5.938	18.750	0.123	0.123
1.8	2.375	22.500	0.124	0.124

Pigment Testing

All four of the sets of pigments were sent to be tested at a Sherwin-Williams R&D facility. Initial testing was focused on measuring total solar reflectance (TSR) and NIR values for the pigments. Due to intellectual property restrictions imposed by Sherwin-Williams, further information regarding the testing of these samples cannot be made public.

Coating Design

Based on feedback from Sherwin-Williams after the pigment testing, it was decided that only coatings made using the $Cr_{2-x}Fe_xO_3$ (black) pigments would be tested for the time being. A common epoxy resin (EPON™ Resin 828) was chosen to be the base of the coatings. For each of the six $Cr_{2-x}Fe_xO_3$ pigments, 4 grams of pigment, 4 grams of resin, and 2 grams of acetone were combined. The pigment-to-binder ratio was chosen as 1:1 based on the procedure followed in the paper by Giable George, V.S. Vishnu, and M.L.P. Reddy. The acetone was then added to thin down the coating to a more workable viscosity. These coating samples were prepared in scintillation vials and shaken by hand to mix.

Prior to application, 5.54 grams of the hardener (EPIKURE™ Curing Agent 3164) was added to each of the coating samples to result in an AHEW:EEW ratio of 1:1. The vials were then shaken by hand to mix and drawn down onto aluminum Q-panels using a 120 µm (~4.7 mils) drawdown bar. The panels were cleaned with acetone and blown clear of dust prior to application of the coatings. After the first few drawdowns, there seemed to be an issue with bubbles on some of the panels, and so 1 drop each of BYK-141 (defoamer) and BYK-333 (wetting agent) were added to each coating sample; this seemed to resolve the issue. Five repeats were made for each sample.

The x = 1.5 and 1.8 pigment samples had issues with drawdowns at 120 µm. It appeared that the pigment particles were larger than 120 µm and so the resulting drawdowns had little-to-no pigment left behind on the panels. It was unclear whether this phenomenon was due to differences in pigment formulation, a pigment dispersion issue, or caused by some other factor. To correct this issue, these coating samples were applied using a 150 µm (~6 mils) drawdown bar instead of the 120 µm bar.

Control panels were drawn down using a control coating that was made following the exact same procedure as was used for all the sample pigments. The black control pigment was pure Fe_3O_4. The control coating was drawn down at both 120 µm and 150 µm so that accurate comparisons could be made between all the samples.

The panels were left to dry in a fume hood overnight before being baked in an oven at 120°C for 2 hours on the following day. After drying, numerous defects were revealed on some of the panels. When it came to test, only panels with minimal defects were used.

Coating Testing

Testing the effectiveness of these "cool" pigments on preventing heating caused by solar radiation was the objective of a different project that accompanies the one presented in this paper. A report published in 2020 by Ashleigh Carpenter focuses on the testing and results that follow this project.

For the testing, small "houses" were made out of polystyrene foam, and these "houses" were heated by lamps designed to mimic solar radiation. The coating panels made from the $Cr_{2-x}Fe_xO_3$ (black) pigments were placed on top of the "houses", and temperature data from inside the "houses" was recorded over time. In this way, the effectiveness of the "cool" pigments – compared to the control pigment – at preventing internal heating of the structures was evaluated. For more information regarding this testing, see the report by Ashleigh Carpenter.

Data and Results

Pigment Results

All four sets of the synthesized pigments exhibited good color and homogeneity. For the first set of pigments, $Cr_{2-x}Fe_xO_3$ (black), the powder ranged from dark grey (x = 0.00) to light grey (x = 1.00) prior to being placed in the high-temperature furnace. Upon removal from the furnace, the powder had changed color from grey to teal, with each x-value having a distinct color. Pictures of the powder before and after the high-temperature furnace can be seen in Figure 1.

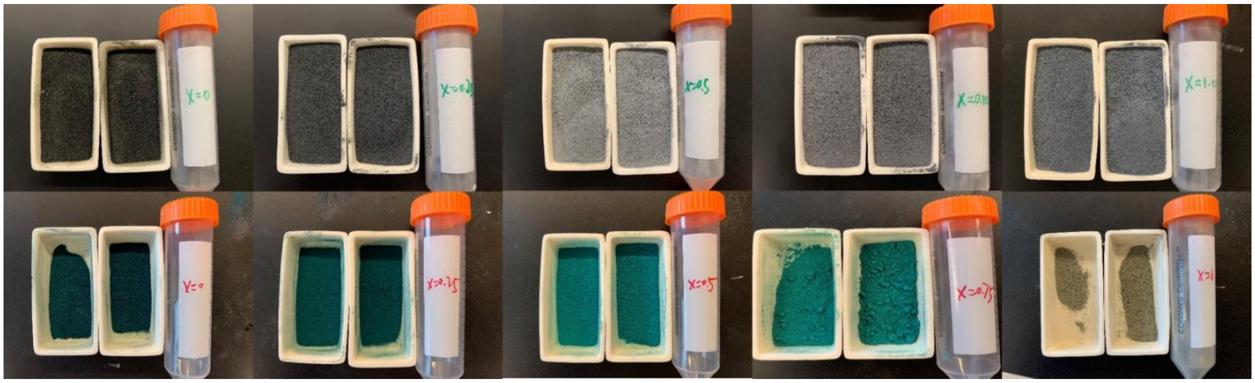

Figure 1: Pictures of the $Co_{1-x}Mg_xCr_2O_4$ pigments before (top) and after (bottom) being put in the high-temperature furnace. The pigments are arranged with x = 0.00 on the far left and x = 1.00 on the far right.

For the second set of pigments, $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue), the powder ranged from grey (y = 0.5) to dull yellow (y = 2.0) prior to being placed in the high-temperature furnace. Upon removal from the furnace, the powder had changed into an assortment of blues, with y = 0.5 (the least aluminum and therefore showing the most resemblance to the pigments in Figure 1) appearing as a teal color, all the way to y = 2.0 appearing as a bright blue. Pictures of the powder before and after the high-temperature furnace can be seen in Figure 2.

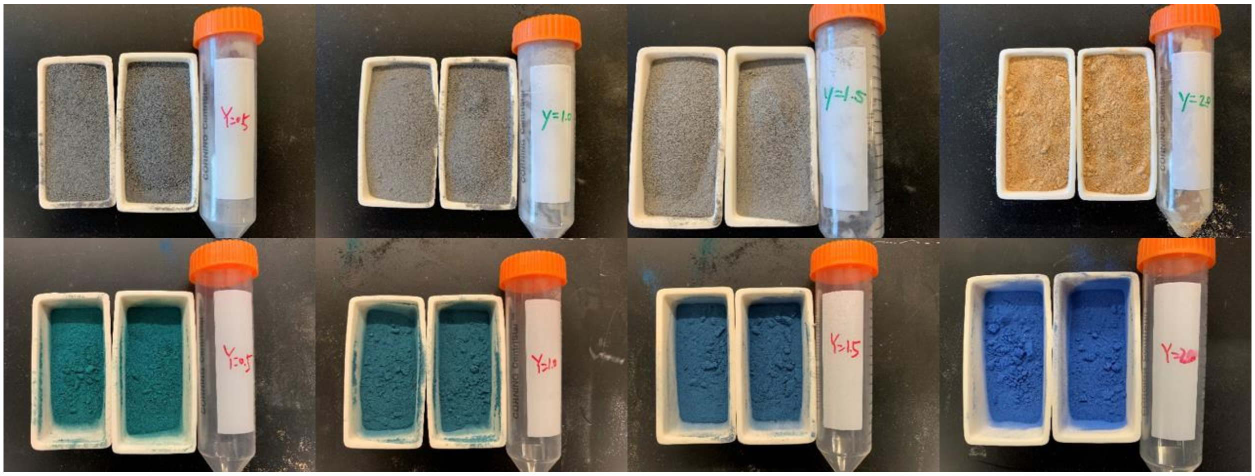

Figure 2: Pictures of the $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ pigments before (top) and after (bottom) being put in the high-temperature furnace. The pigments are arranged with y = 0.5 on the far left and y = 2.0 on the far right.

For the third set of pigments, $Ti_{1-x-y}Ni_xSb_yO_2$ (yellow), all of the powders appeared very light green in color prior to being placed in the high-temperature furnace. Upon removal from the furnace, the powders had changed color from light green to yellow, and it was difficult to distinguish color differences between the samples. Pictures of the powder before and after the high-temperature furnace can be seen in Figure 3.

Figure 3: Pictures of the $Ti_{1-x-y}Ni_xSb_yO_2$ pigments before (top) and after (bottom) being put in the high-temperature furnace. The pigments are arranged with x = 0.12 and y = 0.08 on the far left and x = 0.03 and y = 0.02 on the far right.

For the fourth set of pigments, $Cr_{2-x}Fe_xO_3$ (black), the powders varied in color from green (x = 0.3) to red (x = 1.8) prior to being placed in the high-temperature furnace. Upon removal from the furnace, the powders had changed color from red/green to dark grey, and it was somewhat difficult to distinguish color differences between the samples. Pictures of the powder before and after the high-temperature furnace can be seen in Figure 4.

Figure 4: Pictures of the $Cr_{2-x}Fe_xO_3$ pigments before (top) and after (bottom) being put in the high-temperature furnace. The pigments are arranged with x = 0.3 on the far left and x = 1.8 on the far right.

Due to intellectual property restrictions imposed by Sherwin-Williams, only a small amount of information regarding the results of TSR and NIR testing can be made public. Exact numbers and figures will not be presented in this report, but the results will be discussed in a limited fashion in the Discussion and Analysis section below.

Coating Results

Full data and results for the coating testing are given in the report by Ashleigh Carpenter and so will not be presented here. However, the results will be briefly discussed in the Discussion and Analysis section below.

Discussion and Analysis

Visually, the colors of the four sets of pigments show promise at potentially providing a wider color-range for “cool” coatings than that of white or off-white. Maybe most notably, the idea that a dark grey or black pigment, such as $Cr_{2-x}Fe_xO_3$, could be used in a “cool” coating opens the door for numerous color possibilities.

For the $Co_{1-x}Mg_xCr_2O_4$ (teal) pigments, NIR reflectance showed slight increases with increasing magnesium content (increasing x-values), but the NIR reflectance values for all of the samples remained relatively low without any aluminum being present. The $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue) pigments all exhibited higher NIR reflectance values than the $Co_{1-x}Mg_xCr_2O_4$ (teal) pigments, and NIR reflectance values increased with increasing aluminum content (increasing y-values). These results indicate that some amount of aluminum is necessary to obtain high levels of NIR reflectance, and that higher levels of magnesium relative to cobalt seem to improve NIR reflectance. Based on this, future testing could experiment with keeping aluminum and magnesium levels high while adjusting cobalt/chromium levels, or even while adding other reagents into the pigment. Also, for these pigments, the differences in color were visually significant, and work could be done to determine the optimal color desired for different "cool" coatings, while maintaining a high level of NIR reflectance. In a laboratory setting, using the sol-gel process to synthesize these pigments was much more time-consuming than the method used for the other pigments; work could be done to see if using a different method to synthesize these pigments was able to speed up the process without sacrificing the resulting quality of pigment.

The $Ti_{1-x-y}Ni_xSb_yO_2$ (yellow) pigments exhibited NIR reflectance values much higher than those of the $Co_{1-x}Mg_xCr_2O_4$ (teal) or $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue) pigments, but the values did not surpass those of currently available NIR-reflective yellow pigments. Because of this, this set of pigments does not show as much promise for further use as the other pigments do. NIR reflectance values showed slight increases with increasing titanium content (decreasing x and y values). If other, similar pigments are tested in the future, these results could be used to justify using a high titanium content in the formulation of those pigments.

The $Cr_{2-x}Fe_xO_3$ (black) pigments exhibited relatively high NIR reflectance values compared to other commercial black pigments, and NIR reflectance tended to increase with increasing iron content (increasing x-values). This set of pigments seems to show the most promise out of all the pigments tested, and future work will likely be done to further improve NIR reflectance.

Results from testing the panels made with the $Cr_{2-x}Fe_xO_3$ (black) pigments, and the control panels made with Fe_3O_4, indicate that the pigments synthesized in this project were successful at preventing heating inside the test "houses". The testing demonstrated a surprisingly low level of repeatability; however, a slight trend was observed indicating that increasing x-values seemed to increase the effectiveness at preventing heating. These results match the results from the NIR reflectance testing. Although, as these results were not completely clear, it is possible that with the setup used for the testing, standard noise/variation somewhat masked the underlying differences between the sample coatings. For more information regarding these results, see the report by Ashleigh Carpenter.

Conclusions and Recommendations

The goal of this project was to research several sets of pigments and their potential to be used in “cool” coatings. First, four sets of pigments were synthesized: $Co_{1-x}Mg_xCr_2O_4$ (teal), $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue), $Ti_{1-x-y}Ni_xSb_yO_2$ (yellow), and $Cr_{2-x}Fe_xO_3$ (black). The first two sets of pigments were synthesized using a Pechini-type sol-gel method followed by baking in a high-temperature furnace. The second two sets of pigments were synthesized by blending dry reagents together and then baking the mixture in the high-temperature furnace.

All the pigments were then tested by a Sherwin-Williams research and development facility to measure TSR and NIR data. NIR results for the first two sets of pigments, $Co_{1-x}Mg_xCr_2O_4$ (teal) and $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue), revealed that NIR reflectance tended to increase with magnesium and aluminum content. The $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue) pigments show promise for use in “cool” coatings and will likely be the subject of future testing. NIR results for the third set of pigments, $Ti_{1-x-y}Ni_xSb_yO_2$ (yellow), revealed that NIR reflectance tended to increase with increasing titanium content, and these pigments exhibited relatively high NIR reflectance, but were still outperformed by similar pigments already commercially available. NIR results for the fourth set of pigments, $Cr_{2-x}Fe_xO_3$ (black), revealed that NIR reflectance tended to increase with increasing iron content, and this set of pigments showed the most promise out of the group for use in “cool” coatings.

Sample coatings were then made from the $Cr_{2-x}Fe_xO_3$ (black) pigments by mixing the pigments in a 2:2:1 ratio by volume with epoxy resin and acetone respectively. Very small amounts of defoamer and wetting agents were also added to the coatings. Hardener was added in a 1:1 AHEW:EEW ratio, and the coatings were drawn down onto aluminum Q-panels using either a 120 µm or 150 µm drawdown bar. After curing in an oven, these sample panels were tested against control panels using an Fe_3O_4 pigment to determine whether the $Cr_{2-x}Fe_xO_3$ (black) pigments would work in a small-scale setup designed to mimic the heating of buildings by solar ration. The panel testing was the focus of another project done in conjunction with this one, and information regarding the testing and results can be found in a paper published in 2020 by Ashleigh Carpenter.

It is recommended that further work be done to improve upon the coating formulation in this project. More extensive testing could then be done comparing these novel "cool" pigments to other commercially available pigments and their impact on various coating properties (e.g. color, stability, corrosion protection, etc.). The $Cr_{2-x}Fe_xO_3$ (black) pigments seemed to show the most promise out of all the pigments tested, and so this set of pigments should be a major focus moving forward. More work should also be done on the $Co_{0.25}Mg_{0.75}Cr_{2-y}Al_yO_4$ (blue) pigments, and on any pigments like these that may also exhibit high levels of NIR reflectance.

Design Constraints

Intellectual Property

As mentioned previously, intellectual property restrictions played a significant role in this project. Because this project was carried out in conjunction with Sherwin-Williams, any information regarding the testing methods and the subsequent results has been carefully guarded. This makes it difficult to give readers a complete understanding of the results of this project, which much time and effort went into reaching. However, these restrictions are important as they play a major role in incentivizing experimental projects such as this one. Without intellectual property restrictions, this project and any project similar to it would likely not be carried out, at least to the same extent as they have been.

Safety

Safety is a major focus of any scientific endeavor, and for good reason. In the process of working to improve or expand on previous knowledge and technology, it is important to make sure the result is not more harm than good. In this project, proper personal protective equipment (PPE) was worn at all times and general laboratory safety techniques were used. This included maintaining proper storage of chemical reagents and products, and carrying out laboratory work under a fume hood whenever possible. None of the aspects of this project (the process for synthesizing the pigments, the pigments themselves, coatings made from the pigments, and testing procedures for those coatings) seem to be any more hazardous to the environment or dangerous to personal safety than other procedures/products already common in the coatings industry.

Function

When carrying out projects such as this one, it is important not to lose sight of the final product that the new technology could be useful for. All of the pigments synthesized and tested in this project are done so with the idea that they have potential to be used in novel “cool” coatings. These coatings could be used for both commercial and residential buildings to save money spent on cooling, and could lead to a decrease in energy demands regionally, or even globally. The early testing to evaluate these pigments was carried out with these goals in mind. If any of the pigments fail to accomplish this primary objective to some reasonable extent, more time and money spent on those pigments would likely end up wasted.

Acknowledgements

This project was performed under the direction of Dr. Qixin Zhou and Cheng Zhang; their help in performing experiments and critiquing the process was incredibly valuable. A fellow student, Ashleigh Carpenter, was also very helpful in assisting throughout the course of this project. All the testing was either performed in Dr. Zhou’s lab in NCERCAMP at the University of Akron, or at Sherwin-Williams’ Minneapolis R&D facility.

References

1. Ürge-Vorsatz, D.; Cabeza, L. F.; Serrano, S.; Barreneche, C.; Petrichenko, K., Heating and cooling energy trends and drivers in buildings. *Renewable and Sustainable Energy Reviews* **2015,** *41*, 85-98.

2. Santamouris, M., Cooling the buildings–past, present and future. *Energy and Buildings* **2016,** *128*, 617-638.

3. Richardson, T. J., *Shreir's corrosion*. Elsevier: 2009.

4. Zhang, C.; Wang, H.; Zhou, Q., Waterborne isocyanate-free polyurethane epoxy hybrid coatings synthesized from sustainable fatty acid diamine. *Green Chem.* **2020,** *22* (4), 1329-1337.

5. Zhang, C.; Wang, H.; Zeng, W.; Zhou, Q., High Biobased Carbon Content Polyurethane Dispersions Synthesized from Fatty Acid-Based Isocyanate. *Ind. Eng. Chem. Res.* **2019,** *58* (13), 5195-5201.

6. Zhang, C.; Wang, H.; Zhou, Q., Preparation and characterization of microcapsules based self-healing coatings containing epoxy ester as healing agent. *Prog. Org. Coat.* **2018,** *125*, 403-410.

7. Wang, H.; Zhang, C.; Zeng, W.; Zhou, Q., Making alkyd greener: Modified cardanol as bio-based reactive diluents for alkyd coating. *Prog. Org. Coat.* **2019,** *135*, 281-290.

8. Zhang, C. PIGMENTED POLYURETHANE/POLYSILOXANE HYBRID COATINGS FOR CORROSION PROTECTION. University of Akron.

9. Malshe, V. C.; Bendiganavale, A. K., Infrared reflective inorganic pigments. *Recent Patents on Chemical Engineering* **2008,** *1* (1), 67-79.

10. Santamouris, M.; Synnefa, A.; Karlessi, T., Using advanced cool materials in the urban built environment to mitigate heat islands and improve thermal comfort conditions. *Solar Energy* **2011,** *85* (12), 3085-3102.

11. Synnefa, A.; Santamouris, M.; Akbari, H., Estimating the effect of using cool coatings on energy loads and thermal comfort in residential buildings in various climatic conditions. *Energy and Buildings* **2007,** *39* (11), 1167-1174.

12. Parker, D. S.; Barkaszi Jr, S. F., Roof solar reflectance and cooling energy use: field research results from Florida. *Energy and Buildings* **1997,** *25* (2), 105-115.

13. Levinson, R.; Berdahl, P.; Akbari, H., Solar spectral optical properties of pigments—Part I: model for deriving scattering and absorption coefficients from transmittance and reflectance measurements. *Sol. Energy Mater. Sol. Cells* **2005,** *89* (4), 319-349.

14. Bao, W.; Ma, F.; Zhang, Y.; Hao, X.; Deng, Z.; Zou, X.; Gao, W., Synthesis and characterization of Fe3+ doped Co0. 5Mg0. 5Al2O4 inorganic pigments with high near-infrared reflectance. *Powder Technol.* **2016,** *292*, 7-13.

15. George, G.; Vishnu, V.; Reddy, M., The synthesis, characterization and optical properties of silicon and praseodymium doped Y6MoO12 compounds: environmentally benign inorganic pigments with high NIR reflectance. *Dyes. Pigm.* **2011,** *88* (1), 109-115.