Effect of Different Polymers on the Efficiency of Water-Borne Methyl Amine Adduct as Corrosion Inhibitor for Surface Coatings

BADRAN M. BADRAN,[1] HEBA A. MOHAMMED,[1] HESHMAT A. AGLAN[2]

[1] Department of Polymers and Pigments, National Research Center, Cairo, Egypt

[2] College of Engineering, Architecture, and Physical Sciences, Tuskegee University, Tuskegee, Alabama 36088

Received 23 January 2001; accepted 31 October 2001

ABSTRACT: Styrene/acrylic emulsion copolymer and water-based short oil urethane alkyd resin were used as binders to prepare water-based, environmentally friendly paints by using 0.5% emulsified methylamine adduct as corrosion inhibitor. The choice of the two above-mentioned binders was based on the fact that styrene/acrylic emulsion copolymer is a nonconvertible binder, whereas short oil urethane alkyd resin is a convertible binder. The physical, chemical, mechanical, and corrosion properties of the paint films were evaluated and compared with a commercially known anticorrosive water-based paint. It was found that the prepared paints have unique desirable properties such as the following: they do not contain anticorrosive pigments (which contain heavy metals in their main chemical structure); they are solvent-free; and they can be produced to match any color. Corrosion tests on the films of the formulated paints revealed that the short oil urethane alkyd resin is superior to the styrene/acrylic copolymer. Moreover, the corrosion inhibition properties of the paint films prepared from both binders are comparable with the commercially available paints containing anticorrosive pigments. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 879–885, 2002

INTRODUCTION

Water-borne coatings continue to attract growing attention and importance to replace solvent-based paints. Water-borne two-component polyurethane coatings that met or exceeded the performance levels of typical solvent-based systems were prepared and evaluated.[1] A key advantage was the use of isocyanate crosslinkers normally employed in solvent-borne systems without any modification or chemical change. The isocyanates could simply be stirred in by hand before application. Blending of the isocyanate crosslinkers offered a wide formulation latitude in the resultant water-borne coatings.

Funke et al.[2] found that the rate-determining step for coating failure, in terms of corrosion protection, involves the formation of an aqueous conducting phase at the metal/coating interface. Many workers[3–6] have agreed with Pangelinan and Rhodes[12] that this step in high barrier coatings is electrolyte diffusion, under various conditions and resin systems. Others have attributed oxygen,[8] solvents,[9,10] or water permeation[11,12] as the rate-determining step.

Pangelinan and Rhodes[12] demonstrated, by using SEM, that the barrier properties do not exist because of the highly porous microstructures of many water-based coatings. These porous micro-

---

Correspondence to: H. A. Aglan (aglanh@tusk.edu).

Contract grant sponsor: U.S.–Egypt Science and Technology Joint Project.

Journal of Applied Polymer Science, Vol. 85, 879–885 (2002)

Table I Emulsion Paint Ingredients

Ingredient	Description/Properties	Source
Binders		
Styrene/acrylic	Emulsion	DMS Resins, Netherlands
Short oil urethane	Water–soluble alkyd polymer	DMS Resins, Netherlands
Corrosion inhibitors		
Methyl amine adduct	5% by mass, epoxidized	Ref. 18
Pigments and fillers		
Titanium dioxide, R-902	91% TiO_2, 2% SO_2, and 4.5% Al_2O_3	DuPont Co.
Talc	Particle size: 5 μm	General Co. for Trading and Chem., Egypt
Additives		
Disperse-Ayd W-30	Dispersing agent, aqueous	Daniel Products, USA
Sodium polyphosphate	Wetting agent	Heliopolis Co. for Chemical Industries, Egypt
Ethylene glycol	Coalescing agent	Heliopolis Co. for Chemical Industries, Egypt
Torysol LAC	Leveling agent	Troy Chemical Co., USA
Ethanol amine	PH stabilizer, pH 8–9	El-Gomhoreya Chem. Co.
Polyol DF 3163	Antifoaming agent	Daniel Prod. Co, USA
Urethane-based thickener	Thickener and rheology modifier	Allied Colloids Co., Egypt
Acticide SPX	Biocide	Thor Chem. Co., USA
Dapro 7007	Chelating catalyst, used as crosslinker for alkyd resin	Daniel Products Co., USA

structures of the water-borne coating adversely affect their barrier properties. However, such deficiency can probably be addressed by improving the cohesive resistance of the coatings. The effective corrosion resistance of water-borne coatings, because they are porous to electrolytes, will have to be judged by the appropriate mode of corrosion protection. Water-borne coatings that rely on passivation, for example, would be expected to perform poorly in salt-water immersion service because electrolyte readily destroys passivity. Additionally, elevated temperatures would accelerate the loss of passivity. Conversely, passivated water-borne coatings are more likely to perform satisfactorily in atmospheric exposures.

Pekcan et al.[13] found that the process of slow polymer chain interdiffusion between particulates is necessary for optimal film properties. Several ways for alleviating these gaps have included: adjusting the particulate size distribution by Fernando,[14] promoting crosslinking by Daniels and Klein,[15] choosing optimal surfactant additives by Chen et al.,[16] and adding solvent coalescing aids by Winnik et al.[17] It is clear, however, that these remedies have not resulted in perfect coalescence for commercial water-borne coatings.

In the present work, two different water-based polymers were used as binders. Styrene/acrylic emulsion copolymer is a nonconvertible binder and has very high resistance to water uptake and desirable physical/mechanical properties. Short oil urethane alkyd resin is a convertible binder and has excellent adhesion properties with high abrasion resistance. A concentration of 0.5% of emulsified methylamine adduct, which was proven to be the optimum amount, was used for both binders. The physical, chemical, mechanical, and corrosion properties of the paint films were evaluated and compared with a commercially known anticorrosive water-based paint.

MATERIALS AND TECHNIQUES

Materials

The materials used in this research are listed in Table I, which summarizes the required ingredients needed to prepare the emulsion paint system from each binder.

Techniques

Preparation of Adducts, Paints, and Test Samples

Formulations of Emulsion Paints. Emulsion paint formulations were prepared in two stages.

Table II Test Methods

Property	Test Method	Property	Test Method
Viscosity	ASTM 562	Synthetic sea water	Ref. 22
Drying time	Ref. 20	Corrosion resistance	ASTM D 1653
Dry film hardness	ASTM D3363	Corrosion scratch	Ref. 23
Dry film thickness	Ref. 21	Blistering test	ASTM 714
Surface preparation	ASTM D 1653	Alkali resistance	ASTM D 1647
Ductility	DIN 50 101	Acid resistance	ASTM B 287
Bending	ASTM 1737	Water uptake	Ref. 24
Dry film adhesion	ASTM 3359	Weight loss	Ref. 25

The first stage was high-speed stirring of filler, pigment, dispersing agent, and water. The second stage was low-speed stirring of the emulsion polymer, water, leveling agent, antifoaming agent, thickener, and biocide with the mixed ingredients from the first stage. The emulsified inhibitor was added during the second stage. The pH of the medium was adjusted to 8–9 by using ethanol amine.[19]

Sample Preparation and Paint Application. Carbon steel with a nominal thickness of 1 mm was used as the substrate in the corrosion tests. Samples of dimensions 3 × 3 cm were machined for weight loss tests and 5 × 7 cm were machined for the corrosion resistance, blister, and corrosion scratch tests. Tin plates were used as substrate for the bending test, and glass plates were used for the adhesion and hardness tests. All the substrates were prepared according to ASTM D 1653. Paints were applied to the substrates and all tests were performed after 7 days to make sure that the paints were completely dried.

Testing and Evaluation

The formulated emulsion paints and their films were tested and evaluated according to the standards given in Table II.

RESULTS AND DISCUSSION

Two different water-based polymers, styrene/acrylic emulsion copolymer and short oil urethane alkyd resin, were used as binders to prepare water-based, environmentally friendly paints using 0.5% emulsified methylamine adduct as corrosion inhibitor. The choice of the above-mentioned two binders was based on the fact that styrene/acrylic emulsion copolymer is a nonconvertible binder, whereas short oil urethane alkyd resin is a convertible binder. The methylamine adduct was prepared by reacting epoxidized soybean oil with methylamine which has been emulsified[18] and added to different emulsion paint formulations to study its effect as corrosion inhibitor for carbon steel.

Paint Formulation

The basic formula, given in Table III, is considered blank. It does not contain any of the prepared inhibitors or any type of anticorrosive pigments. Titanium dioxide and talc were used as inert pigment and extender, respectively. At first, styrene/acrylic emulsion copolymer was used. The pigment/binder ratio was 1.31 by mass. The solid content of the blank was 57.9%. Second, styrene/acrylic emulsion copolymer was replaced by water-soluble short oil urethane alkyd to study the effect of different binders on the efficiency of the added methyl amine adduct. In addition, a comparison was carried out between the prepared emulsion paints containing the optimum amine adduct concentration (0.5% by mass) and a commercial product under the trade name Hydro-Corrostabil FRD No. 90, which is a product of Brifa Maling Co., Denmark.

Physical, Chemical, Mechanical, and Corrosion Test Results

The physical, chemical, and mechanical properties for the paint formulation under investigation are summarized in Table IV. As can be seen from this table, all the emulsion paint formulations possess good adhesion, hardness, and ductility. The emulsion paint film containing styrene/acrylic emulsion copolymer had the highest hardness values, whereas the Brifa sample (a commer-

Table III Blank Formulation Based on Styrene/Acrylic Emulsion Copolymer

High-Speed Stirring		Low-Speed Stirring	
Composition	Weight (g)	Composition	Weight (g)
Water	10.0	Styrene/acrylic *or* short oil alkyd resin	22.09
Wetting agent	0.2	Plasticizer (DBP)	1.0
Dispersing agent	0.3	Terpentine	1.2
Etylene glycol	2.0	Leveling agent	0.6
TiO_2	16.0	Aliphatic amine inhibitor (g)	—
Talc	13	Water	31.11
Total pigment	29.0	Defoamer	0.5
Defoamer	0.2	Thickener	0.5
Pigment : Binder	1.31	Biocide	0.3
		Ethanol amine	1.0

Note. The actual added weight of styrene/acrylic is 47 g, where its solid content 47%. 22.09 represents the 100% solid mass of styrene/acrylic copolymer, while the actual added weight of short oil urethane alkyd emulsion polymer is 50.21 g, where its solid content 44%. 22.09 represents the 100% solid mass of short oil alkyd resin.

cial paint used for comparison) was the most viscous. With respect to the chemical (acid/alkali)-resistance tests, it was found that all of the paint films passed the acid and alkali resistance tests successfully.

With respect to the corrosion tests, it was observed that the steel surface under the paint films of the blanks was highly tarnished after immersion in artificial seawater for 28 days, indicating that corrosion was severe and the paint films

Table IV Effect of Different Binders on the Physical, Mechanical, Chemical Resistance of Paints, and on the Efficiency of Methyl Amine Adduct as Corrosion Inhibitor

	Styrene/Acrylic-Based Emulsion Paint		Short Oil Alkyd Based Emulsion Paint		
Adduct Conc. (g/100 g)	Blank	0.5 g	Blank	0.5 g	Brifa Sample
Viscosity					
KU	83.1	82.2	81.5	79.7	90.0
cP	820	811	804	788	888
Adhesion[a]	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness[b]	2H	H	H	H	2H
Ductility	6.6	6.9	6.9	7.0	6.6
Bending (0.9 mm)	pass	pass	pass	pass	pass
Acid/alkali resistance	V.g.	V.g.	V.g.	V.g.	V.g.
Water resistance	V.g.	V.g.	V.g.	V.g.	V.g.
Corrosion resistance[c]	h.t.	b	h.t.	b	b.
Degree of blistering[d]	4D	10	2D	10	10
Corrosion scratch tests[e]	F	A	F	A	A

[a] The adhesion of the dry films decreases in the following descending order: Gt0 > Gt1 > Gt2 > Gt3 > Gt4.

[b] Lead pencils supplied with the unit, softest to hardest, are as follows: 6B, 5B, 4B, 3B, 2B, B, HB, H, 2H, 3H, 4H, 5H, 6H.

[c] b, bright surface; v.s.t., very slight tarnishing; s.t, slight tarnishing; m.t., medium tarnishing; h.t., high tarnishing; h.t.p., high tarnishing and pitting.

[d] Graded on a scale from 10 to 0, where 10 is no blistering and 0 is largest blister and frequency denoted by F, M, MD, and D (few, medium, medium dense, and dense).

[e] A–E, corrosion just in the scratch but differ in the adhesion of the film around the scratch; A, the best adhesion, F, bad adhesion; and F^0, bad adhesion with pitting corrosion.

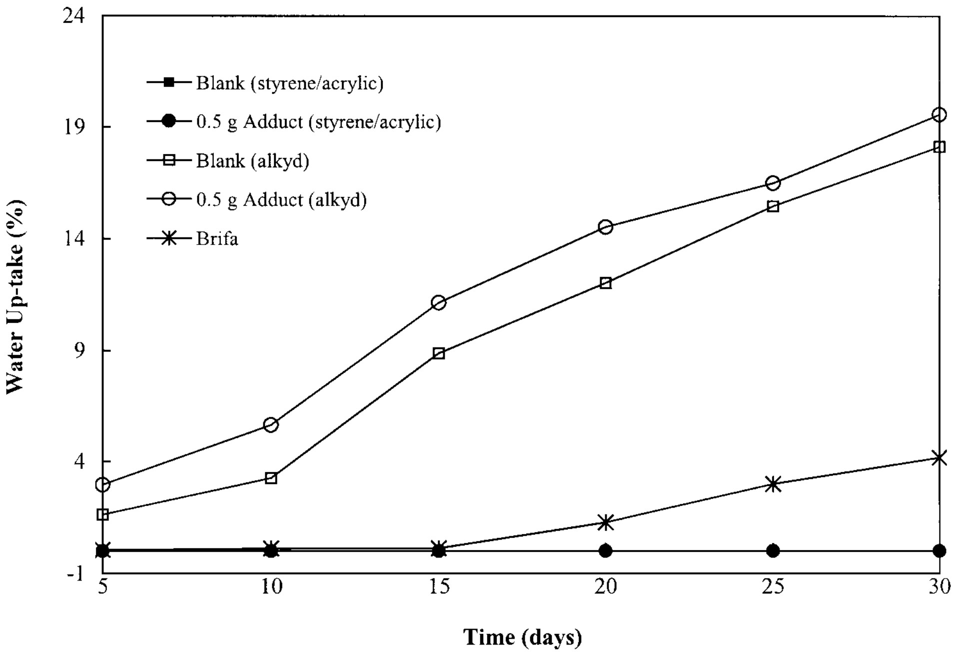

Figure 1 Effect of different polymers on water uptake of the paint.

could not protect the steel surface against corrosion. On the other hand, the steel surface under the paint films containing emulsified methylamine adduct were found to still be bright after the same period of immersion in seawater. This means that the lone pair of electrons of the emulsified methylamine adduct succeeded in making coordinate bonds with the steel surface, compensating the electron deficiency on its surface, at the same time the adduct spread directly on the steel surface as a uniform thin film protecting it against corrosion. This also may explain why the paint film around the scratch (corrosion scratch test) has an adhesion of grade A. This phenomenon can be extended to the degree of blistering on the surface of the paint films. It is also valuable to mention that the obtained results are comparable with those for the commercial one tested.

Water Uptake Results

Water uptake measurements up to 35 days for all paint formulations can be seen in Figure 1. Figure 1 shows that the water uptake of the films containing styrene/acrylic copolymer as binder is almost nil. This is true for the blank as well as for those containing emulsified methylamine adduct. This may be attributed to the chemical composition of the mentioned copolymer, as it does not contain any hydrophilic group in its main structure. On the other hand, the water uptake of the films containing short oil urethane alkyd resin, with and without methylamine adduct, increases with the immersion period; it reached about 19% of the original mass of the paint film after immersion for 30 days in artificial seawater. This phenomenon can be attributed to the presence of the polar (OH) groups in the main chain of the short oil alkyd resin and the nitrogen atom of the urethane group (—NH—COOR).

Weight Loss Results

The weight loss measurements of steel panels under the paint films coated with the paints containing styrene/acrylic emulsion copolymer and short oil urethane alkyd emulsion polymer, as well as the Brifa sample, after immersion in artificial sea water for 60 days are shown in Figure 2. It can be seen from this figure that carbon steel under the blank formulations showed the highest values of weight loss over all the immersion period (60 days) as predicted. The weight loss of the steel panels coated by paint films containing short oil urethane alkyd resin as binder was always less than those coated with paint films using styrene/acrylic copolymer binder, even in the absence of methyl amine adduct. Thus, the protective properties of these two binders decrease in the following descending order: short oil urethane alkyd

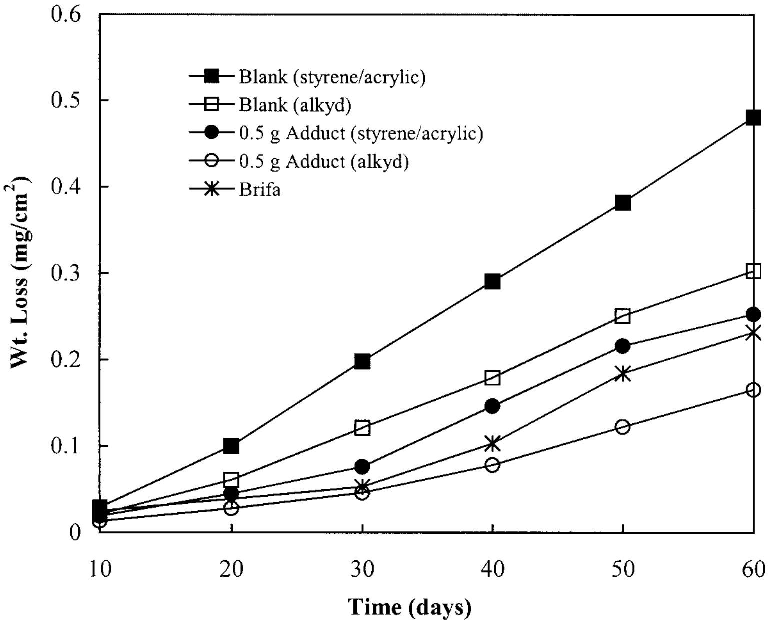

Figure 2 Effect of different polymers on weight loss of the coated metal substrates.

emulsion polymer > styrene/acrylic emulsion copolymer. This is may be attributed to the large number of nitrogen atoms in the urethane groups, contained in the main chain of short alkyd resin, which may increase the coordination with the steel surface inhibiting the arrival the corrosive groups to the steel substrate.

Mechanism of Corrosion Inhibition

Examination of the performance of the two polymers used reveals that although the paint films, containing styrene/acrylic copolymer as binder, have the lowest water-uptake values, the steel under them experienced more weight loss than those under paint films containing short oil urethane alkyd resin, which has the highest water uptake. Thus, the films prepared from styrene/acrylic copolymer provide low corrosion protection. Styrene/acrylic copolymer paint films adhere physically to the steel substrates. This allows the corroding groups to penetrate underneath the paint film, although the film itself does not absorb water. Short oil urethane alkyd resin, on the other hand, has a large number of nitrogen atoms containing lone pairs of electrons. This makes their films absorb water more than those films prepared from styrene/acrylic copolymer, which does not contain any polar group. However, the lone pair of electrons of the nitrogen atom of the short oil urethane alkyd resin can create strong coordination with the steel substrate. This compensates for some of the electron deficiency on the steel substrate, which inhibits the corrosion process on the surface under the paint films formulated from the short oil urethane alkyd resin.

CONCLUSION

Highly efficient anticorrosive, water-based, environmentally friendly paints using styrene/acrylic emulsion copolymer or short oil alkyd water-soluble polymer were prepared with 0.5% methylamine adduct as corrosion inhibitor. These paints are free from any heavy metals or volatile organic compounds. It was found that the protective properties of short oil urethane alkyd water-soluble polymer are higher than that of styrene/acrylic emulsion copolymer. It was also found that these paints can compete successfully with commercially available coatings.

This work was sponsored by the U.S.–Egypt Science and Technology Joint Project. The U.S. funding was provided by the USDA.

REFERENCES

1. Buckley, W. O.; Marianne, K.; Paint Ink Intl 1998, Federation of Societies for Coatings Technology, Jan/Feb, 12.

2. Funke, W. J Coatings Technol 1986, 58, 79.
3. Maitland, C. C.; Mayne, J. E. O. Official Dig 1962, Sep, 972.
4. Parks, J.; Leidheiser, H., Jr. Ind Eng Chem Prod Res Dev 1986, 25, 1.
5. Scully, J. R. J Electrochem Soc 1989, 136, 979.
6. Bellucci, F.; Khamis, E.; Nagarkar, P. V.; Searson, P. C.; Schussler, A.; Seturia, S. D.; Latanision, R. M. Corrosion Engineering in the Packaging of Electronic, Magnetic and Optical Devices; Proceeding of the International Symposium on Corrosion Science and Engineering; Vol. II; Federation of Societies for Coatings Technology, 1989, p 491.
7. Funke, W.; Haagen, H. Ind Eng Chem Prod Res Dev 1978, 17, 50.
8. Cheever, G. D. J Coatings Technol 1989, 60, 61.
9. Ryntz, R. A.; Jones, W. R.; Czarnecki, A. J Coatings Technol 1992, 64, 29.
10. Brasher, D. M.; Nurse, T. J. J Appl Chem 1954, 4, 96.
11. Van Westing, E.; Ferrari, G. M.; de Wit, J. H. Proceedings of the 2nd International Symposium on Electrochemical Impedance Specifications; 1992.
12. Pangelinan, A. B.; Rhodes, P. R. Annual Meeting of the Societies for Coatings Technology; Federation of Societies for Coatings Technology, Atlanta, GA, Oct. 27–29, 1993.
13. Pekcan, O.; Canpolat, M.; Gocmen, A. Eur Polym J 1993, 29, 115.
14. Fernando, R. H. Prog Org Coat 1991, 19, 359.
15. Daniels, E. S.; Klein, A. Prog Org Coat 1991, 19, 359.
16. Chen, Y. C.; Dimonie, V.; El-Asser, M. S. J Appl Polym Sci 1992, 45, 487.
17. Winnik, M. A.; Wany, Y.; Haley, F. J Coat Technol 1992, 64, 51.
18. Razik, H. M. A. Ph.D. Thesis, Cairo University, Faculty of Science, 1998.
19. Ash, M.; Ash, I. A Formulary of Paints and Other Coatings; Vol. 1, George Godwin Ltd.: London, 1978.
20. Gardner, H. A.; Sward, G. G. Anniversary Catalog, 13th ed.; Paul N. Gardner Co., 1964; p 516.
21. Gardner, H. A.; Sward, G. G. Anniversary Catalog, 13th ed.; Paul N. Gardner Co., 1964; p 636.
22. Warmwell, F. J. Iron Steel Inst 1948, 160, 250.
23. Modular Training Manual; Selection and Industrial Training Administration, Ltd.: London, 1971, Vol. IIIa, pp 267–276.
24. Funke, W. J. Oil Color Chem Assoc 1967, 50, 942.
25. Abou-Khalil, M. A. Ph.D. Thesis, Cairo University, Faculty of Science, 1972.