

# Amphiphilic Maleic Acid Copolymers as Corrosion Inhibitors for Aluminum Pigment

B. MÜLLER,<sup>1</sup> A. PAULUS,<sup>1</sup> B. LETTMANN,<sup>2</sup> U. POTH<sup>2</sup>

<sup>1</sup> Fachhochschule Esslingen–Hochschule für Technik, Chemieingenieurwesen/Farbe-Lack-Umwelt, Kanalstrasse 33, D-73728 Esslingen, Germany

<sup>2</sup> BASF Coatings AG, Glasuritstrasse 1, D-48165 Münster, Germany

Received 12 November 1997; accepted 18 December 1997

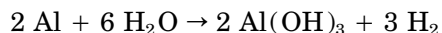
**ABSTRACT:** Aluminum pigments react in aqueous alkaline media (e.g., water-borne paints) by the evolution of hydrogen. Maleic acid copolymers, which were synthesized by copolymerization of maleic acid anhydride, styrene, and acrylic esters (ethyl-, *n*-butyl-, *n*-hexyl-, *n*-dodecyl-, and *n*-octadecyl acrylate) inhibit this corrosion reaction. With the increasing chain length of the ester alcohol of the acrylate monomer, the evolved hydrogen volume decreases (i.e., the corrosion inhibiting effect increases). There seems to be a potential correlation between the number of carbon atoms of the ester alcohol of the copolymers and the evolved hydrogen volumes. With the addition of 0.5 wt % of the copolymers with *n*-butyl, *n*-hexyl, *n*-dodecyl-, and *n*-octadecyl acrylate no hydrogen evolution was observed at pH 8 within 21 days (complete corrosion inhibition). Conductivity measurements of aqueous copolymer solutions indicate that with an increasing chain length of the ester alcohol, the copolymers possibly associate by hydrophobic bonding. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2169–2174, 1998

**Key words:** styrene-maleic acid-acrylic ester copolymers; aluminum pigment; aqueous alkaline media; corrosion inhibition

## INTRODUCTION

Lamellar aluminum pigments (“aluminum flakes”) have been used in solvent-borne metallic paints or inks for many years. Water-borne metallic base coats were introduced, especially in the automotive industry, to reduce the emission of organic solvents to the atmosphere during paint application.<sup>1</sup> Organic binders for water-borne paints usually contain carboxyl groups (acid number about 50 mg KOH/g) and have to be neutralized to salts by amines to become water soluble or water dispersible. Therefore, the pH value of water-borne paints is about 8.<sup>1</sup> One of the problems of water-borne metallic base coats is the corrosion reaction

of the aluminum pigment with the alkaline aqueous paint medium, which causes the formation of hydrogen (detailed studies about the corrosion reactions of different types of aluminum pigments have been presented elsewhere<sup>2,3</sup>):



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 grey.<sup>4</sup> Therefore, inhibition of this corrosion reaction is necessary. The commonly established stabilization methods for aluminum pigments (chromatic treatment and stabilization with organic phosphorus compounds) show some disadvantages like reduced intercoat adhesion after a humidity test (organic

Correspondence to: B. Müller.

**Table I** Data of Synthesized Aqueous Copolymer Solutions

Copolymer Abbreviation	Acrylate Ester Alcohol	Solid Content (wt %)	pH Value	Viscosity Appearance	Acid Number <sup>a</sup> (mg KOH/g)	Molecular Mass <sup>b</sup> ( $M_n \times 10^3$ g/mol)
Copo 2	Ethyl	30	5.7	Low viscous	145	4.3
Copo 4	Butyl	33	6.1	Gel-like	140	3.3
Copo 6	Hexyl	32	6.3	Gel-like	150	3.7
Copo 12	Dodecyl	35	6.1	High viscous	153	4.3
Copo 18	Octadecyl	21	6.9 <sup>c</sup>	Solid, waxy	150	5.2
Copo 4A	Butyl	30	6.5	Low viscous	146	NM
Copo 4B	Butyl	29	6.8	Low viscous	150	NM

NM, Not measured.

<sup>a</sup> The acid number refers to solid copolymer (acid number calculated on monomer composition, 172 mg KOH/g).

<sup>b</sup> The molecular masses were determined before the hydrolysis of the copolymers by gel permeation chromatography.

<sup>c</sup> Aqueous solution with 1 wt % Copo 18.

phosphorus compounds); the chromatic treatment is problematic because chromate(VI) is carcinogenic.<sup>4</sup> Therefore, alternative nontoxic methods for the inhibition of this corrosion reaction are required.

Recent studies reported the inhibition of corrosion of aluminum pigment by styrene-maleic acid (S-MA) copolymers<sup>5-7</sup>; S-MA copolymers are supposed to be nontoxic. Low-molecular weight S-MAs (molecular mass  $\leq 60,000$ ) were superior when compared to high-molecular weight S-MA copolymers (molecular mass  $\geq 100,000$ ).<sup>7</sup> Generally, the corrosion inhibiting effect of S-MA copolymers increases with decreasing acid number.<sup>6,7</sup> Furthermore, S-MAs were also good corrosion inhibitors for zinc pigment in aqueous alkaline media.<sup>8,9</sup> All examined S-MA copolymers<sup>5-9</sup> were commercial products used for many different applications. Therefore, the objective of the present study was the synthesis of low molecular weight S-MA copolymers "tailor-made" for corrosion inhibition of aluminum pigments. The starting point for the improvement of the properties of S-MA copolymers was the observation that the corrosion inhibiting effect of amphiphilic molecules with chelating head groups was better when compared to the respective chelating agents (head groups).<sup>10</sup> So, one may assume that the corrosion inhibiting effect of maleic acid copolymers could be improved by the introduction of long alkyl side chains into the copolymer that should lead to amphiphilic copolymers or at least to polymeric surfactants.<sup>11</sup> Such copolymers should be synthesized by free-radical copolymerization of MA anhydride (MAA), styrene, and acrylic esters with long-chain ester alcohols.

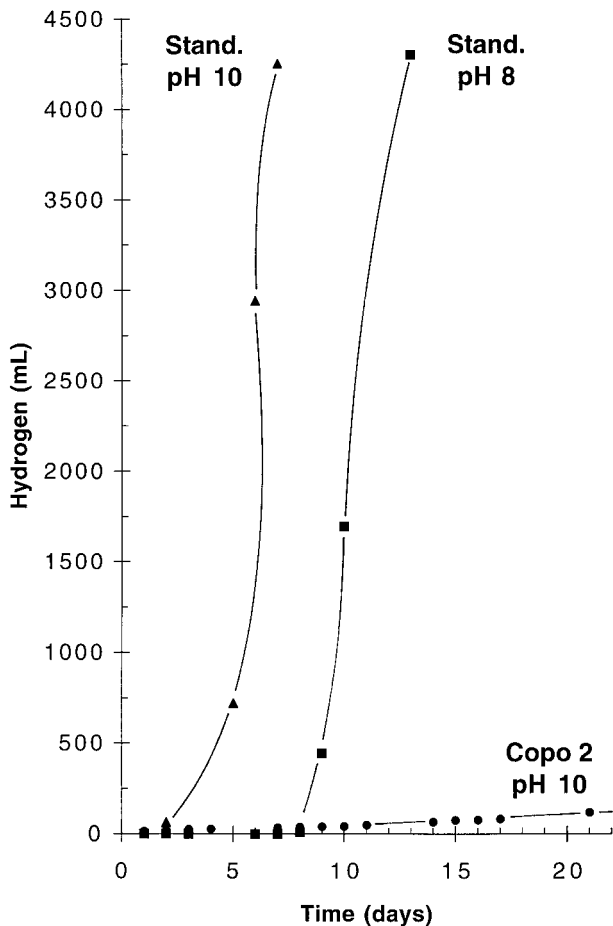
The first part of the present study is the synthe-

sis of copolymers of MAA, styrene, and acrylic esters with various ester alcohols. The second part is the assessment of these copolymers as possible corrosion inhibitors for aluminum pigment in aqueous alkaline media.

## EXPERIMENTAL

### Copolymerization

The copolymers (terpolymers) were synthesized by free-radical copolymerization of MAA, styrene, and acrylic esters with various ester alcohols in methyl isobutyl ketone (MIBK) using *tert*-butylperoxy-2-ethyl-hexanoate (TBPEH) as initiator. The weight ratio of MAA : styrene : acrylic ester was 15 : 15 : 70; the weight ratio of monomer mixture : MIBK was 60 : 40. Five different acrylic esters were used: ethyl- (Copo 2), *n*-butyl (Copo 4), *n*-hexyl (Copo 6), *n*-dodecyl (Copo 12), and *n*-octadecyl acrylate (Copo 18). The MIBK was heated to 110°C in a nitrogen atmosphere. Then the initiator solution (7 wt % TBPEH calculated on the monomer mixture) was added over a period of 4.75 h. Fifteen minutes after the beginning of the initiator addition of the monomer mixture was started and fed over a period of 4 h. The batches were held for an additional 2 h at 110°C. The anhydride copolymers were hydrolyzed by the addition of appropriate amounts of desalinated water and 2-(dimethylamino)ethanol (dimethylethanolamine, DMEA); after these additions the batches were refluxed for 2 h. Then the MIBK was removed by distillation under reduced pressure. The

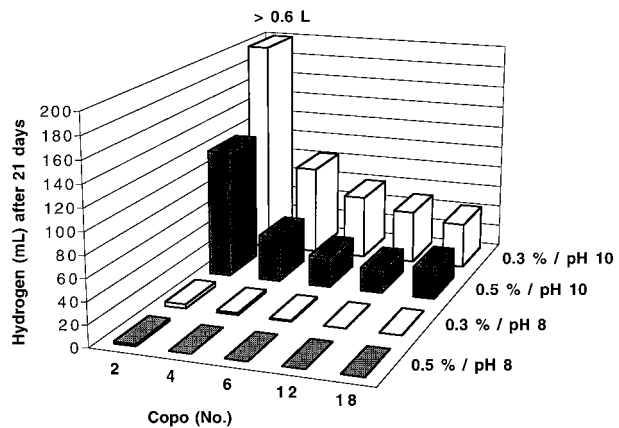


**Figure 1** Time dependency (days) of the hydrogen evolution in water/butyl glycol at pH 8 and 10 of the standard aluminum pigment dispersions (without inhibitor) and with the addition of 0.5 wt % of Copo 2 (pH 10).

data of the aqueous copolymer solutions are recorded in Table I.

### Gas-Volumetric Test Method

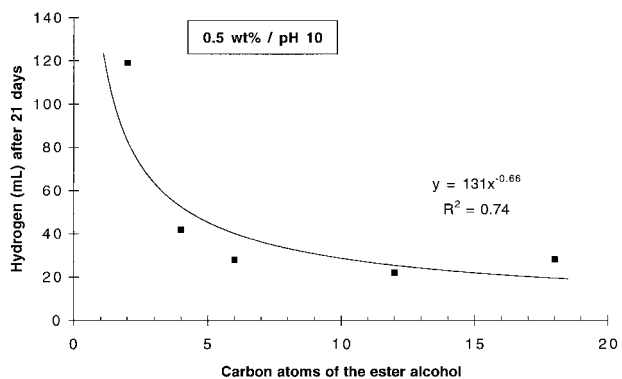
An unstabilized nonleafing aluminum pigment paste for solvent-borne metallic base coats was used, which contained 65 wt % aluminum (specific surface about 5 m<sup>2</sup>/g solids, Brunauer–Emmett–Teller method) and 35 wt % hydrocarbon solvent. The corrosion medium was a mixture of desalinated water and butyl glycol in a ratio of 9 : 1. To improve the wetting of the hydrophobic aluminum pigment paste by the aqueous medium, 2.0 wt % of a wetting agent (adduct of 10 mol of ethylene oxide to nonylphenol) was added. The pH of the solvent mixture was raised to 10 (alternatively 8.0) with DMEA. Butyl glycol is the most common



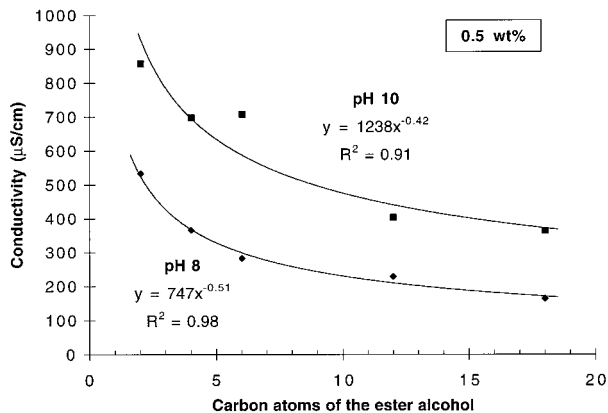
**Figure 2** Comparison of hydrogen volumes evolved from dispersions of an aluminum pigment in water/butyl glycol at pH 8 and 10 within 21 days with the addition of 0.3 and 0.5 wt % of different copolymers.

organic cosolvent, and DMEA is a commonly used amine in water-borne paints. Then 5.0 g aluminum pigment paste was dispersed in 100 mL of the aqueous solvent mixture for 5 min using a magnetic stirrer. Copolymers were dissolved in concentrations of 0.30 and 0.50 wt % (solid polymer) in the corrosion medium before the dispersion of the aluminum pigment; if necessary, the pH value was adjusted again.

The temporal progress of the corrosion reactions was studied daily by volumetric measurement of the evolved hydrogen over a period of 21 days at room temperature. The hydrogen volume by the complete reaction of the aluminum pigment was determined previously as 4.24 L (average value out of 29 gas-volumetric tests, maximum deviation 8%, mean deviation 3%).<sup>2</sup>



**Figure 3** Hydrogen volumes (after 21 days) evolved from dispersions of an aluminum pigment in water/butyl glycol at pH 10 versus number of carbon atoms of the ester alcohol of the acrylic ester monomer in the added copolymers (0.5 wt %).



**Figure 4** Electrical conductivity of aqueous copolymer solutions (0.5 wt %) versus the number of carbon atoms of the ester alcohol of the acrylic ester monomer in the copolymers.

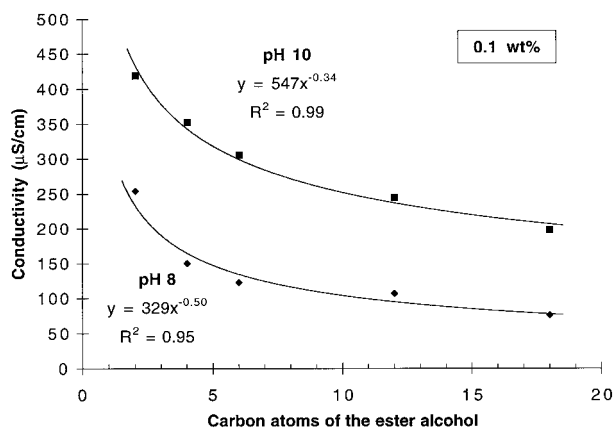
## RESULTS AND DISCUSSION

Figure 1 shows the hydrogen evolution of the standard aluminum pigment dispersions (without polymer) at pH 8 and 10, which reacted completely in 1 (pH 10) or 2 (pH 8) weeks. Within the first day (pH 10) and the first 7 days (pH 8) of the corrosion reaction, no evolution of hydrogen was observed (standards, Fig. 1). After this latency period, the corrosion reaction initiated with a high rate.<sup>3</sup> At pH 8 a longer latency period was observed then at pH 10, but after initiation of the corrosion reaction the rate at pH 8 and 10 was approximately the same (Fig. 1). So the length of the latency period depends on the pH value but not the corrosion rate.<sup>2,3</sup> Furthermore, Figure 1 shows the hydrogen evolution of an aluminum pigment dispersion with the addition of 0.5 wt % of Copo 2 at pH 10, which inhibited the corrosion reaction of the aluminum pigment well.

All gas-volumetric results with the addition of 0.5 and 0.3 wt % of S-MA-acrylic ester copolymers are summarized in Figure 2. (For clarity only the hydrogen volumes after 21 days are plotted.) Figure 2 shows that with increasing copolymer addition, the evolved hydrogen volumes decrease, which was mostly observed with the addition of S-MA copolymers.<sup>6</sup> Moreover, the hydrogen volumes evolved at pH 8 are lower than at pH 10, which is typical for low molecular weight S-MA copolymers.<sup>7</sup> With the addition of 0.3 and 0.5 wt % of Copo 12 and 18 no hydrogen evolution was observed at pH 8 within 21 days (complete corrosion inhibition); with Copo 4 and 6 complete cor-

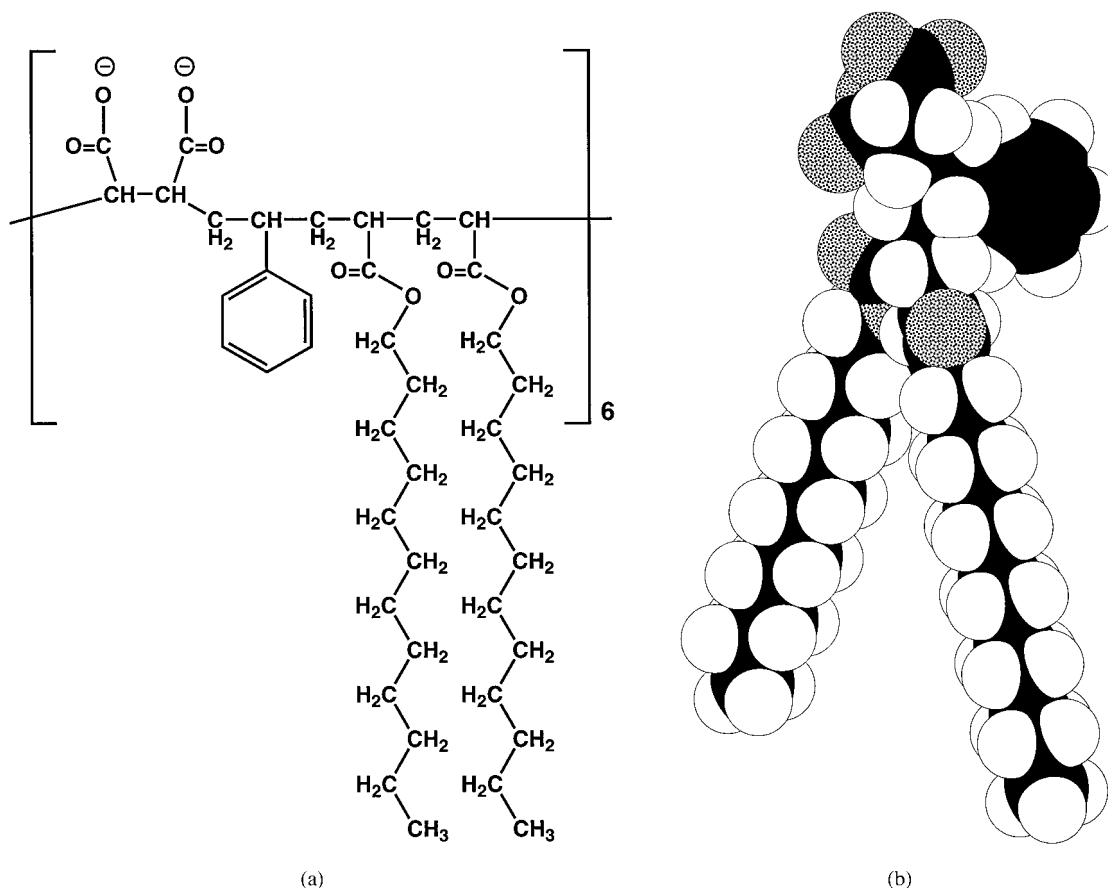
rosion inhibition at pH 8 was observed only with a 0.5 wt % addition. These results are improvements when compared to commercial S-MA copolymers in which the lowest hydrogen volume evolved was 11 mL at pH 8.<sup>5</sup> Furthermore, it is obvious (Fig. 2) that with an increasing chain length of the ester alcohol of the acrylate monomer, the evolved hydrogen volume decreases (i.e., the corrosion inhibiting effect increases). Figure 3 shows that there seems to be a potential correlation between the number of carbon atoms of the ester alcohol of the S-MA-acrylic ester copolymers and the evolved hydrogen volumes. A similar observation was made with the corrosion inhibition of aluminum pigment by different esters of gallic acid (gallates).<sup>10</sup> With increasing chain length of the ester alcohol (methyl-dodecyl) of the gallates, the surface activity and the corrosion inhibiting effect increased.<sup>10</sup> A very good exponential correlation ( $R^2$ : 0.96–0.99) between the number of carbon atoms of the ester alcohol and the evolved hydrogen volumes was obtained with the gallates.<sup>10</sup>

The appearance of the aqueous copolymer solutions (Table I) shows that with the increasing chain length of the ester alcohol of the acrylic ester (Copo 2–18), the flowability decreases. So one may assume that with increasing chain length of the ester alcohol the amphiphilic copolymers possibly associate by hydrophobic bonding.<sup>12</sup> This assumption was justified by the measurement of the electrical conductivity of diluted aqueous copolymer solutions (Fig. 4). It is obvious that with increasing chain length of the ester alcohol of the S-MA-acrylic ester copolymers the conductivity



**Figure 5** Electrical conductivity of aqueous copolymer solutions (0.1 wt %) versus the number of carbon atoms of the ester alcohol of the acrylic ester monomer in the copolymers.

## Copo 12

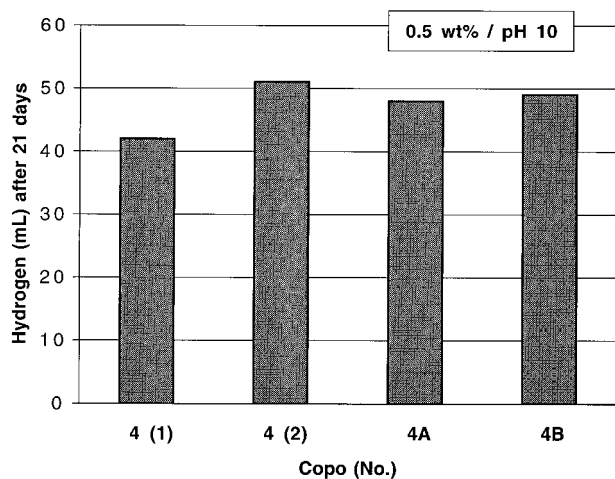


**Figure 6** Simplified presentation of (a) a structural formula and (b) a space-filling model of Copo 12.

decreases, and again a potential correlation between the number of carbon atoms of the ester alcohol and the conductivity of the aqueous solutions is observed (Fig. 4). If the concentration of the dissolved copolymers is reduced to 0.1 wt %, the potential correlation is even better (Fig. 5). Because the acid numbers of all copolymers are approximately equal (Table I), the decreasing conductivity should be caused by decreasing ionic mobility of the copolymer polyanions, possibly because of hydrophobic bonding. To visualize the amphiphilic character of the copolymers with long-chain ester alcohols, a simplified structural formula and a space-filling model of Copo 12 is presented in Figure 6; the molar ratio of MAA : styrene : dodecyl acrylate is about 1 : 1 : 2.

In a second test series two more copolymers based on Copo 4 with decreasing amounts of *n*-butyl acrylate and increasing amounts of styrene

were synthesized. The weight ratio of MAA : styrene : *n*-butyl acrylate was 15 : 15 : 70 (Copo 4), 15 : 35 : 50 (Copo 4A), and 15 : 55 : 30 (Copo 4B). The data of the aqueous copolymer solutions are also recorded in Table I; the flowability of the two new copolymer solutions (Copo 4A and 4B) is improved when compared to Copo 4. The gas-volumetric results at pH 10 with the addition of 0.5 wt % of Copo 4, 4A, and 4B are summarized in Figure 7. (For clarity only the hydrogen volumes after 21 days are plotted.) The test with Copo 4 was carried out twice to show the reproducibility of the gas-volumetric test method. It is obvious (Fig. 7) that within the limits of measuring accuracy there is no difference between Copo 4, 4A, and 4B. Therefore, one may assume that the amount of acrylic ester in the copolymers can be reduced to get better flowable copolymer solutions.



**Figure 7** Comparison of hydrogen volumes evolved from dispersions of an aluminum pigment in water/butyl glycol at pH 10 within 21 days with the addition of 0.5 wt % of different copolymers. The test with Copo 4 was carried out twice.

## CONCLUSIONS

MA copolymers were synthesized by free-radical copolymerization of MAA, styrene, and acrylic esters with various ester alcohols: ethyl, *n*-butyl, *n*-hexyl, *n*-dodecyl, and *n*-octadecyl acrylate. The weight ratio of MAA : styrene : acrylic ester was 15 : 15 : 70.

These copolymers inhibit the hydrogen corrosion reaction of aluminum pigment in aqueous media at pH 8 and 10. With increasing chain length of the ester alcohol of the acrylate monomer, the evolved hydrogen volume decreases (i.e., the corrosion inhibiting effect increases). There seems to be a potential correlation between the number of carbon atoms of the ester alcohol of the

copolymers and the evolved hydrogen volumes. With the addition of 0.5 wt % of the copolymers with *n*-butyl, *n*-hexyl, *n*-dodecyl, and *n*-octadecyl acrylate, no hydrogen evolution was observed at pH 8 within 21 days (complete corrosion inhibition).

Conductivity measurements of aqueous copolymer solutions indicate that with increasing chain length of the ester alcohol the copolymers possibly associate by hydrophobic bonding.

The authors are grateful to BASF Coatings AG for the approval of this publication.

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