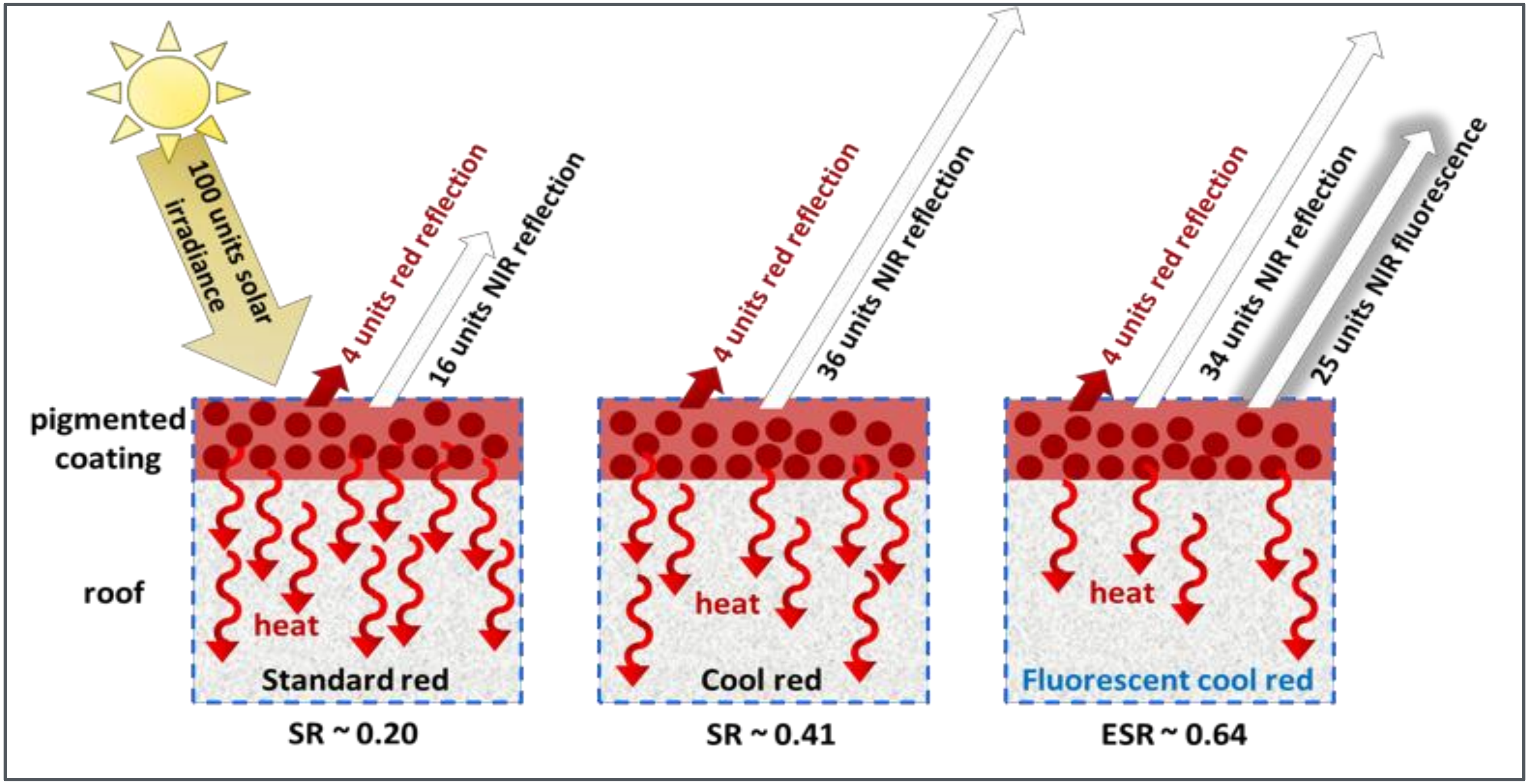
Fluorescent Pigments for High-Performance Cool Roofing

2014 Building Technologies Office Peer Review



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Project Summary

Timeline:

Start date: October 1, 2013 (NEW PROJECT)

Planned end date: September 30, 2014

Key Milestones

1. 200g Dark Red Pigment, End Q1
2. Additional Pigments Identified, End Q2
3. 500g of 2 New Pigments, End Q3
4. ESR Measured on New Cool Roof Coating, End Q4

Key Partners:

PPG Industries, Inc.	Lawrence Berkley National Lab

Budget:

Total DOE $ to date: $474,132

Total future DOE $: $0

Project Goal:

This project will develop novel dark-colored, cool pigments that combine near-infrared (NIR) fluorescence with NIR reflectance. These novel pigments will obtain unprecedented effective solar reflectance (ESR) values for dark-colored coatings to be used in the Building Envelope segment.

Target Market/Audience:

Residential Roofing Sector

Purpose and Objectives

Problem Statement: State of the art solar reflectance and therefore building performance is limited by the nature of the NIR pigments used in cool roof coatings.

Target Market and Audience: The target market is the steep metal roof market. Residential market roofs in Climate Zones 4 & 5 could save 124 TBTU by deploying traditional cool roof technology*. By scaling this savings with the fluorescent pigment improvement, the savings increases to 165 TBTU.

Impact of Project: PPG is already supplying Cool Roof products into the market. By developing novel pigments and incorporating them into roof coatings, we have the ability to increase the energy savings from Cool Roof applications. Since color is important, this project investigates how we can provide a range of different pigment options. This project is a proof of concept, that can lead to subsequent government or private investment to bring this technology to the market. We are measuring progress by the ESR achieved in the lab-scale prototype coatings. The ESR goal for dark coatings is 0.5 to 0.7.

* R. Levinson, The case for cool roofs, LBNL (May 7, 2012)

Approach

Approach: This one-year project is divided into two phases: Pigment Development/Characterization, and Coating Formulation and Testing. LBNL will screen and, synthesize candidate materials using various techniques, including combustion synthesis; then characterize their absorbance, reflectance, and fluorescence properties. PPG will optimize the processing and doping of promising materials in conjunction with LBNL, and to produce them in sufficient quantities to support coating evaluation.

Key Issues: Fluorescent pigment materials are sometimes hard to produce, or expensive. Some materials do not disperse into paints easily. Color shift is not acceptable.

Distinctive Characteristics: LBNL has developed a scaled-up method to synthesize the first red pigment. PPG has process capabilities to further scale-up certain pigment methods.

This is a research project, working to solve a hard problem.

Progress and Accomplishments

Lessons Learned: Scale-up of pigment production and incorporation of pigments into coatings were not straightforward.

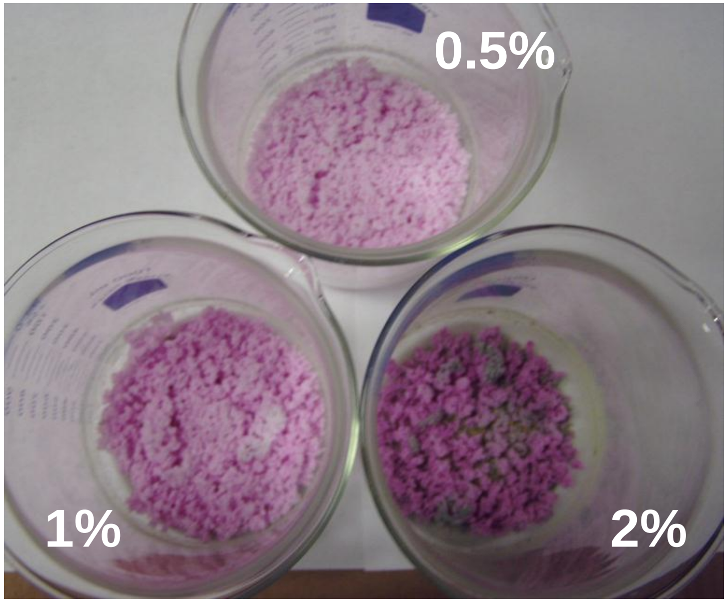
Accomplishments: Two tasks related to initial pigment production completed. First task to incorporate new pigment into coatings ongoing, prolonged. Tasks for additional pigments started. Phase 2 tasks have not started.

Market Impact: Coatings based on these pigments can satisfy consumer demand for dark colors on building surfaces, and contribute to achieving the DOE's goal of building envelope energy savings of 20% compared to 2010 levels. Use of these coatings can save as much as 0.17 Quads annually, worth approximately $1.3B/year in the new or retrofit residential roofs market in the warm and hot U.S. climates.

Awards/Recognition: Nothing to report at this time.

Synthesize red pigment (Al_2O_3:Cr) via combustion synthesis

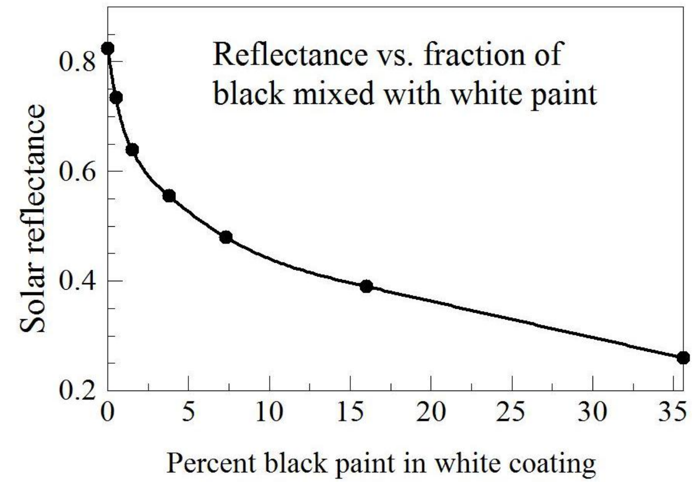
- Kingsley *et al*. recipe
- Metal nitrates + urea + water, 500 °C furnace temp. → 2 g
  - Solution dehydrates
  - Ignition to ~ 1500 °C
- Recipe doubled, doping increased, raise temp. → 4 g
- 2nd doubling, boiling time ▲ to 10 min. increase urea → 8 g
- 3rd doubling, increase urea again, 540 °C → 16 g
- **Production of 200 g - milestone**
- Key issues
  - Ruby fluoresces at 693, 694 nm – deep red
  - By-product (gamma-Al_2O_3:Cr) is greenish yellow; no fluorescence
  - Synthesis of darker red (smaller particles) at lower temp. leads to excessive by-product

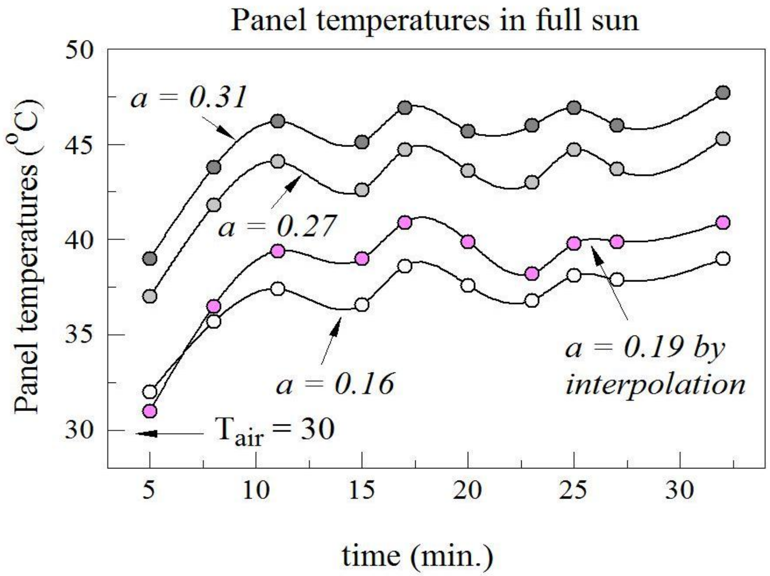


500°C furnace temp; 0.5%, 1%, and 2% doping

Effective Solar Reflectance (ESR) determination

- Calibrated non-fluorescent samples prepared: mixture of white and black paint on metal substrates
- Spectrometer determines SR
- Temperature measurements taken outside in full sun
- Solar absorptance a of unknown fluorescent sample determined by interpolation
- ESR = 1 - a





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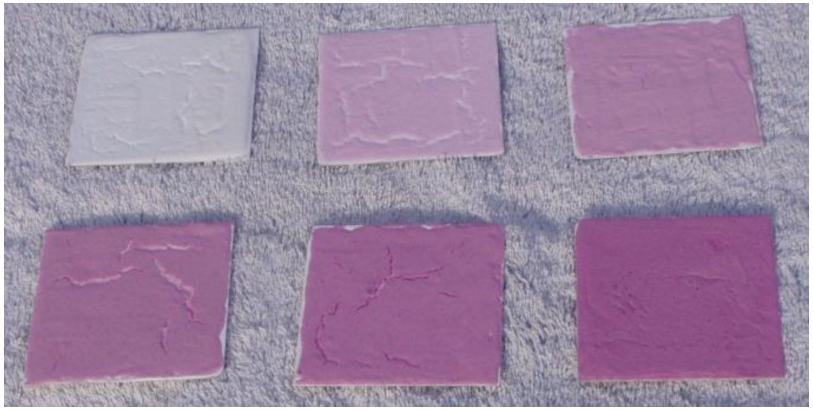
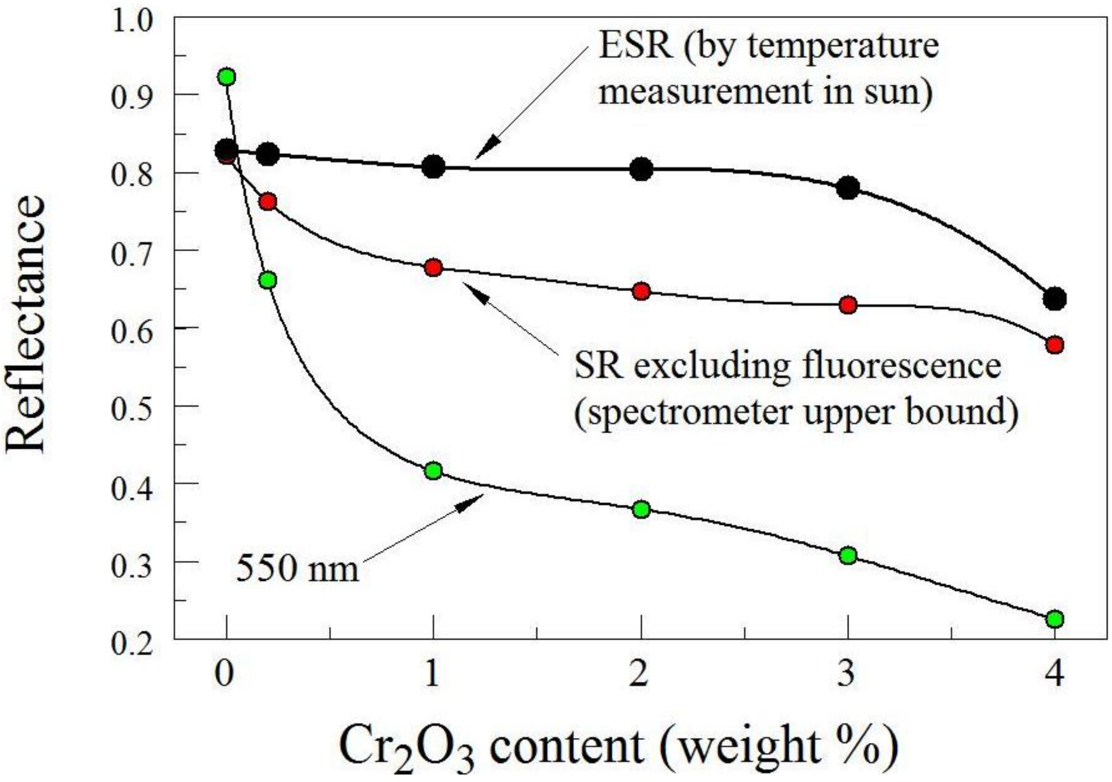
Results for 5 mil (125 µm) handmade coatings over white

- Pigments mixed with acrylic polymer and applied with spatula





- ESR value high up to 3% doping
- 550 nm curve shows visual brightness
- Performance of commercial coatings will not be quite as high

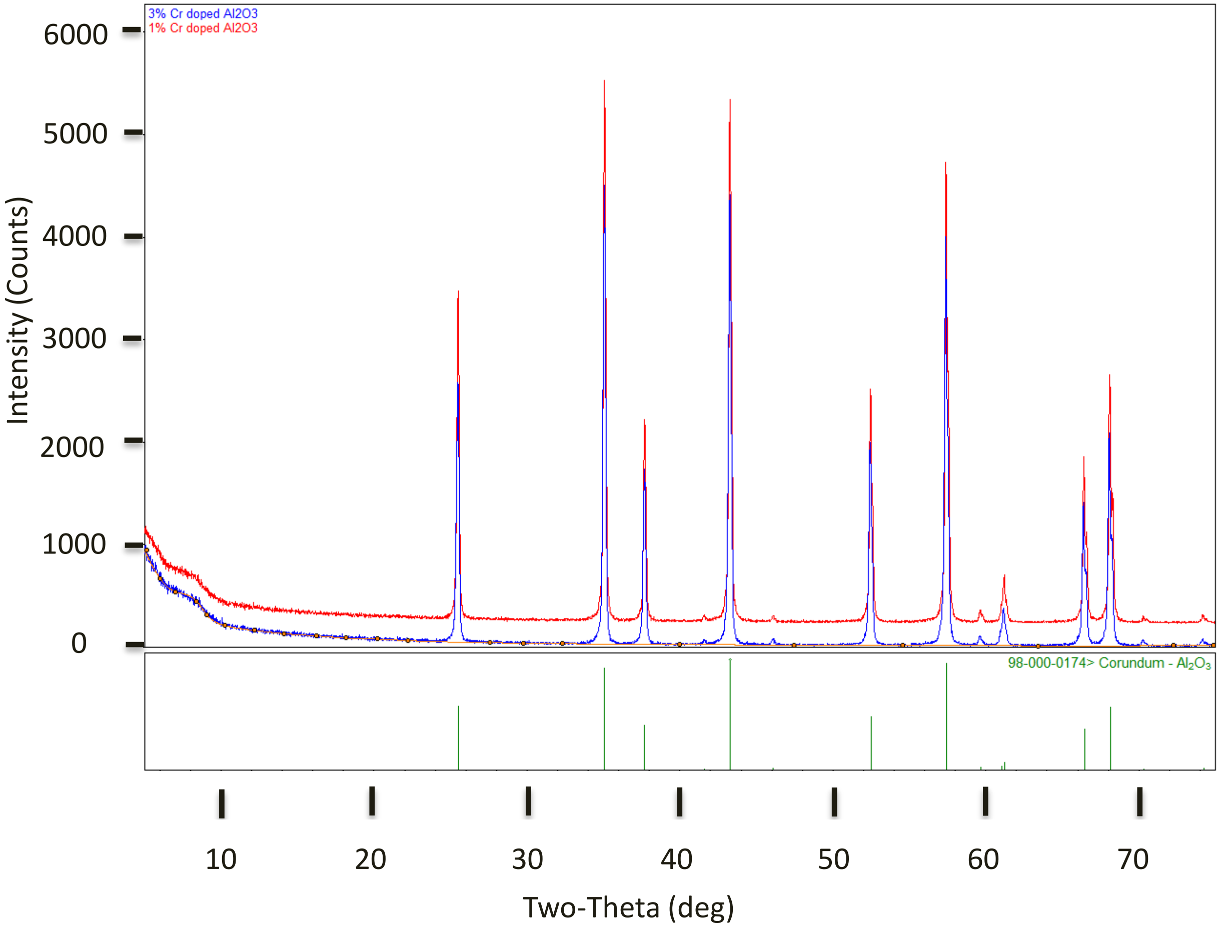
Current list of additional prospective pigments

- Egyptian blue, $CuCaSi_4O_{10}$, 900-1000 nm
- YAG:Nd – $Y_3Al_5O_{12}:Nd^{3+}$, 1060 nm
- Cd(S,Se,Te) –direct band gap, wide range of wavelengths
- Zn(O,S,Se,Te) – emission below band gap, includes $ZnS:Sn^{2+}$, also ZnS doped with Mn, Te
- $LiAlO_2:Fe^{3+}$, 700-800 nm, need dopant for VIS absorption
- α-SrO · $3B_2O_3$:Sm, deep red, 300-550 nm absorption
- $CaS:Yb^{2+}$, 750 nm

- Criteria: quantum efficiency, cost, stability, toxicity, etc.

Characterization of red pigment from LBNL

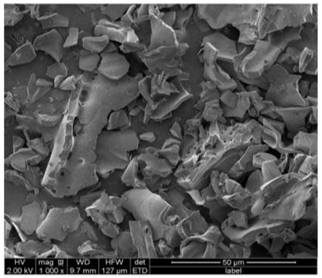
XRD

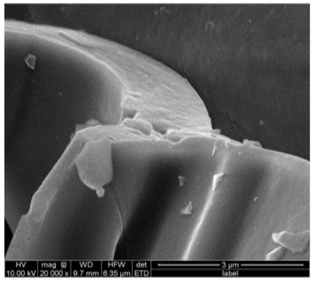


XRF

X-ray fluorescence measurements on 1 and 3% Cr_2O_3 doped Al_2O_3 showed the expected composition

SEM





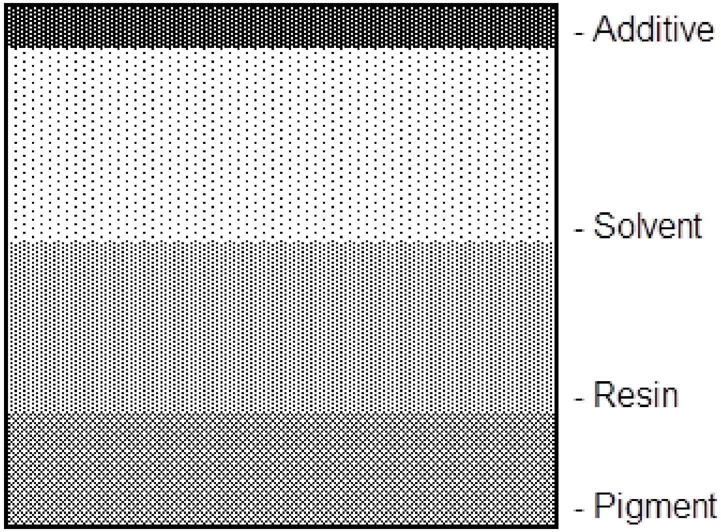
Data acquired by SEM and x-ray diffraction suggest that large crystalline particles are generated during the combustion synthesis of $Cr:Al_2O_3$

X-ray diffraction patterns of two samples of Al_2O_3 from LBNL doped with 1 and 3% of Cr showed the presence of α-Al_2O_3 – the desired phase of Cr doped Al_2O_3 for near IR fluorescence

Incorporating Pigments into Paint

Paint Consists of

- Binder
  - Resin
  - Polymer
  - Vehicle
- Pigment
- Additives
- Solvent



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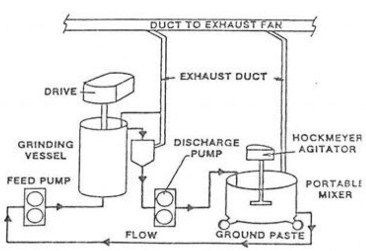
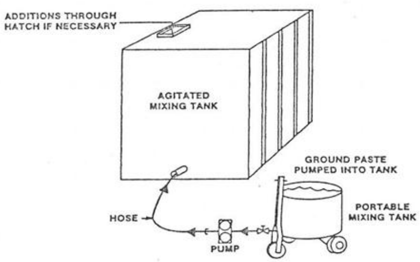
Incorporating Pigments into Paint

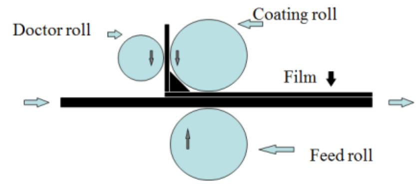
Pigment dispersion with high speed dispersing blade or grind media



→ Letdown with additional resins/additives/ solvents



→ Apply coating to substrate (spray, roll, dip, etc.)



→ Cure coating (ambient or heat)

↓ Test coating

Incorporation of Al_2O_3:Cr into Paint

- To be properly incorporated into a coating, a tint base containing Al_2O_3:Cr was prepared.
- A tint base is comprised of a grind resin, dispersing/wetting agent, solvent and pigment.
- These ingredients are mixed in a stainless steel vessel using a flat blade stirrer[1] and zirconia grind media.
- The pigment dispersion settled rapidly, suggesting a poor dispersion of the pigment. Also, the dispersion was contaminated with a gray color
- **Problem**: Al_2O_3:Cr has a Mohs hardness of 9, which is harder than both stainless steel (5.5-6.3) and zirconia (8). This difference in hardness makes it challenging to properly disperse the Al_2O_3:Cr using conventional pigment dispersion methods
- **Plans**: disperse pigment in a PTFE container that will be able to absorb the energy from the Al_2O_3:Cr. Some contamination from the plastic and zirconia may still occur, but the contaminants will be colorless and have no impact on the properties of the coating.

[1]http://www.cbmills.com/images/lab-mills.jpg

Project Integration and Collaboration

Project Integration: LBNL has identified a number of interesting alternate pigments that will be incorporated into paint shortly. Many of these do not have the same dispersion issues found in the first pigment. PPG has a large pool of resources looking at the dispersion issue, which are providing a number of options for this pigment.

Partners, Subcontractors, and Collaborators: In phase 2, we will look at new synthesis techniques to increase the ability to produce pigments. Many of the new pigments may be available from commercial sources.

Communications: The project team is meeting monthly, or more as needed. We are meeting with our sponsor quarterly.

Next Steps and Future Plans

Next Steps: Complete Phase 1 activities, selecting the most promising candidate pigments (from a performance and processing perspective) for further development in Phase 2.

- Evaluate Al_2O_3: Cr as a commercial cool fluorescent pigment
- Screen other candidate pigments for feasibility
- Spectral fluorescence characterization
- Coating formulation and testing – ESR, mechanical and chemical stability
- Replace combustion synthesis with faster processes
- Invite participation of one or more pigment manufacturers

Future Plans: Enhance BTO's Cool Roof mission by addressing limitations of pigments (efficiency, stability, toxicity…); address other roofing types and even automotive applications

REFERENCE SLIDES

Project Budget

Project Budget: $530,165 (PPG + LBNL, including cost share)
Variances: Work is progressing slightly slower than planned, leading to a slightly reduced level of spending.

Budget History					
FY2013 (past)		FY2014 (current)		FY2015 (planned)	
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
	$0	$474,132	$56,033	$0	$0

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Project Plan and Schedule

WBS	Task Name	Duration	Start	Finish	% Complete	Baseline Start
1	**Phase 1**	**174 days**	**10/1/13**	**5/31/14**	**50%**	**10/1/13**
T 1	Synthesize dark red pigment via combustion synthesis	83 days	10/1/13	1/23/14	100%	10/1/13
T 2	Develop and document consistent testing methodologies	57 days	10/1/13	12/18/13	90%	10/1/13
T 3	Validate performance of dark red pigment in conventional coatings	86 days	11/1/13	2/28/14	50%	11/1/13
T 4	Evaluate additional candidate pigment materials	152 days	11/1/13	5/31/14	45%	11/1/13
T 5	Synthesize dark-colored pigments	109 days	1/1/14	5/31/14	0%	1/1/14
2	**Phase 2**	**131 days**	**4/1/14**	**9/30/14**	**0%**	**4/1/14**
T 6	Scale-up pigment synthesis with plasma reactor	88 days	4/1/14	7/31/14	0%	4/1/14
T 7	Incorporate pigments into metal roof coatings and evaluate cool roof performance	87 days	4/1/14	7/30/14	0%	4/1/14
T 8	Pre-commercialization of pigments with qualified pigment manufacturer	66 days	7/1/14	9/30/14	0%	7/1/14
T 9	Technology-to-Market Strategy	22 days	9/1/14	9/30/14	0%	9/1/14
3	**Milestones**	**204 days**	**12/18/13**	**10/1/14**	**0%**	**11/1/13**
M a	Two hundred grams of dark red pigment	0 days	1/23/14	1/23/14	99%	11/1/13
M b	A consistent and reproducible test methodology	0 days	12/18/13	12/18/13	90%	1/1/14
M c	A dark red coating will be formulated	0 days	3/1/14	3/1/14	0%	2/3/14
M d	Provide initial estimates	0 days	12/31/13	12/31/13	100%	12/31/13
M e	10 additional pigments synthesized	0 days	6/2/14	6/2/14	0%	6/2/14
M f	Produce other pigments	0 days	6/2/14	6/2/14	0%	6/2/14
M g	Five hundred gram batches	0 days	8/1/14	8/1/14	0%	8/1/14
M h	Potential manufacturing partner identified	0 days	10/1/14	10/1/14	0%	10/1/14
M i	ESR of pigments measured	0 days	7/31/14	7/31/14	0%	7/31/14
M j	Update BTO prioritization tool	0 days	10/1/14	10/1/14	0%	10/1/14