

# Styrene Copolymers with Carboxyl Groups as Corrosion Inhibitors for Zinc Pigments in Aqueous Alkaline Media

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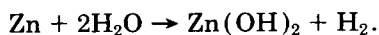
## SYNOPSIS

Zinc pigments react in aqueous alkaline media (e.g., water-borne paints) by the evolution of hydrogen. Low molecular weight styrene–maleic acid and styrene–acrylic acid/styrene–acrylate copolymers can inhibit this corrosion reaction of zinc pigments in a mixture of water and butyl glycol in the ratio 9 : 1 at a pH value of 10 (ammonia). High molecular weight styrene–maleic acid copolymers are only very poor corrosion inhibitors. This was proved by volumetric measurement of the evolved hydrogen. There seems to be a correlation between the content of carboxyl groups of the low molecular weight styrene–maleic acid and styrene–acrylic acid/styrene–acrylate copolymers and the evolved hydrogen volume in ammoniacal aqueous medium: The lower the acid number of the styrene copolymers, the lower is the evolved hydrogen volume. Low molecular weight styrene copolymers neutralized with dimethylethanolamine inhibit the corrosion reaction much better than with ammonia.

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## INTRODUCTION

The starting point for this work are zinc pigments<sup>1</sup> which are used in anticorrosion paints. Water-borne paints reduce significantly the emission of organic solvents to the atmosphere during the paint application. 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 values of water-borne paints are about 8–9. One of the problems of water-borne anticorrosion paints with zinc pigments is the corrosion of the zinc pigments in the alkaline aqueous paint medium, which causes the formation of hydrogen (a detailed study of the corrosion of different types of zinc pigments in aqueous alkaline media is presented in Ref. 2):



Therefore, an inhibition of this corrosion reaction is necessary. Zinc pigments can be stabilized by addition of chromate (VI),<sup>3</sup> which is, however, carcinogenic. So, alternative nontoxic methods for the inhibition of this corrosion reaction are required.

Recent studies reported the inhibition of corrosion of aluminum pigments (for decorative metallic paints) in alkaline aqueous media by polymers with carboxyl groups like polyacrylic acids,<sup>4</sup> low<sup>5</sup> and high molecular weight<sup>6</sup> styrene–maleic acid copolymers, and a styrene–acrylic acid copolymer<sup>5</sup>; these polymers are supposed to be nontoxic. Styrene–maleic acid copolymers showed an excellent corrosion inhibiting effect with respect to aluminum pigments in aqueous alkaline media.<sup>5,6</sup> There was also a correlation between the acid number of the styrene–maleic acid copolymers and the evolved hydrogen volume: The lower the acid number, the lower was the evolved hydrogen volume.<sup>5,6</sup> No influence of the molecular weight of the styrene–maleic acid copolymers on their corrosion-inhibiting effect with respect to aluminum pigments in aqueous alkaline media was found.<sup>5,6</sup> Contrarily, with addition of poly(acrylic acid)s as corrosion inhibitors for aluminum pigments, the corrosion inhibiting effect de-

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creased strongly with increasing molecular weight of the poly(acrylic acid)s.<sup>4</sup> The results with aluminum pigments in aqueous alkaline media led to the question of whether polymers are also able to inhibit the corrosion of zinc pigments in aqueous alkaline media.

The subject of the present study is the assessment of styrene-maleic acid copolymers and styrene-acrylic acid/styrene-acrylate copolymers as alternative corrosion inhibitors for zinc pigments in an aqueous alkaline medium.

## EXPERIMENTAL

An unstabilized paste of a platelike leafing zinc pigment ("zinc flakes")<sup>2</sup> for solvent-borne paints, which contains 10 wt % hydrocarbon solvent, was used (specific surface about 8 m<sup>2</sup>/g: BET method); 8.76 g of such a paste was dispersed for 5 min with a magnetic stirrer in 100 mL of a mixture of water and butyl glycol in the ratio 9 : 1 (butyl glycol is the most common organic cosolvent in water-borne paints). To improve the wetting of the hydrophobic zinc paste by the aqueous medium, 2 wt % of a wet-

ting agent (adduct of 10 mol of ethylene oxide to nonylphenole) was added. To accelerate the corrosion reaction, the pH of the solvent was raised to 10 with ammonia, a commonly used amine for water-borne air-drying paints. The temporal progress of the corrosion reaction was studied by volumetric measurement of the evolved hydrogen. The standard zinc pigment dispersion (without corrosion inhibitors) reacted completely to a nearly colorless precipitate (presumably zinc hydroxide) within about 3 weeks at room temperature; the hydrogen volume by complete reaction of the zinc pigment was determined to 2.51 L (average value of 22 gas-volumetric tests, maximum deviation 11%, mean deviation 5%).<sup>2</sup>

The data of the examined copolymers according to the specifications of the suppliers were recorded in Table I. The solid copolymers were converted into their soluble salts by heating 2 wt % copolymer in water plus an appropriate amount of ammonia; 0.5 wt % (referring to solid polymer) of each copolymer was dissolved in the solvent mixture. After that, the pH value was adjusted to 10 and the zinc pigment was dispersed. Then, the hydrogen evolution was measured daily over a period of 5 weeks at room temperature.

**Table I** Data of Styrene-Maleic Acid Copolymers (S-MA), a Styrene-Acrylic Acid Copolymer (S-AA), and Styrene-Acrylate Copolymers (S-A) According to the Specifications of the Suppliers

Copolymer Abbreviation	Molecular Mass <sup>a</sup> (g/mol)	Acid No. (mg KOH/g)	Glass Temperature (°C)	Styrene : MAA (Mol Ratio)	Esterification (Partial Ester)
S-MA 1	1600	465-495	154	1 : 1	None
S-MA 2	1700	255-285	124	1 : 1	Partial ester <sup>b</sup>
S-MA 3	2500	165-205	44	1 : 1	Partial ester <sup>b</sup>
S-MA 4	1700	335-375	124	2 : 1	None
S-MA 5	1900	200-240	110	2 : 1	Partial ester <sup>b</sup>
S-MA 6	1900	265-305	125	3 : 1	None
S-MA 7	105,000	175	No data	1 : < 1	Partial ester <sup>b</sup>
S-MA 8	180,000	185	No data	1 : < 1	Partial ester <sup>b</sup>
S-MA 9	350,000	405	No data	1 : 1	None
S-MA 10	400,000	500-540	No data	1 : 1	None
S-AA	1200	260-280	97	1 : 1 <sup>c</sup>	None
S-A 1	1300	235	70		
S-A 2	1800	250	57		
S-A 3	4200	110	58		
S-A 4	5000	225	76		
S-A 5	9200	150	79		
S-A 6	10,000	200	88		

Suppliers: S-MA 1-6: Elf Atochem; S-MA 7-9: Monsanto; S-MA 10: Leuna; S-AA: BASF; S-A 1 and 6: Morton; S-A 2-5: SC Johnson.

<sup>a</sup> The molecular masses are approximate data.

<sup>b</sup> S-MA 2, 3, 5: The exact esterification is not specified by the supplier. S-MA 7: methyl/butyl-partial ester; S-MA 8: methyl/isobutyl-partial ester.

<sup>c</sup> Styrene : acrylic acid.

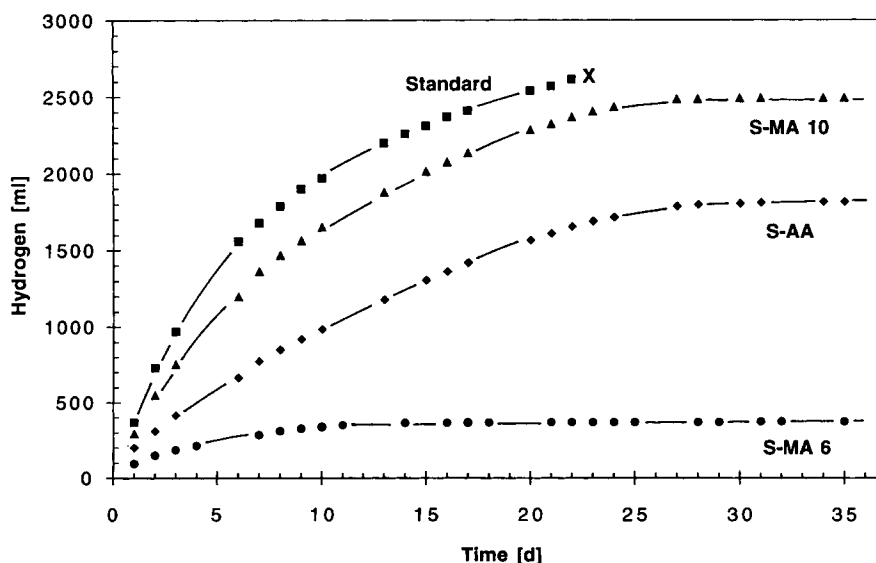
## RESULTS AND DISCUSSION

Figure 1 shows the temporal progress of the corrosion reaction determined by volumetric measurement of the evolved hydrogen with addition of 0.5 wt % of S-MA 6 (good corrosion inhibitor), S-AA (poor corrosion inhibitor), and S-MA 10 (very poor corrosion inhibitor), which were typical for zinc pigment dispersions with addition of copolymers. Also shown, for comparison, is the time dependency of the hydrogen evolution of the standard zinc pigment dispersion (without corrosion inhibitor) which had completely reacted after 22 days.<sup>2</sup> Volumetric measurement of the corrosion reaction of all zinc pigment dispersions with addition of copolymers showed the same time dependency of the hydrogen evolution (see Fig. 1). First, a rapid evolution of hydrogen was observed; after this period, the corrosion rate slowed down (inhibition of the corrosion reaction).

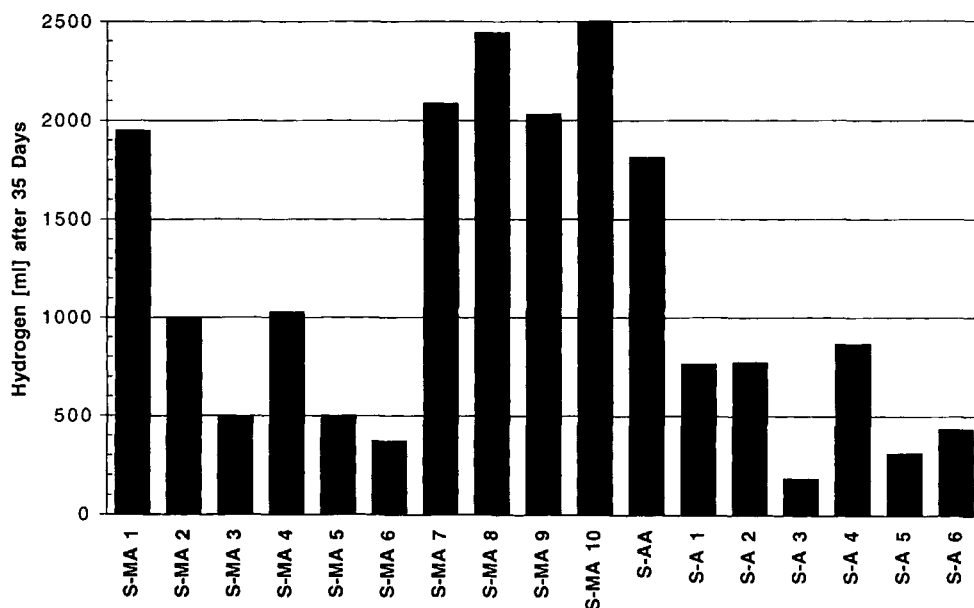
All gas-volumetric results with addition of 0.5 wt % of copolymers are summarized in Figure 2 (for clarity, only the hydrogen volume after 5 weeks is plotted). It is obvious (Fig. 2) that all high molecular weight styrene-maleic acid copolymers (S-MA 7-10) were only very poor corrosion inhibitors with respect to the zinc pigment, whereas the low molecular weight styrene-maleic acid copolymers with the exception of S-MA 1 inhibited the corrosion reaction. (The poor corrosion inhibiting effect of S-MA

1 is discussed below [Fig. 3].) This is different from the observations made with aluminum pigments where high and low molecular weight styrene-maleic acid copolymers were excellent corrosion inhibitors.<sup>5,6</sup> Also, the styrene-acrylate copolymers inhibited the corrosion reaction of the zinc pigment (Fig. 2). Furthermore, there seems to be a correlation between the acid number of the examined low molecular weight copolymers and the evolved hydrogen volume (Fig. 3): The lower the acid number, the lower was the evolved hydrogen volume. The straight line in Figure 3 was calculated by linear regression; the certainty of the correlation ( $R^2$  value) of 0.62 indicates that the correlation is not very strong. With styrene-maleic acid copolymers and aluminum pigments, the certainty of the correlation between the acid number and the evolved hydrogen volume was much better ( $R^2$ : 0.86-0.94).<sup>5,6</sup> This correlation (Fig. 3) explains the poor corrosion inhibiting effect of S-MA 1 because of its high acid number: 465-495 mg KOH/g (Table I).

The overall corrosion inhibition of zinc pigments in ammoniacal aqueous media by copolymers is noteworthy but not sufficient for an application in water-borne paints because ammonia greatly accelerates the corrosion reaction of zinc.<sup>2</sup> The reason for this acceleration is the solubility of zinc oxide in aqueous solutions of ammonia and ammonium ions.<sup>2,7</sup> In water-borne paints also, other amines like dimethylethanolamine (DMEA) can be used which



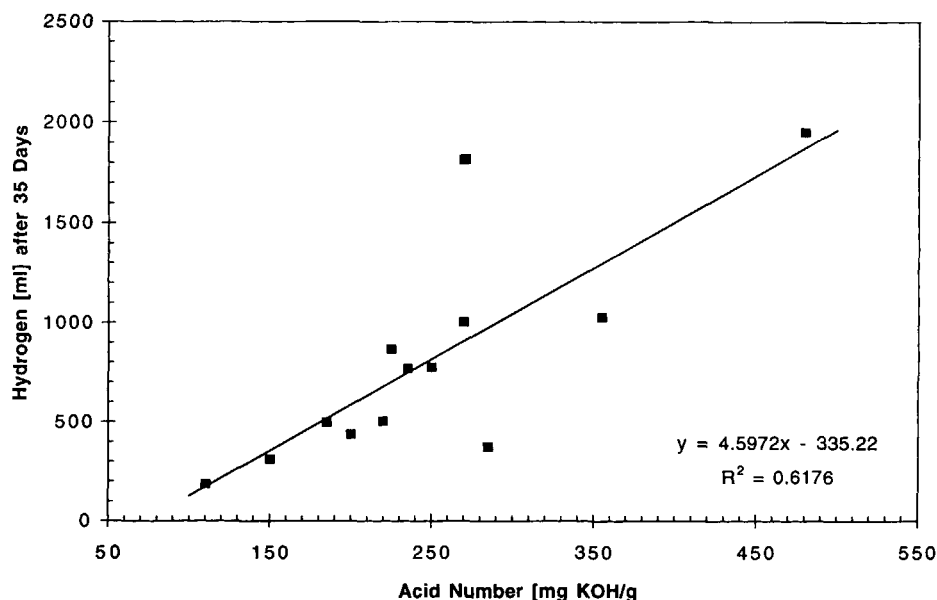
**Figure 1** Time dependency (days) of the hydrogen evolution in water/butyl glycol at pH 10 (ammonia) of the standard zinc pigment dispersion (without inhibitor) and with addition of 0.5 wt % of the styrene-maleic acid copolymers S-MA 6 and S-MA 10 and the styrene-acrylic acid copolymer S-AA. (X) Complete reaction of the zinc pigment.



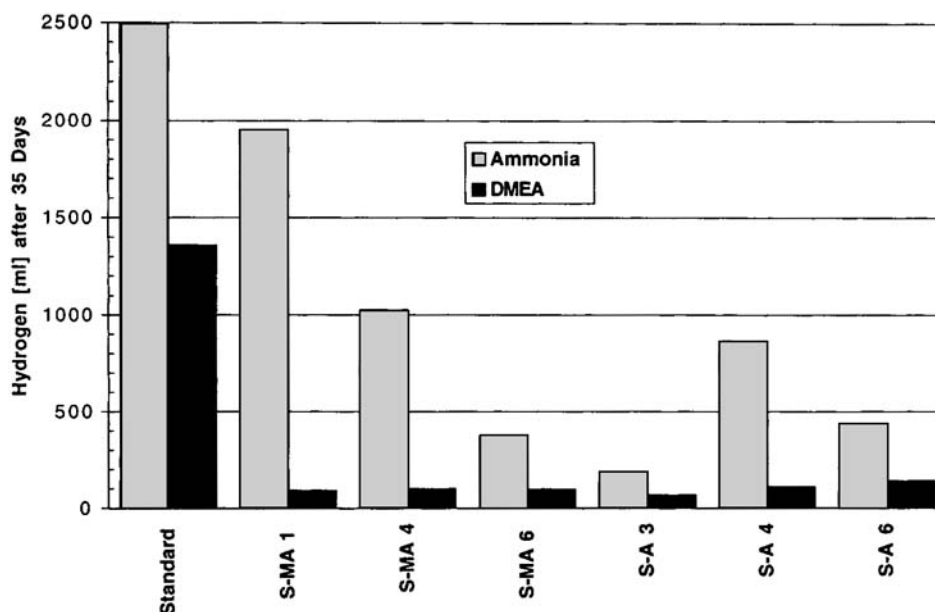
**Figure 2** Comparison of hydrogen volumes evolved from dispersions of a zinc pigment in water/butyl glycol at pH 10 (ammonia) within 35 days with addition of 0.5 wt % of different styrene copolymers.

do not accelerate the corrosion reaction of zinc pigments to the same extent as does ammonia.<sup>2</sup> In a second series, the pH values of six zinc pigment dispersions with addition of 0.5 wt % of the styrene-maleic acid copolymers S-MA 1, 4, and 6 and of the

styrene-acrylate copolymers S-A 3, 4, and 6 were raised to 10 with DMEA (the solid copolymers were dissolved in water with addition of DMEA). The gas-volumetric results of these experiments are presented in Figure 4 (for clarity, only the hydrogen



**Figure 3** Hydrogen volumes (after 35 days) evolved from dispersions of a zinc pigment in water/butyl glycol at pH 10 (ammonia) vs. acid number (average values) of the added low molecular weight styrene copolymers (0.5 wt %). Linear regression and  $R^2$  value were calculated with MS-Excel 5.0.



**Figure 4** Comparison of hydrogen volumes evolved from dispersions of a zinc pigment in water/butyl glycol at pH 10 (ammonia and DMEA, respectively) within 35 days of the standard zinc pigment dispersions (without inhibitor) and with addition of 0.5 wt % of the styrene-maleic acid copolymers S-MA 1, 4, and 6 and the styrene-acrylate copolymers S-A 3, 4, and 6 (neutralized with ammonia and DMEA, respectively).

volume after 35 days is plotted). Also shown, for comparison, are the hydrogen volumes of the standard zinc dispersions (without a corrosion inhibitor) with, respectively, DMEA and ammonia (pH 10) and of the zinc dispersions with addition of 0.5 wt % of S-MA 1, 4, and 6 and S-A 3, 4, and 6 with ammonia (pH 10). The superiority of the copolymers neutralized with DMEA is obvious (Fig. 4). For an exact comparison of the gas-volumetric results with addition of different amines, protective values, as published by Horner and Meisel,<sup>8</sup> have to be calculated, because the standard zinc pigment dispersions (without inhibitors) with ammonia and DMEA evolve different hydrogen volumes (see Fig. 4). All protective values with addition of 0.5 wt % of S-MA 1, 4, and 6 and S-A 3, 4, and 6 are calculated on the basis of the hydrogen volume evolved after 22 days because the standard zinc pigment dispersion with ammonia has completely reacted after 22 days. It should be noted that with addition of effective corrosion inhibitors the hydrogen volume after 22 days is nearly the same as after 35 days (e.g., S-MA 6; see Fig. 1); an exception is the poor corrosion inhibitor S-MA 1:

$$\text{Protective value}^8: J = \frac{V_0 - V}{V_0} \times 100\%$$

$V_0$  is the hydrogen volume evolved from the standard zinc dispersions (without inhibitor) after 22 days (ammonia: 2.51 L; DMEA: 1.35 L), and  $V$ , the hydrogen volume evolved from zinc dispersions with addition of copolymers (after 22 days).

The calculated protective values are summarized in Table II. It is obvious (Table II) that the corrosion inhibiting effect of the copolymers neutralized with DMEA is much better than with ammonia. These

**Table II Protective Values of Styrene-Maleic Acid Copolymers (S-MA) and Styrene-Acrylate Copolymers (S-A) Neutralized with Ammonia or Dimethylethanolamine (DMEA) at pH 10 After 22 Days**

Copolymer Abbreviation	Protective Value (%)	
	Ammonia	DMEA
S-MA 1	37	93
S-MA 4	61	93
S-MA 6	85	93
S-A 3	93	95
S-A 4	67	92
S-A 6	84	90

results show the potential of the corrosion inhibition of zinc pigments by the copolymers presented in this study.

In the system carboxylic acid (weak acid)/ammonia (weak base), more or less ammonia can be used without changing the pH significantly. As ammonia accelerates, the corrosion reaction very strong; it is important for a good reproducibility of the gas-volumetric results to use the exact amount of ammonia as in the experiment before. Gas-volumetric tests with DMEA are less sensitive because DMEA is less corrosive; so, the reproducibility of gas-volumetric results with DMEA is very good.

## CONCLUSIONS

It was shown that low molecular weight styrene-maleic acid and styrene-acrylic acid/styrene-acrylate copolymers inhibit the corrosion reaction of zinc pigments in aqueous alkaline media (pH 10/ammonia); high molecular weight styrene-maleic acid copolymers were only very poor corrosion inhibitors.

There seems to be a correlation between the content of carboxyl groups of the low molecular weight styrene-maleic acid and styrene-acrylic acid/styrene-acrylate copolymers and the evolved hydrogen volume in ammoniacal aqueous medium: The lower the acid number of the styrene copolymers, the lower is the evolved hydrogen volume. With dimethyleth-

anolamine as the neutralizing agent, the corrosion-inhibiting effect of low molecular weight styrene-maleic acid and styrene-acrylate copolymers can be very much improved.

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