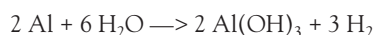


Stabilization of Aluminum Pigments in Aqueous Alkaline Media by Styrene Copolymers

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INTRODUCTION

Aluminum pigments have been used in solvent-borne metallic paints or inks for many years.¹ Waterborne metallic color coats have been introduced to the automotive industry to reduce the emission of organic solvents to the atmosphere during the paint application.² One of the problems of waterborne metallic color coats is the corrosion reaction of the aluminum pigments with the alkaline aqueous paint medium (pH value about 8), which causes the formation of hydrogen³:



Furthermore, the color of the paint changes from silver to gray.³ Therefore, an inhibition of this corrosion reaction is necessary. An overview about different stabilization methods for aluminum pigments is presented in reference (3). The commonly established stabilization methods (chromatic treatment and stabilization with organic phosphorus compounds) show some disadvantages such as reduced intercoat adhesion after humidity test (organic phosphorus compounds); the chromatic treatment is problematic because chromium (VI) compounds are carcinogenic.³ Therefore, alternative methods for the inhibition of this corrosion reaction are required.

The corrosion reaction of the aluminum pigment in aqueous alkaline media can be inhibited by adding corrosion inhibitors like chelating agents⁴ or antioxidants.⁵ Another possibility is the stabilization by polyacrylic acids,⁶ which are well-known paint additives (e.g., dispersing agents) and are, therefore, suited for an application in waterborne metallic paints. It was pointed out⁶ that the corrosion inhibiting effect of polyacrylic acids has a maximum at low molecular masses and decreases with increasing molecular mass; polyacrylic acids with molecular masses of 178,000-250,000 are only poor corrosion inhibitors. Better results as with addition of polyacrylic acids are obtained with maleic acid copolymers and especially with an olefin-maleic acid copolymer⁶; therefore, a positive influence of hydrophobic olefin co-monomers on the corrosion inhibiting effect of maleic acid copolymers was presumed in this study.⁶ Styrene is a hydrophobic monomer and can be copolymerized easily with acrylic acid or maleic acid. Different styrene-acrylic acid or styrene-maleic acid⁷ copolymers (S-MA) are available on the raw material market. These copolymers are used as dispersing agents, binders for printing inks, and for many other applications.

Aluminum pigments react in alkaline aqueous media (e.g., waterborne metallic paints) with the evolution of hydrogen. Low- and high-molecular weight styrene-maleic acid copolymers inhibit the corrosion of aluminum pigments in a mixture of water and butyl ether of ethylene glycol at a pH value of 10 very effectively and are much better corrosion inhibitors than high-molecular weight polyacrylic acids or a styrene-acrylic acid copolymer. There is a correlation between the composition of the styrene-maleic acid copolymers and the evolved hydrogen volume: the lower the acid number the lower the hydrogen volume—resulting in a higher corrosion inhibiting effect.

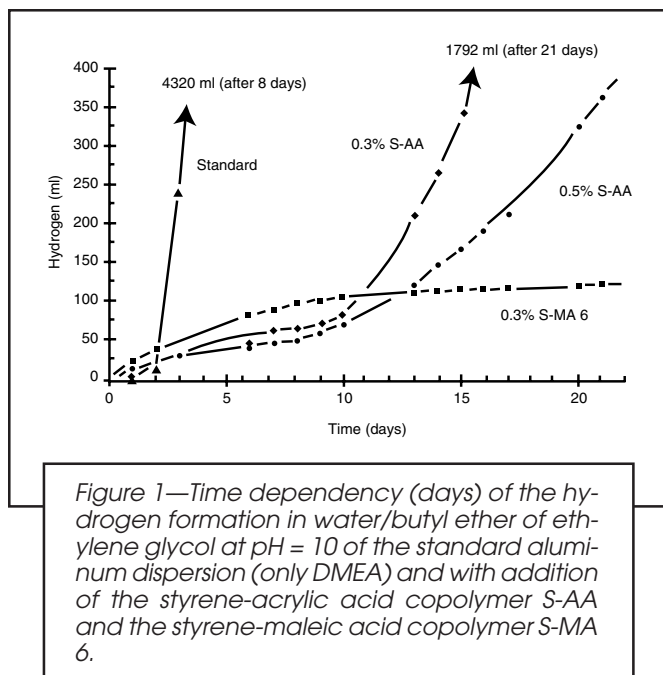
The subject of the present investigation is the assessment of styrene-maleic acid copolymers and a styrene-acrylic acid copolymer as possible adequate corrosion inhibitors for aluminum pigments in alkaline aqueous medium.

EXPERIMENTAL

Stability Test

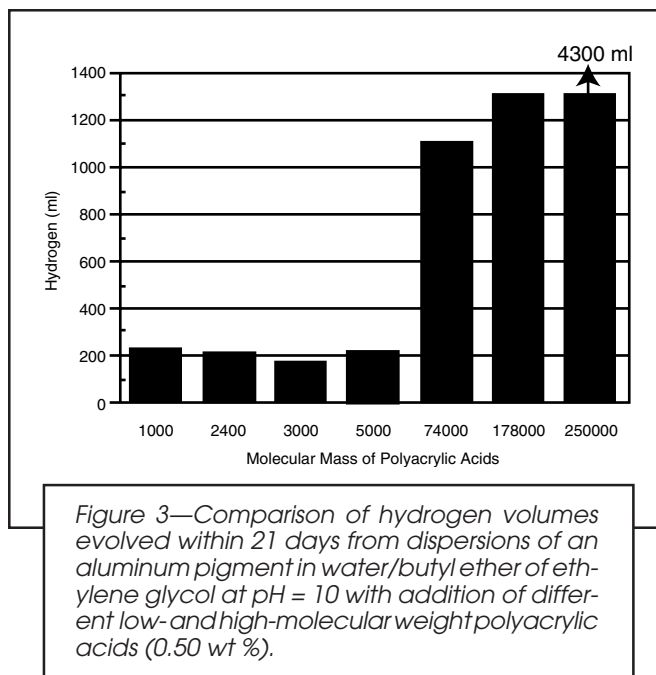
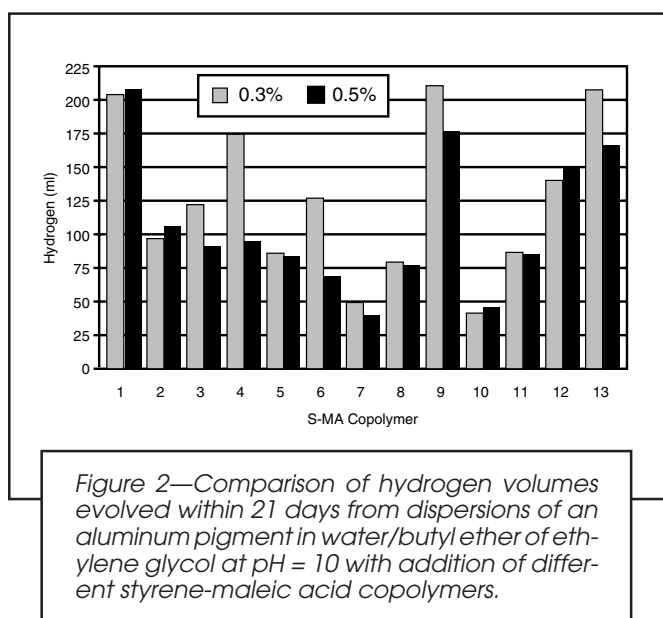
An unstabilized nonleafing aluminum pigment paste for solvent-borne metallic paints, which contains 65 wt % aluminum and 35 wt % hydrocarbon solvent, is used (specific surface about 5 m²/g). Five grams of such a paste are dispersed for five minutes by a magnetic stirrer in a glass beaker in 100 ml of a mixture of water and butyl ether of ethylene glycol in the ratio 9:1. To improve the wetting of the hydrophobic aluminum paste by the aqueous medium, 2 wt % of a wetting agent (adduct of 10 moles of ethylene oxide to nonylphenole) is added. To accelerate the corrosion reaction, the pH of the solvent is raised to 10 with 2-(dimethylamino)ethanol (dimethylethanolamine, DMEA), a commonly used amine

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for waterborne baking enamels. This unstabilized dispersion reacts to a colorless precipitate (presumably aluminumhydroxide) in approximately one week at room temperature. With addition of suitable corrosion inhibitors that were dissolved in the solvent mixture before addition of the pigment these aluminum pigment dispersions are stable for more than 10 weeks and keep their metallic sparkle.⁴⁻⁶

The commercial copolymers of styrene and maleic acid anhydride and the styrene-acrylic acid copolymers (see Table 1) are converted into their soluble salts by heating them in water with addition of an appropriate amount of DMEA. The stability test is carried out with all styrene-maleic acid copolymers (S-MA 1-13) and the styrene-acrylic acid copolymer (S-AA) summarized in Table 1 (addition level 0.30 resp. 0.50 wt %).



Gas Volumetry

In the second step, the temporal progress of the corrosion reaction is studied by volumetric measurement of the evolved hydrogen over a period of 21 days at room temperature.⁴⁻⁶ The hydrogen volume by total turnover of the aluminum pigment is calculated to 4.3 L. All styrene-maleic acid copolymers (S-MA 1-13) and the styrene-acrylic acid copolymers (S-AA) summarized in Table 1 are tested (additional level 0.30 resp. 0.50 wt %). Furthermore, seven polyacrylic acids⁶ with molecular masses from 1,000 to 250,000 are tested for comparison (addition level 0.50 wt %).

RESULTS AND DISCUSSION

Stability Test

First, the influence of the wetting agent (adduct of 10 moles of ethylene oxide to nonylphenole) on the stability of the aqueous aluminum pigment dispersions is examined because without wetting agent the dispersibility of the hydrophobic aluminum paste in water/butyl ether of ethylene glycol = 9:1 is not sufficient. In a mixture of water and butyl ether of ethylene glycol in the ratio 1:1, the aluminum pigment is dispersible without wetting agent; the stability of this dispersion at pH 10 (DMEA) is one to two weeks. With addition of 0.5, 1.0, 1.5, 2.0, and 3.0 wt % of the wetting agent (adduct of 10 moles of ethylene oxide to nonylphenole), the stability of the five aluminum pigment dispersions in water/butyl ether of ethylene glycol = 9:1 at pH 10 (DMEA) is about one week. So, it can be concluded that the wetting agent used in this study has no significant influence on the stability of the aqueous aluminum pigment dispersions.

The addition of 0.30 resp. 0.50 wt % of the styrene-maleic acid copolymers S-MA 1-13 (Table 1) inhibit the corrosion of aluminum pigments at pH 10 very effectively. The aluminum pigment dispersions are stable for more than 10 weeks; they keep their silver sparkle and are easily redispersible.

Aluminum pigment dispersions with addition of 0.30 resp. 0.50 wt % of the styrene-acrylic acid copolymer (S-AA, Table 1) show stabilities of only 8-10 weeks; S-AA seems to be a less effective corrosion inhibitor than the styrene-maleic acid copolymers.

Gas Volumetry

Volumetric measurement of the evolved hydrogen is a better method to differentiate between good and poor corrosion inhibitors than the qualitative stability test. Figure 1 shows the typical time dependency of the hydrogen evolution with addition of an effective corrosion inhibitor (S-MA 6) and a poor corrosion inhibitor (S-AA). Also shown, for comparison, is the time dependency of the hydrogen evolution of the standard aluminum dispersion (without corrosion inhibitor) which has completely reacted after eight days. Within the first two days of the corrosion reaction, the standard aluminum dispersion evolves less hydrogen (latency period⁸) than dispersions with addition of the copolymers (see Figure 1). A similar time dependency of the hydrogen evolution was observed with addition of polyacrylic acids.^{6,8} The neutralized carboxylic groups of the polymer react with the aluminum surface which cause an enhanced evolution of hydrogen within the first days.⁸ This reaction may lead to a protective layer on the aluminum surface which can inhibit the corrosion reaction. The comparison of the time dependency of the hydrogen evolution within 21 days with addition of the styrene-maleic acid copolymer S-MA 6 and the styrene-acrylic acid copolymer S-AA (see Figure 1) clearly shows the superiority of the styrene-maleic acid copolymer; all examined styrene-maleic acid copolymers show the same type of time dependency of the hydrogen evolution as S-MA 6.

All gas-volumetric results with addition of 0.30 and 0.50 wt % of S-MA copolymers are summarized in Figure 2 (for

Table 1—Data of the Styrene-Maleic Acid Copolymers (S-MA) and a Styrene-Acrylic Copolymer (S-AA) According to the Specifications of the Suppliers

Copolymer Abbreviation	Molecular Mass (g/mol)	Acid Number (mg KOH/g)	Styrene:MAA (Mole ratio)	Esterification (Partial ester)
S-MA 1	1,600	465-495	1:1	none
S-MA 2	1,700	255-285	1:1	partial ester ^a
S-MA 3	2,500	165-205	1:1	partial ester ^a
S-MA 4	1,700	335-375	2:1	none
S-MA 5	1,900	200-240	2:1	partial ester ^b
S-MA 6	1,900	265-305	3:1	none
S-MA 7	2,300	95-120	3:1	partial ester ^a
S-MA 8	60,000	260-280	2:1	isopropyl
S-MA 9	100,000	500-540	1:1	none
S-MA 10	105,000	175	1:<1	methyl/butyl
S-MA 11	180,000	185	1:<1	methyl/isobutyl
S-MA 12	350,000	405	1:1	none
S-MA 13	400,000	500-540	1:1	none
S-AA	1,200	260-280	1:1 ^c	none

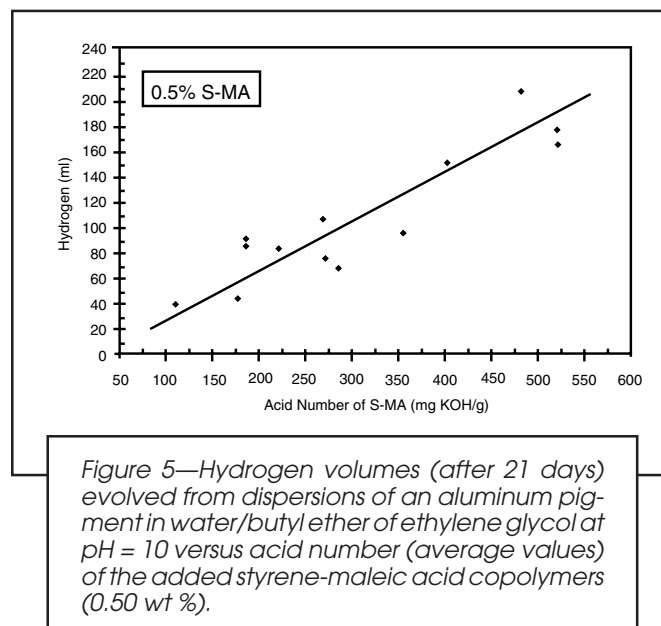
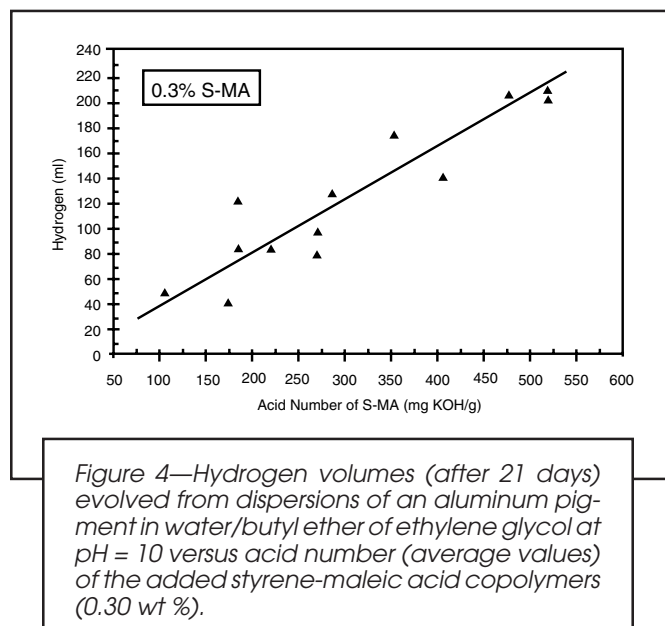
(a) The exact esterification is not specified by the supplier.

(b) The molecular masses are approximate data.

(c) Styrene:acrylic acid.

clarity only the hydrogen volume after 21 days is plotted). It is obvious that no correlation exists between the molecular weight of the styrene-maleic acid copolymers and the evolved hydrogen volume (see Figure 2). This is an important result because with addition of polyacrylic acids there is a correlation between the hydrogen volume evolved after 21 days and the molecular mass of the polyacrylic acids: the higher the molecular mass of the polyacrylic acids the higher the hydrogen volume—that means the lower is the corrosion inhibiting effect (see Figure 3).⁶ The comparison of the hydrogen volumes evolved within 21 days with addition of high-molecular weight styrene-maleic acid copolymers S-MA 8-13 (Figure 2) and high-molecular weight polyacrylic acids (Figure 3) shows the superiority of the styrene-maleic acid copolymers.

Figures 4 and 5 show correlations between the composition of the styrene-maleic acid copolymers and the evolved hydrogen volume (after 21 days): the lower the acid number, the



lower the hydrogen volume. This correlation is only valid within the series of styrene-maleic acid copolymers. Moreover, this fact supports the assumption⁸ that there is a reaction of the neutralized carboxylic groups of the copolymers with the aluminum surface which cause an evolution of hydrogen.

SUMMARY

Styrene-maleic acid copolymers inhibit the corrosion of aluminum pigments in a mixture of water and butyl ether of ethylene glycol at a pH value of 10 very effectively and are much better corrosion inhibitors than high-molecular weight polyacrylic acids⁶ or the styrene-acrylic acid copolymer examined in this study. With styrene-maleic acid copolymers, no correlation of the corrosion inhibiting effect and the molecular mass can be observed. This is important because with polyacrylic acids the corrosion inhibiting effect decreases strongly with increasing molecular mass. However, there is a dependence between the composition of the styrene-maleic acid copolymers and the evolved hydrogen volume: the lower the acid number, the lower the hydrogen volume—that means the corrosion inhibiting effect is higher.

The copolymers examined in this study are commercial products used for many different applications; it should be possible to synthesize styrene-maleic acid copolymers with improved properties “tailor-made” for waterborne metallic paints.

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Appendix—Materials and Suppliers

Material	Product	Supplier
S-MA 1	SMA 1000	Elf Atochem
S-MA 2	SMA 17352	Elf Atochem
S-MA 3	SMA 1440	Elf Atochem
S-MA 4	SMA 2000	Elf Atochem
S-MA 5	SMA 2625	Elf Atochem
S-MA 6	SMA 3000	Elf Atochem
S-MA 7	SMA 3840	Elf Atochem
S-MA 8	Leumal 533/100	Leuna
S-MA 9	Leumal 501/100	Leuna
S-MA 10	SCRIPSET 550	Monsanto
S-MA 11	SCRIPSET 540	Monsanto
S-MA 12	SCRIPSET 520	Monsanto
S-MA 13	Leumal 501 H/100	Leuna
S-AA	Suprapal WS	BASF