Short Communications

Stabilization of Aluminum Pigment in Waterborne Paints

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The corrosion of aluminum pigments in aqueous alkaline paint media, which results in the evolution of hydrgen, can be inhibited by certain substances. The combination of noninhibiting paint resins with three corrosion inhibitors (salicylic acid, a fluorinated phosphate surfactant, and an epoxy ester resin) has been studied. The presence of the resins does not significantly affect the stabilization of the aluminum pigment at pH 10 by the corrosion inhibitors. With the addition of corrosion inhibitors, the hydrogen volume evolved from aqueous aluminum pigment dispersions is surprisingly reduced by stirring. However, when heated to +40°C aqueous aluminum pigment dispersions with inhibitors evolve more hydrogen; at pH 8 the results are still satisfactory even at +40°C.

INTRODUCTION

Lamellar aluminum pigments (“aluminum flakes”) have been used in solventborne metallic paints or inks for many years. Waterborne metallic basecoats are used especially in the automotive industry to reduce the emission of organic solvents to the atmosphere during paint application.[1] Organic binders for waterborne paints usually contain carboxyl groups and have to be neutralized to salts by amines to become water-soluble or water-dispersible. Therefore, the pH values of waterborne paints are about 8.[1] One of the problems with waterborne metallic basecoats is the corrosion reaction of the aluminum pigment with the alkaline aqueous paint medium, which causes the formation of hydrogen (detailed studies of the corrosion reactions of different types of aluminum pigments have been presented elsewhere[2,3]):

$$2\ Al + 6\ H_2O \longrightarrow 2\ Al(OH)_3 + 3\ H_2$$

The evolution of hydrogen during this corrosion reaction may lead to a dangerous pressure buildup in containers. Furthermore, the color of the paint changes from silver to gray.[4] Therefore, inhibition of this corrosion reaction is necessary. Commonly established stabilization methods for aluminum pigments (chromatic treatment and stabilization with organic phosphorus compounds) still show some disadvantages such as reduced intercoat adhesion after humidity test (organic phosphorus compounds); the chromatic treatment is problematic because chromate (VI) is carcinogenic.[4] So, alternative and especially nontoxic methods for the inhibition of this corrosion reaction are required.

We have described various low-molecular weight, oligomeric or polymeric corrosion inhibitors for stabilization of aluminum pigment in aqueous alkaline media previously.[5-12] Up to now the tests were carried out in a simplified model system, that is an aqueous solution of one inhibitor. As paints are multicomponent mixtures, the question is whether the inhibitors found to be effective in the simplified model system[5-12] are also effective in multicomponent systems.[7] Is the efficiency of the inhibitors used as additives affected by paint resins, e.g., saturated polyesters or melamine-formaldehyde resins, by competetive adsorption?

In practice, paints are often mechanically stressed, e.g., by pumps in ring lines. Moreover, elevated temperatures may also damage waterborne metallic paints. So, the second question is whether corrosion inhibitors[5-12] are still effective when mechanically stressed or at elevated temperatures.

The objective of the present study is to test certain corrosion inhibitors for aluminum pigment in mixtures with paint resins, when mechanically stressed or at elevated temperatures.

EXPERIMENTAL

An unstabilized nonleafing aluminum pigment paste for solventborne metallic basecoats, which contains 65 wt% aluminum (average particle diameter 16 μm; specific surface about 5 m^2/g: BET method) and 35 wt% hydrocarbon solvent, was used. The corrosion medium was a mixture of 100 mL of water and butyl glycol (ethylene glycol monobutyl ether) in the ratio 9 : 1. To improve the wetting of the hydrophobic aluminum paste, 2.0 wt% of a wetting agent (adduct of 10 moles of ethylene oxide to nonylphenol) was added. The pH value of the medium was raised to 10 and sometimes to 8 with dimethylethanolamine (DMEA); the high pH value of 10 accelerates the corrosion reaction (see *Figure* 5) and is often better suited for a fast differentiation of corrosion inhibiting effects. Then 5.0 g of the aluminum pigment paste were dispersed in the medium with a magnetic stirrer for five minutes. The progress of the corrosion reaction was examined daily by volumetric measurement of the evolved hydrogen over a period of 21 days usually at room temperature; the gas-volumetric apparatus has been described in detail in this journal.[13] The hydrogen volume by complete reaction of the aluminum

Table 1—Data of the Paint Resins According to the Specifications of the Suppliers

Paint Resin Abbreviation	Description	Acid Number [mg KOH/g][a]
AY	Acrylic resin crosslinkable with amino resins	70-85
EPE	Drying epoxy ester resin (oil content 47%)	70-85
MF	Reactive methylated melamine-formaldehyde resin	About 0
SP	Oil-free linear saturated polyester resin	50-70

(a) Acid number refers to solid resin
Suppliers: AY (Vianova), EPE (Jäger), MF (Dyno-Cytec), SP (Worlée)

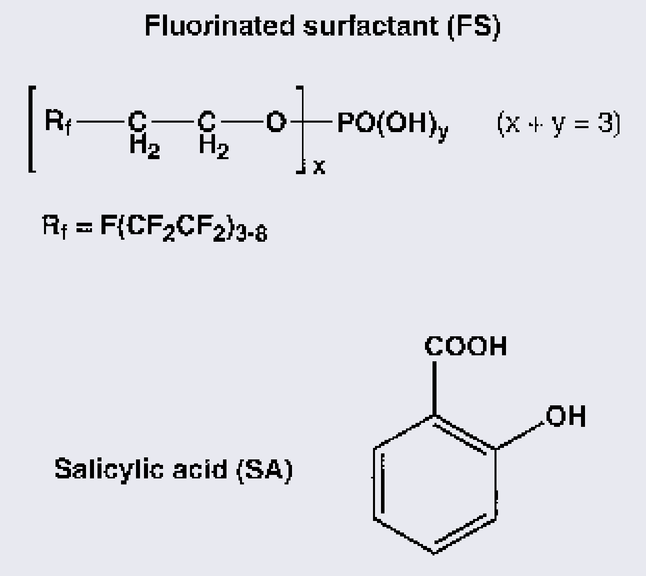

Figure 1—Structures and abbreviations of the low-molecular weight inhibitors.

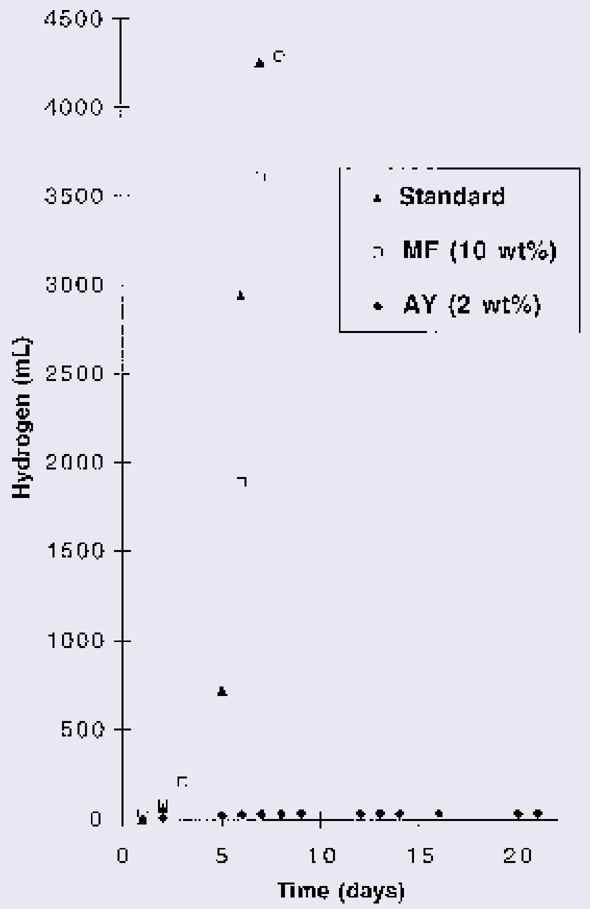

Figure 2—Time dependency of hydrogen formation from dispersions of the aluminum pigment at pH 10 without inhibitor (standard) and with addition of 10 wt% of the melamine resin (MF) or 2.0 wt% of the acrylic resin (AY).

pigment was previously determined to 4.24 L (average value out of 29 gas-volumetric tests).[2]

The two selected low-molecular weight corrosion inhibitors are presented in *Figure* 1. The data of the paint resins examined are recorded in *Table* 1; all addition levels of paint resins refer to solid resin. Corrosion inhibitors and/or paint resins were dissolved in the medium before the dispersion of the aluminum pigment; if necessary, the pH values were adjusted again.

RESULTS AND DISCUSSION

Paint Resins

Figure 2 shows the typical time dependency of the hydrogen evolution with addition of a corrosion inhibiting resin (AY) and a noninhibiting resin (MF) at pH 10. Also shown, for comparison, is the time dependency of the hydrogen evolution of the standard aluminum dispersion (without corrosion inhibitor). Both aluminum pigment dispersions without inhibitors (standard) and with the addition of even 10 wt% of MF react completely within one week at room temperature at pH 10. In contrast, with the addition of 2.0 wt% of AY, the aluminum pigment is well stabilized (*Figure* 2).

The influence of resin concentration is recorded in *Figure* 3 (for clarity only the hydrogen volumes after 21 days are plotted). The epoxy ester resin (EPE) is an excellent inhibitor and the acrylic resin (AY) is a good corrosion inhibitor for aluminum pigment. Increasing resin concentration decreases hydrogen evolution, i.e., corrosion inhibition increases (*Figure* 3).

More details about the corrosion inhibition of an aluminum pigment by paint resins have been reported elsewhere.[7,10-12]

Combination of Paint Resins and Corrosion Inhibitors

The paint resins are a saturated polyester (SP) and a methylated melamine-formaldehyde resin (MF), selected because such resins are used as binders in waterborne metallic paints.[1] A previous study showed that SP does not inhibit the hydrogen corrosion of the aluminum pigment;[11] the inefficency of MF is shown in *Figure* 2. The selected corrosion inhibitors were the chelating agent salicylic acid (SA), see *Figure* 1 and reference 8, a fluorinated surfactant with a phosphate hydrophilic group (FS) see *Figure* 1 and reference 9, and the epoxy ester resin (EPE) see *Table* 1 and *Figure* 3.

In this series of experiments, the standard (without inhibitors) and the non-inhibiting paint resins (SP, MF each 2.0 wt%) were tested first. Then the corrosion inhibitors were examined in the following concentrations: 3.0 mmol/100 mL of SA, 0.50 wt% of FS, and 2.0 wt% of the EPE. Finally, combinations of the noninhibiting paint resins and the corrosion inhibitors were tested. The results of all these gas-volumetric tests are summarized in *Figure* 4. As expected, neither SP nor MF inhibits the corrosion reaction. In contrast, SA is a good inhibitor and FS as well as EPE are excellent inhibitors. Furthermore, *Figure* 4 shows

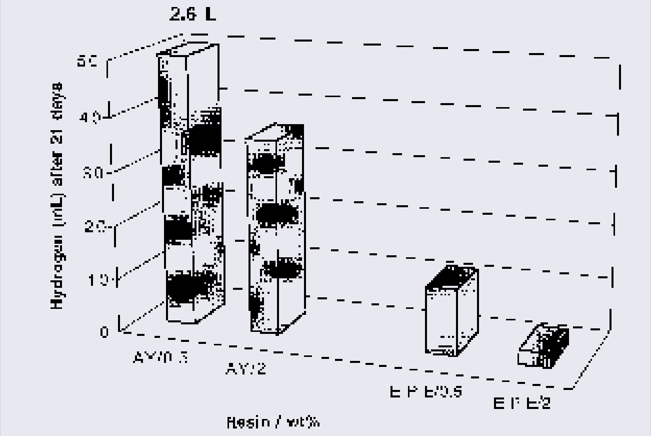

Figure 3—A comparison of hydrogen volumes evolved within 21 days from dispersions of the aluminum pigment at pH 10 with addition of 2.0 and 0.50 wt% of the acrylic resin (AY) or the epoxy ester resin (EPE).

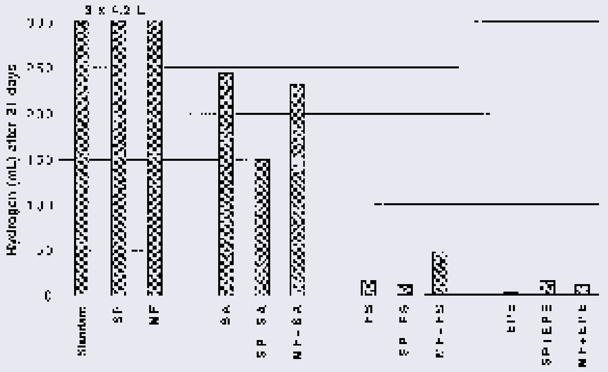

Figure 4—A comparison of hydrogen volumes evolved within 21 days from dispersions of the aluminum pigment at pH 10 without (standard) and with addition of 2.0 wt% of the polyester (SP) or melamine resin (MF), with 3.0 mmol/100 mL of salicylic acid (SA), 0.50 wt% of the fluorinated surfactant (FS) or 2.0 wt% of the epoxy ester resin (EPE). Furthermore, combinations of resins and inhibitors were tested.

that a combination of noninhibiting resins (SP and MF) with the corrosion inhibitors SA, FS, or EPE does not significantly affect the stabilization of aluminum pigment by the corrosion inhibitors. So, it can be assumed that the corrosion inhibitors SA, FS, and EPE are more strongly adsorbed on the aluminum pigment surface than the noninhibiting resins SP and MF.

Influence of Shear Stress and Elevated Temperature

Shear stress was generated in the laboratory by fast stirring with a magnetic stirrer during the whole test period of 21 days at room temperature. Thermal stress was generated by heating of the aluminum dispersion to +40°C during 21 days. Over the same timeframe, a "normal" test was carried out for comparison.

First, the acrylic resin (AY) was tested, see *Table* 1, because acrylic resins are used as binders in waterborne metallic paints[1]; furthermore, AY inhibits the corrosion reaction of the aluminum pigment (*Figures* 2 and 3). The results with 2.0 wt% of acrylic resin are summarized in *Figure* 5. As expected, at the lower pH value of 8 less hydrogen is evolved when compared to pH 10 (*Figure* 5). Surprisingly, the stirred tests evolve the lowest hydrogen volumes at pH 8, as well as pH 10 (*Figure* 5). The tests at +40°C evolve the highest hydrogen volumes in this series. At pH 10 there is complete reaction of the aluminum pigment at +40°C whereas at pH 8 (the usual pH of waterborne metallics[1]) corrosion inhibition by AY is still satisfactory even at +40°C.

In a subsequent series, the low-molecular chelating agent SA was tested with an addition level of 2.0 mmol/100 mL only at pH 8. The results, summarized in *Figure* 6, show that the inhibiting action of SA had the same trends, but not the same magnitude as AY: Again, the highest hydrogen volume was observed at +40°C, and the lowest was observed with stirring (*Figure* 6).

So, stirring of the inhibited aluminum pigment dispersions decreases the hydrogen evolution, i.e., increases the

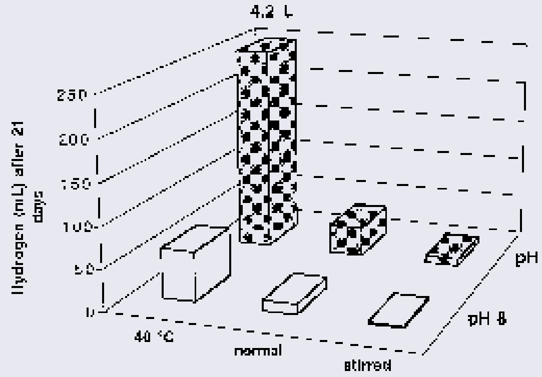

Figure 5—A comparison of hydrogen volumes evolved within 21 days from dispersions of the aluminum pigment at pH 8 and 10 with addition of 2.0 wt% of the acrylic resin (AY) "normal," stirred and at +40°C.

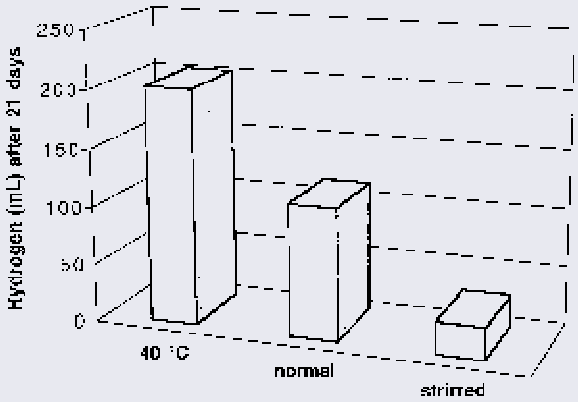

Figure 6—A comparison of hydrogen volumes evolved within 21 days from dispersions of the aluminum pigment at pH 8 with addition of 2.0 mmol/100 mL of salicylic acid (SA) "normal," stirred and at +40°C.

effect of the corrosion inhibitors (*Figures* 5 and 6). In reference 14, the influence of the speed of motion of the medium on the action of corrosion inhibitors has been summarized. Different sources reported different observations[14]; sometimes the corrosion rate increases in stirred media, sometimes the corrosion rate decreases by increasing the rotation speed similar to *Figures* 5 and 6. Within the limits of the experimental results presented in this study, an explanation for the decreased hydrogen evolution of stirred aluminum pigment dispersions is not possible. The effect of stirring on the hydrogen evolution of metal pigment dispersions will be examined more in detail in the future.

CONCLUSIONS

Aluminum pigments corrode in aqueous alkaline paint media with the evolution of hydrogen, which can be inhibited by the addition of oligomeric paint resins (acrylic, epoxy ester) or low-molecular weight inhibitors (salicylic acid, fluorinated phosphate surfactant).

The combination of noninhibiting paint resins (polyester, melamine-formaldehyde) with the selected corrosion inhibitors salicylic acid, fluorinated phosphate surfactant, or epoxy ester resin does not significantly affect the stabilization of aluminum pigment at pH 10 by the corrosion inhibitors. So, it can be assumed that the corrosion inhibitors are more strongly adsorbed on the aluminum pigment surface than the noninhibiting resins.

In practice, waterborne metallic paints are often damaged by elevated temperatures or mechanically stressed, e.g., by pumps in ring lines. As expected, aqueous aluminum pigment dispersions with inhibitors (acrylic resin or salicylic acid) evolve more hydrogen when heated to +40°C; at pH 8 the results are still satisfactory even at +40°C. With the addition of corrosion inhibitors (acrylic resin or salicylic acid), the hydrogen volume evolved from aqueous aluminum pigment dispersions is surprisingly reduced by stirring (simulation of mechanical stress). This effect of stirring on the hydrogen evolution of aluminum pigment dispersions cannot be explained up to now and will be subject of future examinations.

This study shows that stabilization aluminum pigments in aqueous alkaline media by corrosion inhibitors works also in systems relating to practice.

ACKNOWLEDGMENT

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