Inhibited Aluminum Vacuum Metallized Flakes for Waterbased Inks and Coatings

Introduction

Aluminum vacuum metallized flakes (VMF) are widely used to produce mirror-like, metallic effects for a variety of decorative applications (Figure 1). This includes decorative effects in packaging, automotive and consumer electronic markets.

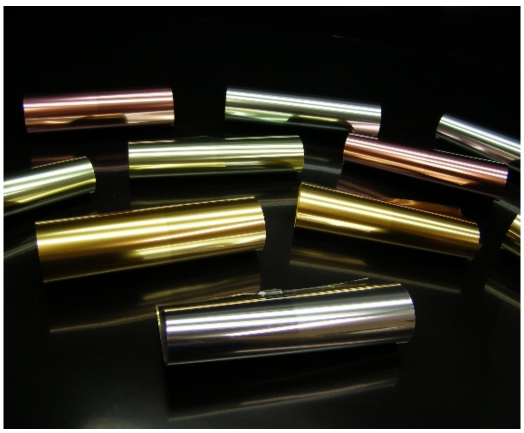

Figure 1. Polyester films coated with aluminum Vacuum Metallized Flake (VMF) coatings.

Often, there is an economic consideration whether to use VMF pigment for a small area of decoration versus using a fully metallized substrate. Depending on the application, there is a threshold coverage, below which it is more economical to decorate with a VMF ink or coating rather than using a fully metallized substrate.

Manufacturing process

VMF pigment is produced by stripping vacuum metallized aluminum from polymer film using a solvent, such as ethyl acetate. This is followed by several process steps that ultimately results in a 10% -20% solids dispersion (Figure 2).

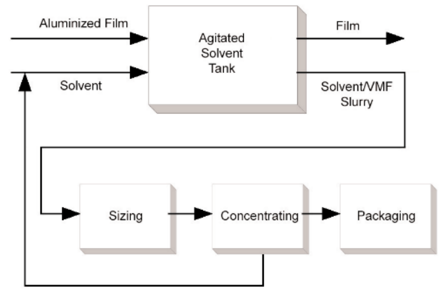

Figure 2. *Vacuum Metallized Flake (VMF) production process*

Prior to metallization, the substrate film is coated with a “release coating” designed to dissolve rapidly in the stripping solvent. Since there will be some residual release coating in the final product, the nature of the release coating can be important for compatibility and post treatment.

Controlling the thickness of the metallized flake is very important to maintain a consistent visual effect. Flake thicknesses are typically between 100 – 400 angstroms. In practice, flake thickness is controlled by the optical density or surface resistivity of the metallized film.

As flake thickness decreases, the appearance becomes darker and the overall reflectivity increases. The greater reflectivity of thinner flakes can be attributed to less light scattering from the flake edges. The scanning electron image in Figure 3 illustrates typical flake dimensions.

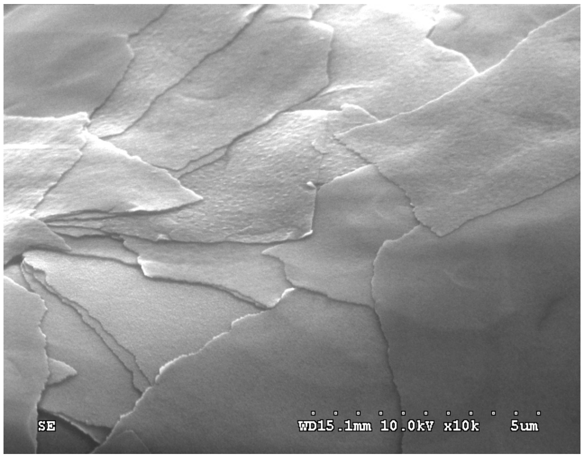

Figure 3. Scanning electron microscope images of VMF pigment.

Formulation basics

Basic formulation strategies for optimizing a mirror effect are:

1. **High pigment/binder (P/B) ratio**: Greater levels of binder tend to dull metallic effect. However, reducing the binder level will also reduce adhesion and rub resistance
   a. For printing applications; typical P/B ratios are 1/1 – 1/2
   b. For coating applications; typical P/B ratios are 2/1 – 1/4
2. **Low total solids:** Greater solvent evaporation and low coating weight produces higher levels of orientation
   a. For printing application; typical total solids are 8% - 15%
   b. For coating applications, typical total solids are 2% -10%

Producing a mirror-like effect is easiest for "second-side" applications where the metallic decoration is applied to the back-side and viewed through a clear substrate. The aluminum flakes are highly oriented at the substrate interface which assists in achieving a mirror-like effect. Typically, "first-side" or surface coated applications, achieve less flake orientation which tends to reduce the potential for a mirror effect.

Aluminum pigment corrosion/stability in waterbased applications

The continued trend toward reduced VOC emissions has driven the use of waterbased ink and coating formulations. This has resulted in a special challenge for aluminum pigments since they are susceptible to corrosion reactions.

In practice, aluminum pigments need some type of inhibition to minimize corrosion in waterbased inks or coatings. This is necessary to minimize the following negative effects of corrosion:

1. Dulling of the metallic effect
2. Hydrogen gas generation ($2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$)

The safety aspects of hydrogen generation are significant. Pressurized containers can explode and potentially cause injury.

There are a variety of inhibitor additives available to minimize aluminum pigment corrosion. These additives fall into categories of anodic and cathodic inhibition. Anodic inhibitors are anionic species (molybdate, phosphate, etc.) that bind to the metal surface and act as a barrier to corrosion reactions. Cathodic inhibitors are metal cations that form surface precipitates on the metal surface. An example of this is Zn^{2+} which forms $Zn(OH)_2$ on the metal surface (1).

Encapsulation with a silica coating can also be effective for reducing the corrosion of aluminum pigments. Encapsulated pigments are prepared by precipitation of silica on the aluminum pigment in a solution of hydrolyzed silicon alkoxides (2). While silica encapsulation is very effective for prevention corrosion, it has the drawback of reducing metallic luster, especially, for pigments with smaller particle sizes.

The surface of aluminum naturally develops a dense 10 – 20 angstrom layer of aluminum oxide that serves as a barrier to additional oxidization (3). When aluminum is exposed to water, this barrier oxide is stable at pH's between 4 – 9 (4). Outside this range, the oxide layer begins breaks down and the rate of corrosion will increase significantly. Therefore, it is important to keep formulation pH's as close to neutral (pH = 7) as possible.

Corrosion/stability testing

The relative stability of aluminum pigments in a waterbased ink or coating can be determined by the measuring the amount of generated hydrogen. Figure 4 shows a method for measuring the volume of hydrogen generated from corrosion.

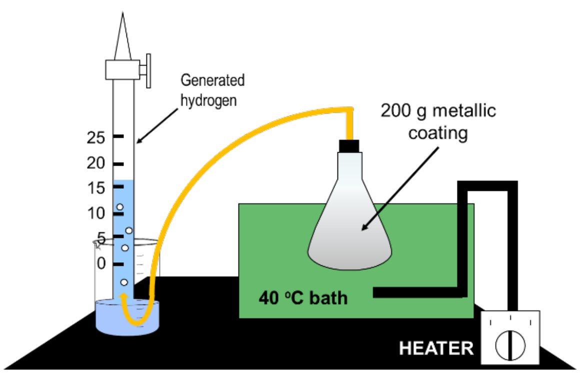

Figure 4. Experimental set-up for measuring evolved hydrogen from aluminum pigment corrosion

A flask containing approximately 200 g of metallic coating or ink is sealed with an outlet feeding into the bottom of an inverted burette filled with water. The generated hydrogen bubbles up the burette displacing water. This allows for easy measurement of the extent corrosion as the volume of generated hydrogen.

Evolved hydrogen volumes are generated at elevated temperatures (40 °C – 50 °C) to simulate worst case conditions. Measurements periods can be as short as several days for QC testing and as long as multiple weeks for detailed studies.

Inhibited aluminum VMF pigment

STARBRITE Reveal 4172-PM is a new, inhibited VMF pigment that can be used in waterbased inks and coatings. Several anodic inhibitors are used to provide a balance of inhibition and formulation compatibility. Anodic inhibitors also have the advantage of best maintaining metallic luster. The metal precipitates from cathodic inhibitors and silica encapsulation both tend to dull the metallic appearance of aluminum pigments. The basic pigment composition is given in Table 1.

Aluminum VMF	17%
Anodic inhibitors	3%
Propylene Glycol Methyl Ether	80%

Table 1. STARBRITE Reveal 4172-PM composition

Figure 5 illustrates the dramatic effect that inhibition treatment has on minimizing corrosion and hydrogen generation. The coating prepared with un-inhibited VMF generated over 400 ml of hydrogen after 1 day at 40 °C. Conversely, the inhibited STARBRITE Reveal 4172-PM only generated only 15 ml of hydrogen after 4 days at 40 °C (standard QC period). This is a manageable level of gas generation that can be accommodated by using vented containers.

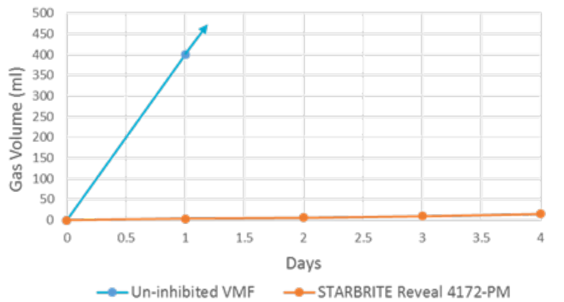

Figure 5: Hydrogen evolution from coatings prepared with inhibited and un-inhibited aluminum VMF pigments

Summary

In summary, the increasing use of waterbased formulations to reduce VOC emissions has presented unique challenges for aluminum VMF pigments in terms of corrosion stability. Fortunately, the use of appropriate corrosion inhibitors provides sufficient corrosion stability for safe usage of waterbased metallic inks and coatings.

References

1. "Principles and Prevention of Corrosion, 2nd Edition"; p 506-508; Denny Jones; Prentice Hall; 1996
2. "A Silane Primer: Chemistry and Applications of Alkoxy Silanes," G.L. Witucki,; J. of Coatings Technology, 65(822), 57-60 (1993).
3. "Oxides and Hydroxides of Aluminum", Karl Wefers and Chamakya Misra; Alcoa Technical Paper No. 19, Revised; 1987.
4. "Corrosion of Aluminum and Aluminum Alloys"; p. 38; Joseph R. Davis; ASM International; 1999