Polymeric Corrosion Inhibitors for Copper and Brass Pigments

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ABSTRACT: Copper and brass pigments corrode in aqueous alkaline media with the absorption of oxygen that can be measured gasvolumetrically. These corrosion reactions can be inhibited by certain polymers; the metallic sparkle and the color of the pigments is preserved. The brass pigment is inhibited more effectively than the copper pigment. Some low-molecular mass styrene–maleic acid (SMA) copolymers are efficient corrosion inhibitors; a low acid number is necessary but not sufficient for corrosion inhibition. At pH 8.5 there is a potential correlation between the acid number of the low-molecular mass SMA and the oxygen volumes absorbed from brass pigment dispersions; oxygen volumes decrease with decreasing acid number. Furthermore, increasing copolymer addition effects an increase of corrosion inhibition. Polyacrylic acids, polyvinyl alcohols and high-molecular mass SMA copolymers are ineffective. The most efficient group of polymers examined in this study are the styrene–acrylate copolymers because by addition of these the overall lowest volumes of oxygen were absorbed by the metal pigments. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 475–483, 2001

Key words: copper and brass pigments; oxygen absorption; corrosion inhibition; styrene–maleic acid copolymers; styrene–acrylate copolymers

INTRODUCTION

Lamellar copper and brass ("gold bronze") pigments are used as metallic pigments especially in printing inks. Waterborne inks significantly reduce the emission of organic solvents to the atmosphere during the printing process. The pH values of waterborne printing inks are slightly alkaline like the pH values of waterborne paints. The change from solventborne to waterborne metallic ink formulations leads to some problems caused by the copper and brass pigments as, e.g., tarnishing (darkening) of the pigments or to an increase of the viscosity of the inks.[1] The reason for these problems is an oxidation respectively corrosion reaction of the copper and brass pigments in the aqueous alkaline printing ink media.[1]

In a previous study, the corrosion reactions of copper and brass (rich gold) pigments in aqueous alkaline media were examined.[2] Copper as well as brass pigment corrode in aqueous alkaline media with the absorption of oxygen, which can be measured gasvolumetrically[2]:

$$2\ Cu + O_2 \rightarrow 2\ CuO$$

$$Cu/Zn + O_2 \rightarrow CuO + ZnO$$

Recent studies reported the inhibition of the hydrogen corrosion of aluminum and zinc pigments in aqueous alkaline media by different

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polymers respectively copolymers.[3–5] The hydrogen corrosion reactions both for aluminum and zinc pigments are inhibited well by addition of certain low-molecular mass styrene–maleic acid copolymers (SMA) and styrene–acrylate copolymers (SA).[3–5] As an empirical rule, low-molecular mass polymers (molecular mass <60,000) inhibit these corrosion reactions better than high-molecular mass polymers.[3,4] So, one may assume that polymers could also inhibit the oxygen corrosion of copper and brass pigments. Moreover, it is an interesting fact that some low-molecular mass SMA and SA are used as binders in waterborne printing inks.

The subject of the present study is the assessment of different polymers as possible corrosion inhibitors for copper and brass pigments in aqueous alkaline media.

EXPERIMENTAL

Unstabilized lamellar leafing pigments for solventborne inks of copper and brass (rich gold; about 70 wt % copper and 30 wt % zinc) with average particle diameters (d_{50}) of 11 μm were tested. The corrosion medium was desalinated water with 2.0 wt % of a wetting agent (adduct of 10 moles of ethylene oxide to nonylphenol) and 2.0 mmol/100 mL ammonium acetate as corrosion stimulator.[2] The pH values of 8.5 and 10 were adjusted with triethylamine (TEA). Metal pigment samples, each 4.0 g, were dispersed in 100 mL of corrosion medium with a magnetic stirrer. The oxygen absorption of the stirred metal pigment dispersions was measured over a period of 21 days at room temperature; the gasvolumetric apparatus (inverted graduated cylinder filled with pure oxygen) has been described in detail elsewhere.[2,6,7]

The standard metal pigment dispersions (without inhibitors) reacted completely with oxygen to mostly dark precipitates within one to six days. Oxygen absorption by complete corrosion reaction:

- Copper pigment 0.71 L (average value out of 75 tests); calculated oxygen absorption by complete conversion 0.76 L.
- Rich gold pigment 0.72 L (average value out of 61 tests); calculated oxygen absorption by complete conversion 0.75 L.

The reasons for the small deviation between measured and calculated oxygen volumes have been discussed previously.[2]

The solid copolymers (SMA and SA) were dissolved in heated water by neutralization with dimethylethanolamine (DMEA) because DMEA dissolves copolymers better as TEA. Each 0.50 and sometimes 2.0 wt % (solids) of polymer was added to the corrosion medium before the dispersion of the metal pigments. The data of the polymers are recorded in Table I. The different groups of polymers are arranged in Table I with increasing molecular mass; only the low-molecular mass SMA which have similar molecular masses are ordered with decreasing acid number.

RESULTS AND DISCUSSION

Polyacrylic Acids (PAA) and Polyvinyl Alcohols (PVAL)

PAA has a very high acid number whereas the acid number of PVAL is zero (Table I). Low-molecular mass PAA (e.g., PAA 1) were good corrosion inhibitors for aluminum pigment but high-molecular mass PAA (e.g., PAA 2) were bad inhibitors.[4,8] PVAL showed no corrosion inhibiting effect on aluminium pigment at all.[4,8] The experimental results with copper and brass pigments with addition of PAA and PVAL are summarized in Figure 1. It is obvious that neither PAA or PVAL inhibited the examined corrosion reactions. So, very high acid number (PAA) as well as zero acid number (PVAL) seems to be unsuitable for corrosion inhibition of copper and brass pigments.

Styrene–Maleic Acid Copolymers

SMA proved to be good corrosion inhibitors both for aluminum[4] and zinc[3,5] pigments; low-molecular mass SMA inhibit these corrosion reactions better than high-molecular mass SMA. The results with copper and brass pigments with addition of SMA are summarized in Figures 2 and 3. It is obvious that all high-molecular mass SMAs (Nos. 6–10) showed no corrosion inhibiting effect whereas some of the low-molecular mass SMA inhibited the corrosion reaction (Figures 2 and 3). The corrosion reaction of the copper pigment is inhibited by SMA 2, 3, and 5 at pH 8.5, and by SMA 1 surprisingly at the higher pH value of 10 (Fig. 2). The corrosion reaction of the brass pigment is inhibited by SMA 5 both at pH 8.5 and 10, by SMA 2, 3, and 4 only at pH 8.5, and again by SMA 1 at pH 10 (Fig. 3). At pH 8.5, the oxygen absorption of the brass pigment with addition of

Table I Data of the Examined Polymers According to the Specifications of the Suppliers[a]

Polymer Abbreviation	Molecular Mass[b] (g/mol)	Acid Number (mg KOH/g)	Styrene : MAA (Mole Ratio)	Esterification (Partial Ester)
1. Polyacrylic acids (PAA)				
PAA 1	1000	780[c]		
PAA 2	100 000	700–750		
2. Polyvinyl alcohols (PVAL)[d]				
PVAL 1	27 000	0[c]		
PVAL 2	31 000	0[c]		
3. Styrene-maleic acid copolymers (SMA)				
3.1. Low-molecular mass SMA				
SMA 1	1600	465–495	1 : 1	None
SMA 2	1700	335–375	2 : 1	None
SMA 3	1900	265–305	3 : 1	None
SMA 4	1700	255–285	1 : 1	Partial ester[e]
SMA 5	2500	165–205	1 : 1	Partial ester[e]
3.2. High-molecular mass SMA				
SMA 6	60 000	260–280	2 : 1	Isopropyl
SMA 7	100 000	500–540	1 : 1	None
SMA 8	105 000	175	1 : < 1	Methyl/butyl
SMA 9	350 000	405	1 : 1	None
SMA 10	400 000	500–540	1 : 1	None
4. Styrene-acrylate copolymers (SA)				
SA 1	1200	260–280		
SA 2	5000	205–225		
SA 3	8500	215		
SA 4	15 500	240		
SA 5	17 250	214		

[a] Suppliers: PAA 1, SA 1: BASF; PAA 2: Röhm; PVAL 1, 2: Hoechst; SMA 1–5: Elf-Atochem; SMA 6, 7, 10: Leuna; SMA 8, 9: Monsanto; SA 2–5: Johnson; higher-molecular mass SA have not been available.
[b] The molecular masses are approximate data.
[c] Calculated on monomer.
[d] Degree of hydrolysis PVAL 1: 98%, PVAL 2: 88%.
[e] The exact esterification has not been specified by the supplier.

the low-molecular mass SMA (Nos. 1–5) decreases with decreasing acid number (Fig. 3); i.e., corrosion inhibition increases. The increase of corrosion inhibition with decreasing acid number of SMA is similar to our results with aluminum pigments[4] and to practical observations in waterborne "gold bronze" printing inks.[1] Figure 4 shows that there seems to be a potential correlation between the acid number and the oxygen volumes absorbed. So, there seems to be a mathematical relationship between composition of the low-molecular mass SMA and their corrosion inhibiting effect. With aluminum pigments a linear correlation between the acid number of SMA and hydrogen volumes evolved has been established; with decreasing acid number, the hydrogen volumes evolved decreased (corrosion inhibition increased).[4]

To corroborate the surprising results with SMA 1 at pH 10, the tests were repeated with the neutralizing agent TEA as usual and additionally with DMEA; Figure 5 shows that the results with SMA 1 were reproducible. Within the limits of measuring accuracy of our test method, the difference between the two tertiary amines TEA and DMEA on corrosion inhibition is approximately negligible (Fig. 5; see also Ref. 2). The effect of pH with SMA 1 on copper and brass pigment is the opposite as observed with aluminum,[4] but similar to the results with zinc[3] pigment. But with zinc *all* examined polymers were more effective at the higher pH value of 10; a discussion of this phenomenon that is related to the isoelectric point of zinc oxide and the high reactivity of zinc metal has been presented elsewhere.[3] The question why with copper and brass pigment only SMA 1 is more efficient at pH 10 and the other low-molecular mass SMA are not, cannot be answered within the limits of the experimental results of this study. It could be of importance that SMA 1

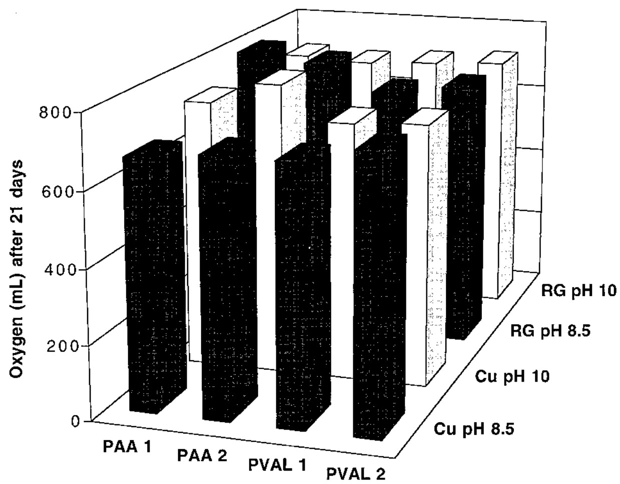

Figure 1 Comparison of oxygen volumes absorbed from aqueous dispersions of copper (Cu) and brass (rich gold: RG) pigments at pH 8.5 and 10 within 21 days with addition 0.5 wt % of different PAA and PVAL.

has as far the highest acid number of all examined low-molecular mass SMA (Table I). Furthermore, Figure 5 shows repeated test with brass pigment and SMA 5; again, the reproducibility of the results is sufficient.

The effect of copolymer concentration is shown in Figure 6. It is obvious that an increase of SMA concentration from 0.50 to 2.0 wt % effects a decreasing oxygen absorption (corrosion inhibition increases). This observation is similar to our results with aluminum[4,9] and zinc[10] pigments.

Provisional results can be stated:

- Corrosion inhibition of the brass pigment by SMA is more effective than for the copper pigment (see Figs. 2 and 3), which is similar to previous results with other copolymers.[6]
- High-molecular mass SMA are ineffective (see Figs. 2 and 3).
- Some low-molecular mass SMA are efficient inhibitors. So, low molecular mass is a necessary but not a sufficient requirement for corrosion inhibition.
- With exception of SMA 1, the corrosion inhibiting effects are better at the lower pH

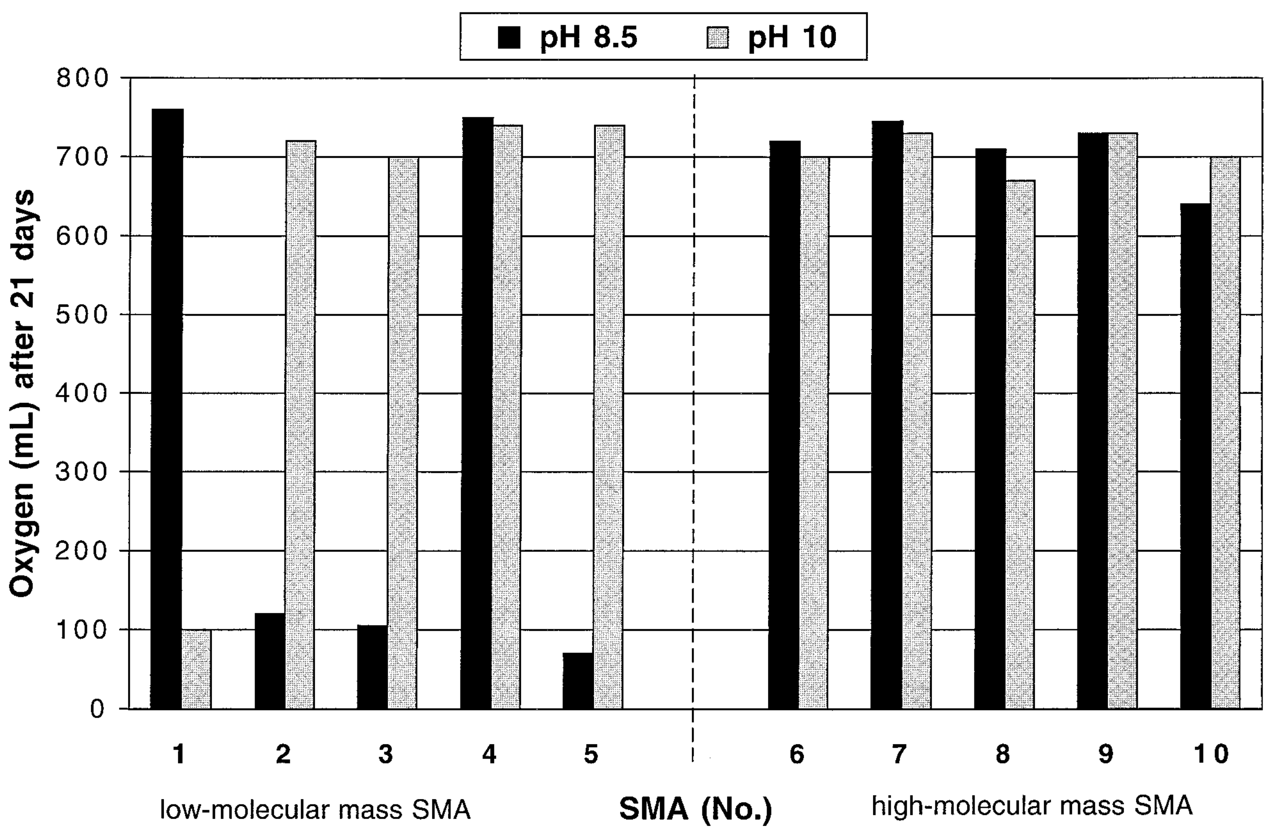

Figure 2 Comparison of oxygen volumes absorbed from aqueous dispersions of the copper pigment at pH 8.5 and 10 within 21 days with addition 0.5 wt % of different SMA.

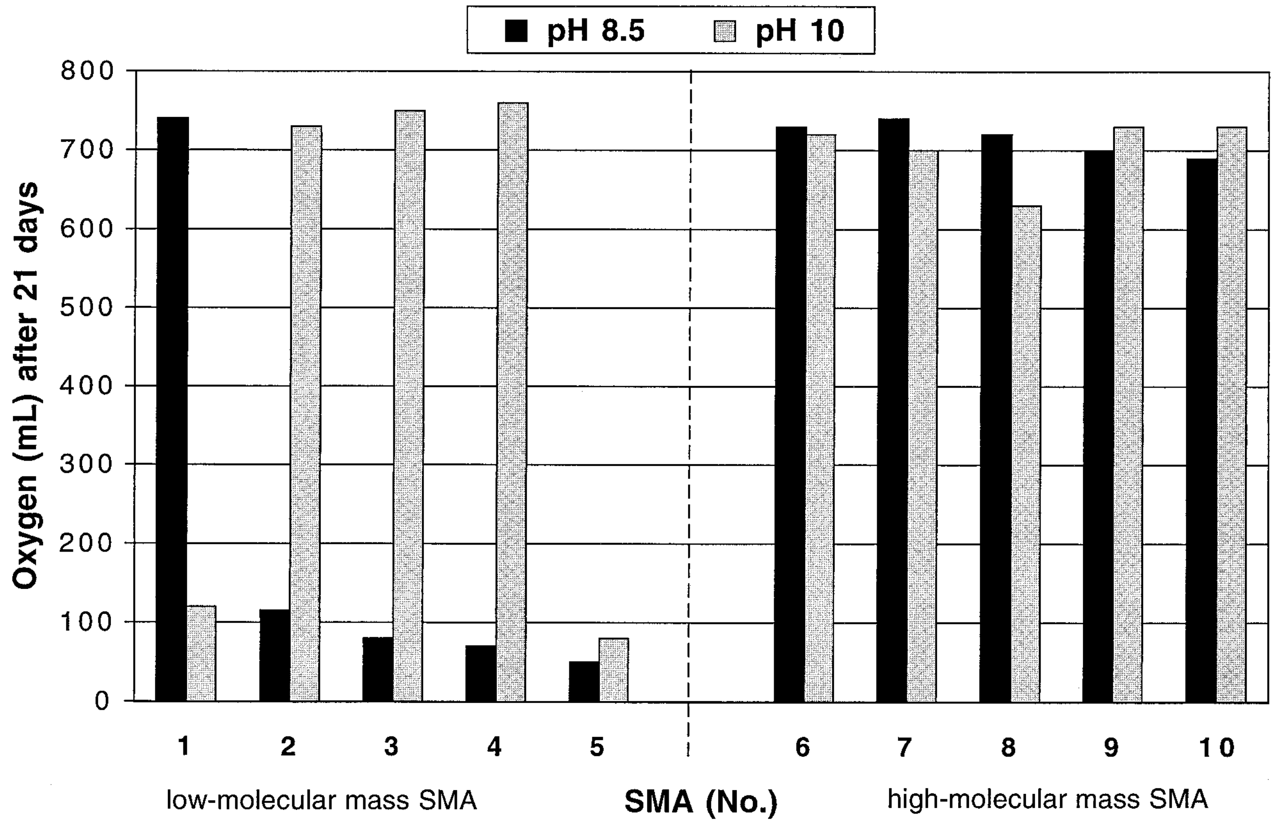

Figure 3 Comparison of oxygen volumes absorbed from aqueous dispersions of the brass pigment at pH 8.5 and 10 within 21 days with addition 0.5 wt % of different SMA.

value of 8.5 as at pH 10, which is similar to the results with low-molecular mass SMA and aluminum pigment.[4]

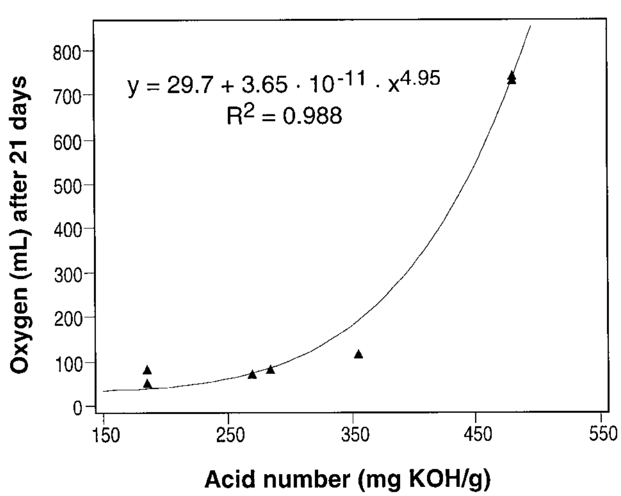

Figure 4 Oxygen volumes absorbed from brass pigment dispersions at pH 8.5 (TEA) vs acid number (average values) of the SMA coplymers 1–5 (0.5 wt %); two tests were repeated (see Fig. 5).

- A low acid number of copolymers is necessary but not sufficient for corrosion inhibition. Only at pH 8.5 is there a potential correlation between the acid number of the low-molecular mass SMA and the oxygen volumes absorbed from brass pigment dispersions; oxygen volumes decrease with decreasing acid number.
- Increasing copolymer addition effects an increase of corrosion inhibition.

Styrene–Acrylate Copolymers

The results with SA are presented in Figures 7 and 8. Only SA 4 is ineffective both with copper and brass pigment. The question why SA 4 is worse than all other SA is difficult to answer; it can only be speculated that the combination of relative high molecular mass and relative high acid number may be the reason (Table I). With addition of SA, no difference between the copper and the brass pigment can be observed (Figs. 7 and 8). Generally, SA seem to be better corrosion inhibitors for copper and brass pigments as SMA.

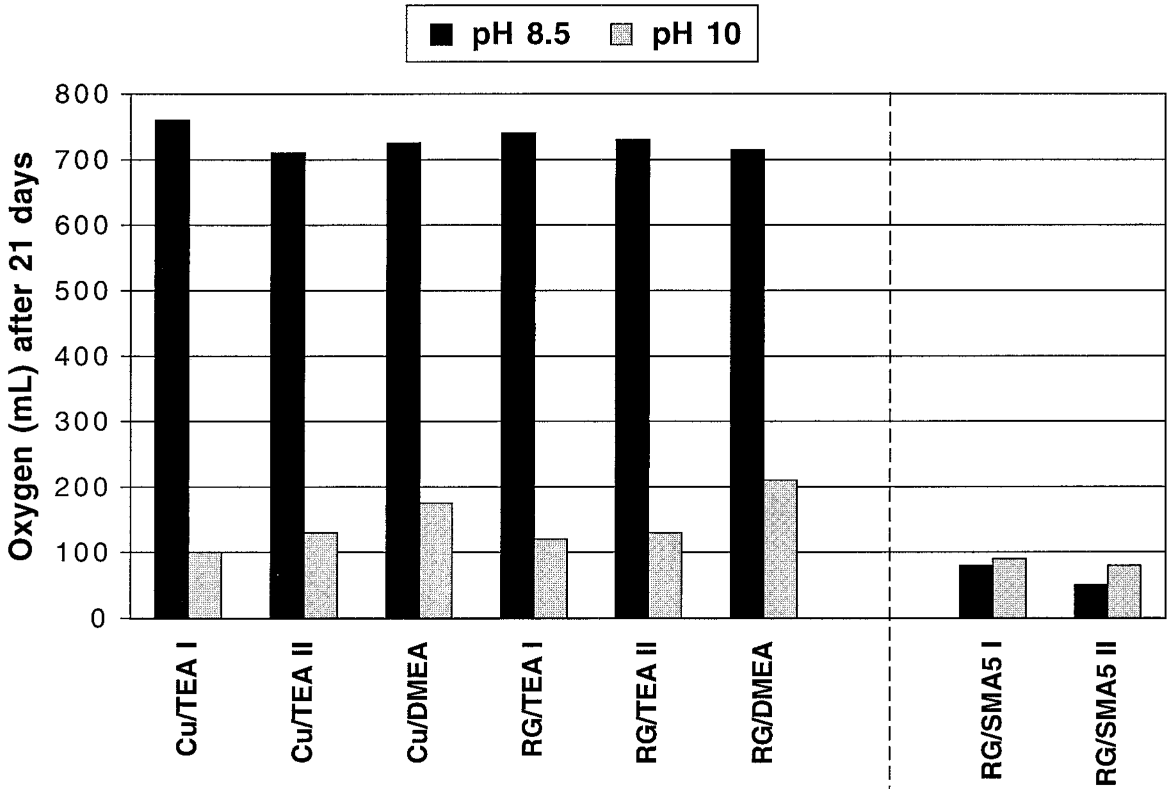

Figure 5 Comparison of oxygen volumes absorbed from aqueous dispersions of copper (Cu) and brass (rich gold: RG) pigments at pH 8.5 and 10 within 21 days with addition 0.5 wt % of SMA 1; pH adjusted with TEA as usual (repeated tests) and DMEA. Furthermore, a reproduction of the experiment with brass and 0.5 wt % SMA 5 (TEA) is shown.

Blank Experiments

In a pure oxygen atmosphere autoxidation of organic compounds (e.g., polyethers or polymers) is possible. Moreover, copper compounds are able to catalyze autoxidation reactions. So, oxygen absorption experiments were carried out at pH 10 (as described above) without addition of metal pigments. To simulate the influence of copper compounds, 2.0 mmol/100 mL of copper(II) sulfate were added to the corrosion medium. Furthermore, the blank experiments with polymers do not contain the wetting agent (polyether). The results of the blank experiments (Fig. 9) show that significant volumes of oxygen (24 mL are equal to 1 mmol oxygen) were absorbed by the polymers and the wetting agent; because of the limits of measuring accuracy especially at low volumes (see Fig. 5), only the upper and lower limit of the oxygen absorption of the seven tested polymers is plotted in Figure 9. The last blank experiment without polymer addition shows that there is also an oxygen absorption by the medium (TEA and ammonium acetate). So, it can concluded, that the corrosion inhibiting effect of the copolymers on copper and brass pigments is even better as observed in Figures 2–8 (above).

CONCLUSIONS

- The corrosion reaction (oxygen absorption) of copper and brass pigments in aqueous alkaline media can be inhibited by certain copolymers; the metallic sparkle and the color of the pigments was preserved.
- Polyacrylic acids, polyvinyl alcohols and high-molecular mass styrene–maleic acid copolymers are ineffective corrosion inhibitors because by addition of these complete corrosion of the metal pigments was observed.
- The most effective group of polymers examined in this study are the styrene–acrylate

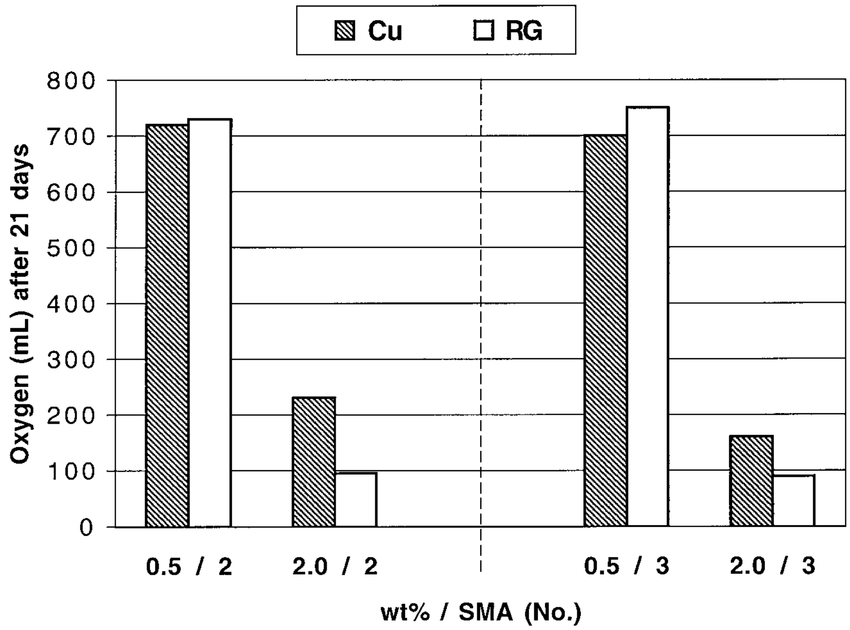

Figure 6 Comparison of oxygen volumes absorbed from aqueous dispersions of copper (Cu) and brass (rich gold: RG) pigments at pH 10 within 21 days with addition 0.5 and 2.0 wt % of SMA 2 and 3.

copolymers because by addition of these the overall lowest volumes of oxygen were absorbed by the metal pigments.

- Some low-molecular mass styrene–maleic acid copolymers are also efficient corrosion inhibitors. The brass pigment (rich gold) is

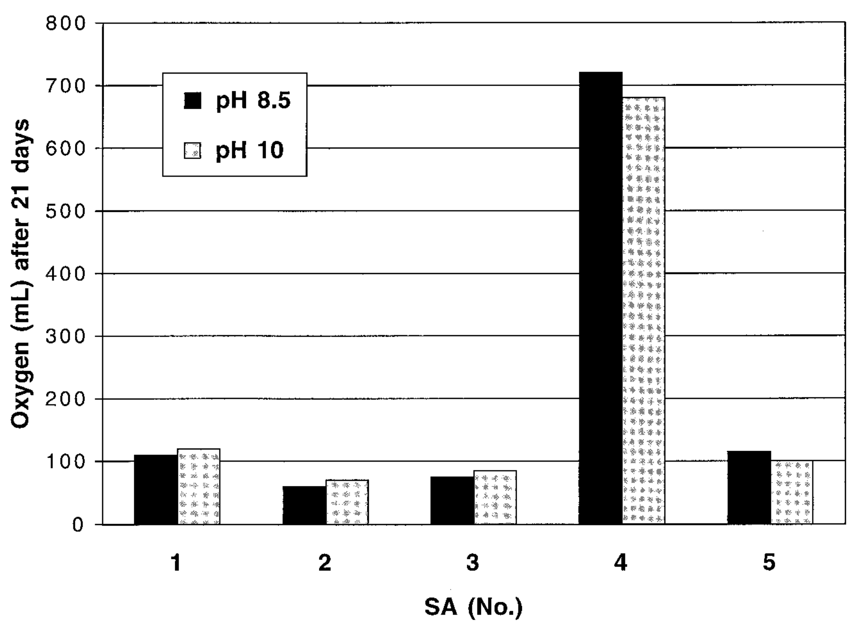

Figure 7 Comparison of oxygen volumes absorbed from aqueous dispersions of the copper pigment at pH 8.5 and 10 within 21 days with addition 0.5 wt % of different SA.

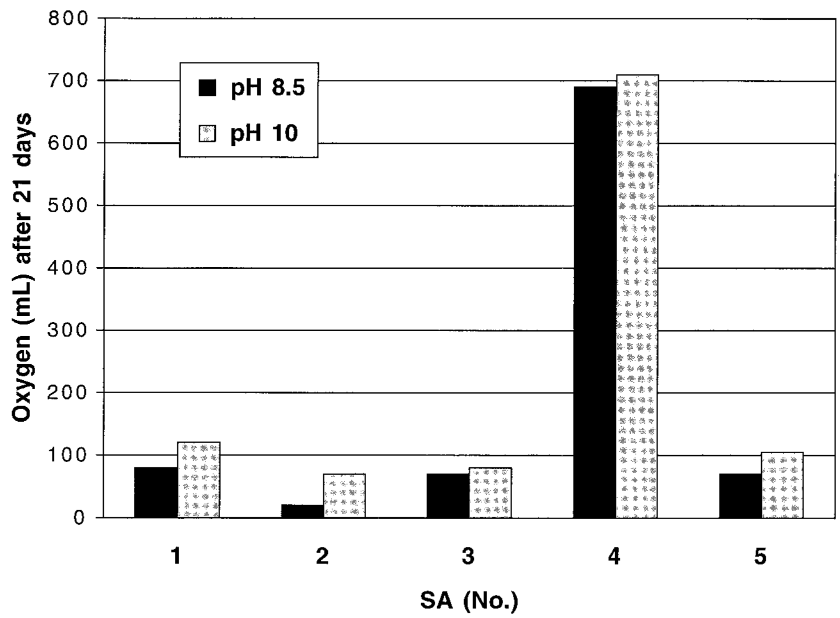

Figure 8 Comparison of oxygen volumes absorbed from aqueous dispersions of the brass pigment at pH 8.5 and 10 within 21 days with addition 0.5 wt % of different SA.

inhibited more effectively than the copper pigment. A low acid number of the copolymers is necessary but not sufficient for corrosion inhibition. Only at pH 8.5 is there a potential correlation between the acid number of the low-molecular mass SMA and the oxygen volumes absorbed from brass pigment dispersions; oxygen volumes

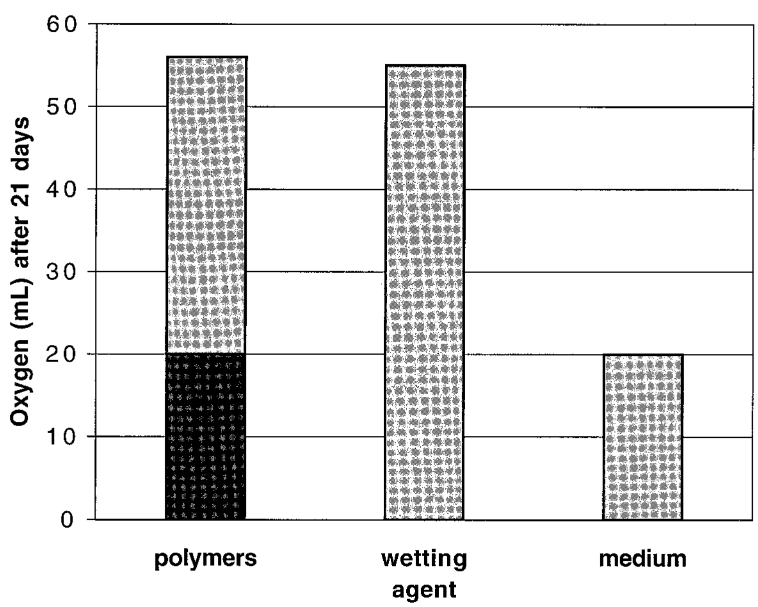

Figure 9 Comparison of oxygen volumes absorbed within 21 days from corrosion media at pH 10 (TEA) with addition of 0.50 respectively 2.0 wt % of seven different polymers (without wetting agent) and with 2.0 wt % of the wetting agent. Furthermore, the oxygen absorption of the medium without polymer and wetting agent is shown. All blank experiments without metal pigments but with 2.0 mmol/100 mL of copper(II) sulfate.

decrease with decreasing acid number. Furthermore, increasing copolymer addition effects an increase of corrosion inhibition.

The copolymers examined in this study are commercial products used for many different applications; it may be possible to synthesize copolymers with improved properties "tailor-made" for waterborne metallic inks (compare Refs. 6 and 9).

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