Eco-Friendly Zero VOC Anticorrosive Paints for Steel Protection

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ABSTRACT: With the growth of the green movement, it is important to prepare environmentally friendly anticorrosive paints to save lot of money, which are lost each year because of corrosion. High molecular weight organic corrosion inhibitor (safe adduct), barrier anticorrosive pigment (safe) and convertible anticorrosive pigment (toxic) are protective elements in paint formulations. Emulsification of the prepared adduct was the way to be applicable in water-borne paints, using mixture of emulsifiers. Surface tension measurements using ring method technique and thermal stability test could characterize the prepared emulsion systems. It was interesting to study the performance of the protective elements in water paint formulations based on short oil water thinned alkyd. Physical and mechanical properties of dry paint films, corrosion tests of the coated steel, water up-take% of the prepared paints, weight loss of steel under paint films after immersion in artificial sea water and corrosion inhibition efficiency of the protective elements were determined. Comparative studies of the protective elements in water-borne paints have been done according to performance, economic feasibility and environmental safety. It was found that zinc chromate as carcinogenic anticorrosive pigment could be replaced by 0.09% of the prepared water-borne corrosion inhibitor (MTDT adduct), 20% micaceous iron oxide (MIO) or their blend. Superior corrosion inhibition efficiency of steel was obtained in case of using MTDT/MIO blend. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1790–1795, 2012

Key words: surfactants; coatings; blends; adhesion; barrier

INTRODUCTION

Corrosion inhibition elements (protective elements) are substances, which lower the corrosion rate after they have been added to a given system, which is presumed to be working under a set of corrosive conditions.[1] These elements may be inorganic pigments as micaceous iron oxide (MIO), which acts as barrier anticorrosive pigment due to its lamellar structure. The action of MIO is purely physical. It provides coatings with high resistance to weathering and atmosphere.[2–4] Chromate forms a protective layer with metal oxides and has passivation effects because of its high oxidation potential. The chemical activity of Zinc chromate is based on the fact that they set a basic pH.[2] The most important inhibitive chromate pigments are the metals of hexavalent chromium such as zinc chromate (zinc tetraoxychromate). Unfortunately hexavalent chromium is toxic and an established human carcinogen.[2,5] It is irritating to eyes, skin, and mucous membranes. Chronic exposure to chromium (VI) compounds can cause permanent eye injury.[6]

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Also corrosion inhibition elements may be organic corrosion inhibitors.[7–14] In this work the organic corrosion inhibitor is a prepared high molecular weight heterocyclic thiol compound containing both nitrogen and sulfur. This kind of corrosion inhibitor has particular interest because of its best inhibition efficiency compared with those containing N or S alone.[1,15–18] Organic corrosion inhibitors have other benefits besides combating rust. They are not toxic. They are applied easily. And that means, they are more worker friendly, safer for the environment, and will help control hazardous material costs, disposal, and handling.

With increasing environmental regulations, water-borne coatings can replace solvent-based coatings with more than 60% of the total volume of coatings produced globally and are projected to grow with annual rate of 5–7% through the next years.[19,20] Protective water-borne paints can be used successfully to protect steel in conjunction with nontoxic chemical inhibition with different emulsion polymers.[21,22]

In choosing the extender pigments and adjusting pigment volume concentration, good results are often obtained if a combination of particle size, shape, low oil, and water absorption are employed, which may improve barrier protection.[23] Typical pigments used include calcium metasilicate, barium sulfate, talc, MIO, and mica.[24]

MATERIALS AND METHODS

Materials

Polyoxyethylene sorbitan monolaurate, HLB 16.7 and sorbitan monolaurate, HLB 8.6 were delivered from Sigma-Aldrich, Germany; Epoxidized soybean oil, oxirane content 6.5% was delivered from Hobum Company, Germany; 5-methyl-1,3,4-thiadiazole-2-thiol (MTDT) was delivered from Sigma-Aldrich, Mwt 167.25 and m.p. 179°C, Germany; short oil alkyd based on linoleic acid rich oils was delivered from DSM Company, Netherland, oil length 25% and solid content 44%; Drier (Dapro 7007), Daniel Products Company, USA; Talc, 60–63% silica, 30–32% magnesium oxide, <1.0% iron oxide, <1.5% calcium oxide and <1.5% aluminum oxide, El- Nasr Phosphate Company, Cairo; titanium dioxide (Rutile R-902), 91% titanium dioxide, 4.5% aluminum oxide, 2% silicon oxide, and 2% additives, Du-Pont Company; MIO, steel gray color, density 4.5 gm/mL, oil absorption 12 g/100 g, Tongling Zhirun Mica Pigment, China; zinc chromate, yellow color, 17% as CrO_3, density 3.8 g/mL, oil absorption 40 g/100 g, Tianjin Jifa Pigments, China; butyl glycol, Fast-evaporation coalescing agent, DOW Company, USA; dispersing and wetting agent, Münzing Chemie, Germany; flash rust inhibitor, Fluka Company, Germany; thickening agent, Münzing Chemie, Germany; Biocide, Troy Chemie GmbH, Germany. The used steel is mild steel alloy. Its chemical composition is 0.08% C, 0.35% Mn, 0.014% P, 0.018% S, 0.17% Si and the rest is Fe.

Methods and experimental

MTDT adduct was prepared by reaction of 1 : 4 of epoxidized soybean oil: thiol, in sealed ampoule and at 190°C for 6 h. The structure and molecular weight of the prepared adduct were confirmed by infra-red spectroscopy (IR) and gel permeation chromatography (GPC), respectively.[14,15] Zero VOC water-borne adduct was prepared by dissolving 20 g MTDT adduct in different concentrations (5–15 g) of sorbitan monolaurate in the dispersed phase. The mixture was added drop by drop to continuous phase of (0.5–5%) polyoxyethylene sorbitan monolaurate in distilled water during high speed stirring, 5000 round per minute (r.p.m.).

Surface tension of the prepared emulsified adduct was measured using ring method technique according to ASTM D 1331-89 (2001). The interfacial tensiometer is calibrated with double distilled water (interface tension at 20°C = 72.6 mN/m). The interfacial tension σ is expressed by $k/4\pi r$, where k is the force necessary to withdraw the ring against interfacial tension, and r corresponds to the average value of outer and inner ring diameter.

The stability of the prepared emulsion was determined thermally by transferring constant volume of the prepared emulsion to test tube. The increasing of 10°C in the temperature of the prepared emulsion was considered to double the rate of most reactions. Therefore, three months at 45–50°C was equivalent to one year at 20–25°C, (also one week at 45–50°C was equivalent to one month at 20–25°C) for many systems.[25]

Emulsion paint formulations[26,27] were prepared in two stages. The first stage was high speed stirring of filler, pigment, dispersing agent, and water. The second stage is low speed stirring of the emulsion polymer, water, antifoaming agent.

Steel panel surface should be cleaned first by acetone and distilled water and polished mechanically with different grades of emery paper.[28] The wet paint was applied on metal or glass panels using film applicator, 100 μm according to ASTM D 823-07.

A measurement of paint film hardness was carried out using pencil hardness tester according to ASTM D 3363-05. After drying of paint film, the coated panels were bent over cylindrical mandrels of diameter 6 mm according to ASTM D522-08.

A representative sample of artificial sea water was prepared[29] by dissolving sodium chloride 27.26 g, magnesium chloride 3.51 g, magnesium sulfate 1.84 g, potassium chloride 0.69 g, sodium bicarbonate 0.11 g, potassium chloride 0.09 g, and calcium sulfate 1.29 g in 1 L of distilled water.

According to ASTM D 1654-08 corrosion resistance and scratch tests were done where, 5 cm × 7 cm of dry coated steel panels were exposed to artificial sea water up to 28 days. At the end of test time, they were washed in distilled water and dried. Rating of Failure at both scribed specimens and unscribed areas was evaluated.

Photos were picked up at the end of corrosion test (28 days). Photographic reference standards were used to evaluate the degree of blistering according to ASTM D 714-09. Alkali and acid resistance tests were done according to DIN 53168.

Determination of water up-take[30] was done, using 3 cm × 3 cm painted, thin plastic panels. The panels were removed from the water at intervals of 5, 10, 15, 20, 25, and 30 days. The percentage of water up-take was then plotted against time.

Weight loss measurements were done according to ASTM D 2688-05 where, steel panels of area 3 cm × 3 cm were weighted before coating. The dry coated panels were immersed in a chamber containing artificial seawater. The specimens were successively removed after intervals of 10, 20, 30, 40, 50, and 60 days. The panels were reweighed after removing the paint film and corrosion products on the surface of the metal. The weight loss values were calculated in mg/cm^2.

RESULTS AND DISCUSSION

In this work four different anticorrosive water-borne paints (P2, P3, P4, P5) were prepared to reduce the corrosion of steel in addition to blank (control) water-borne paint formula (P1) free from protective elements. Prepared organic corrosion inhibitor with zero volatile organic compound (zero voc emulsified MTDT adduct) and two kinds of anticorrosive pigments (zinc chromate and MIO) were the protective elements in this work, in addition to blank formula which based on water thinned short oil alkyd (convertible polymer). Blend of both MIO and organic corrosion inhibitor were incorporated in water-borne paint formula. Comparative studies have been done according to performance, economical feasibility and environmental safety of the prepared anticorrosive paints containing protective elements.

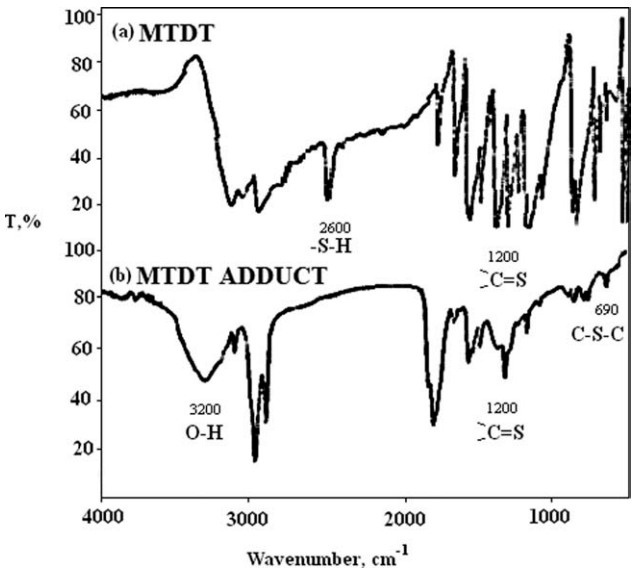

Figure 1 IR chart of (a) MTDT & (b) MTDT ADDUCT.

Preparation of zero VOC water-borne organic corrosion inhibitor

The reaction of MTDT with epoxidized soybean oil (Ep-So) was carried out at temperature 190°C and for 6 h in sealed glass ampoule. The prepared adduct was confirmed by infra-red spectroscopy , where the thiol band at 2600 cm^{-1} disappeared and a new band at 3200 cm^{-1} of the hydroxyl group was appeared, which is very characteristic of the prepared adduct as shown in Figure 1. Also chromatography technique (GPC) showed increase of molecular weight, with $M_{w1} = 1740$, $M_{n1} = 446$, $PDI_1 = 3.9$ of MTDT adduct comparing to Ep-So with $M_{w2} = 1226$, $M_{n2} = 845$, PDI2 = 1.45 and $M_2 = 1000$ of where, M_w, M_n, PDI, and M were weight-average molecular weight, number average molecular weight, polydispersity ($PDI = M_w/M_n$) and theoretical molecular weight, respectively.[14] The prepared MTDT adduct is soluble in aromatic solvents and insoluble in water and has suitable features to be corrosion inhibitor.

The most important step in preparation of zero VOC water-borne MTDT adduct is to convert MTDT adduct into water dispersible form to be applied in water-borne paints. Many trials have been done to emulsify thiols, but unfortunately xylene was used in emulsification to decrease hydrogen bonding between viscous adducts molecules.[14] At the present work zero VOC emulsified MTDT adduct could be prepared using more than one surfactant[31,32] where, emulsification with mixture of emulsifiers resulted in more stable systems compared with those containing single emulsifier. As mentioned in methods and experimental section, many emulsion systems of MTDT adduct were prepared according to the concentrations of both polyoxyethylene sorbitan monolaurate, in the continuous phase and sorbitan monolaurate in the dispersed phase. Finally 5% of polyoxyethylene sorbitan monolaurate, HLB 16.7 in the continuous phase and 15 g of sorbitan monolaurate, HLB 8.6/20 g MTDT adduct in the dispersed phase, pH $\geq$ 8, could produce stable emulsion for six months. Surface tension of the prepared emulsion was measured using Pt ring technique and it was found to be 50.2 mN/m.

Anticorrosive water-borne paints and comparative studies

Many emulsion paint formulations based on water thinned short oil alkyd with different concentrations of the emulsified MTDT adduct were prepared and examined by corrosion tests to determine the optimum concentrations range. Finally, concentrations ranging from 0.08 to 0.12 g MTDT adduct per 100 g paint formulation showed optimum corrosion inhibition of steel.

It is interesting to prepare some anticorrosive water-borne paints and to study their efficiencies. Four anticorrosive emulsion paint formulations were prepared. Blank formulas (P1) neither contained anticorrosive pigments nor emulsified MTDT adduct and based on water thinned short oil alkyd. Paint formula P2 contains 20% of zinc chromate ($ZnCrO_4$) as anticorrosive convertible pigment. Paint formula P3 has 20% of MIO as barrier anticorrosive pigment. Paint formula P4 has 0.09% of emulsified MTDT adduct as solid (within the optimum concentration range). Finally P5 contains blend of both 20% MIO and 0.09% of emulsified MTDT adduct. Ammonium benzoate was added as flash rusting inhibitor to all formulations to prevent flash rusting, which occurs in water-borne coatings due to the direct contact of water to ferrous metal surface during drying. Pigment/binder ratio of all paint formulations was 1.84

TABLE I
Anticorrosive Water-Borne Paint Formulations

Paint formula Composition, g		P1	P2	P3	P4	P5
Mill base	TiO_2	20.00	–	–	20.00	20.00
	Zn CrO_4	–	20.00	–	–	–
	MIO	–	–	20.00	–	20.00
	Talc	15.00	15.00	15.00	15.00	15.00
	Water and Additives[a]	16.00	16.00	16.00	16.00	16.00
Water thinned Alkyd (as 100% solid)		19.00	19.00	19.00	19.00	19.00
Emulsified MTDT adduct (as 100% solid)		–	–	–	0.09	0.09
Drier		0.30	0.30	0.30	0.30	0.30
Additives[a]		5.00	5.00	5.00	5.00	5.00
Water		24.70	24.70	24.70	24.61	24.61
Total weight, g		100.00	100.00	100.00	100.00	100.00

[a] Additives involve: wetting and dispersing agent, flash rust inhibitor, biocide, antifoaming agent and thickener.

and pH $\geq$ 8. The prepared paint formulations were listed in Table I.

Physical, mechanical, chemical, and corrosion measurements

The results of physical, mechanical, chemical, and corrosion tests of all paint formulations are listed in Table II (Fig. 2).

Compared with the control formula P1, higher hardness was obtained for paint formulations containing $ZnCrO_4$ (P2) and MIO (P3). Formula P4 with the prepared MTDT adduct gave the lowest hardness, while hardness was slightly increased by blending MTDT adduct with MIO in P5 formula. P1, P3, and P4 formulations resisted acid and alkali test while fading of color occurred to P2 formula which contains $ZnCrO_4$. With respect to degree of blistering and corrosion resistant tests, it was clear that $ZnCrO_4$ formula, P2 showed few blistering, corrosion just in the scribe (rating of scribed area was 7) with good adhesion, and 20% of area failure at the end of test period. P3, P4, and P5 formulations, corresponding to MIO, MTDT adduct and their blend formulations showed no blistering, corrosion was just in the scribe (rating of scribed area was 8) with good adhesion and 7–10% of area failure of uncoated steel panels. On the other hand the blank formula, P1 showed few blisters, corrosion just around the scribe with rating 6 of scribed area and 31–40% of area failure at the end of test time.

According the picked up photos of coated steel panels after 28 days of immersion in artificial sea water as shown in Figure 2, it is clear that P3, P4, and P5 formulations, with MIO, MTDT adduct and their blend could resist corrosion and replace the unfavorable toxic zinc chromate.

Water up-take% of paint films up to 30 days has intensively studied. The obtained results were plotted in Figure 3. Maximum water up-take was observed with $ZnCrO_4$ formula, P2, while MIO formula, P3 showed lower water up-take. MTDT adduct formula, P4, gave the lowest water up-take.

Weight loss of mild steel of coated panels was measured and plotted in Figure 4, which declared that, the prepared paint formulations showed corrosion inhibition of steel surface decreased weight loss of steel panels under paints films in the descending order: MTDT/MIO blend formula (P5) > MTDT formula (P4) > MIO formula (P3) > $ZnCrO_4$ formula (P2) > blank formula (P1).

Corrosion inhibition efficiency study of the anticorrosive elements

It is important to study the inhibition efficiency of the prepared anticorrosive water-borne paints

TABLE II
Physical, Mechanical, and Chemical Properties of Paint Films and Corrosion Tests Results

Paint formula Test	P1	P2	P3	P4	P5
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness	3H	4H	4H	2H	3H
Bending, 6mm diameter	Pass	Pass	Pass	Pass	Pass
Acid resistance	v.g.	F.c	v.g.	v.g.	v.g.
Alkali resistance	v.g.	F.c	v.g.	v.g.	v.g.
Water resistance	v.g.	v.g.	v.g.	v.g.	v.g.
Degree of blistering (1)	8F	6F	10	10	10
Rating of unscribed areas (2)	3	5	6	6	6
Rating of scribed areas (3)	6	7	8	8	8
Photos after 28 days immersion			Figure 2		
Water up-take			Figure 3		
Weight loss of steel during 60 days immersion			Figure 4		

1) It is graded on a scale from 10 to 0, where 10 no blistering and 0 for largest blisters and frequency denoted by F, M, MD, and D (few, medium, medium dense, and dense).

2) Rating number 3, 5, and 6 represents area failure of 31–40%, 11–20%, and 7–10%, respectively.

3) Rating number 6, 7, and 8 represents mean creepage from scribe of 2.0–3.0 mm, 1.0–2.0 mm, 0.5–1.0 mm, respectively.

Figure 2 Photos of coated steel panels after 28 days immersion in artificial sea water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containing the anticorrosive elements ($ZnCrO_4$, MIO, MTDT adduct, and MIO/ MTDT adduct).

The percentage of inhibition efficiency could be measured according to general equation[15]:

$$I\ (\%) = \{(W_o - W_i)/W_o\} \times 100$$

where, W_o : weight loss values for metal of paint films without adduct. W_i: weight loss values in the presence anticorrosive elements.

It was clear from Figure 5 that maximum corrosion inhibition efficiency of steel (76.95%) was obtained in case of formula P5 which contains MTDT adduct/MIO blend followed by MTDT adduct formula, P4 which gave high corrosion inhibition efficiency (74.61%) compared with inhibition efficiency of $ZnCrO_4$ (P2) and MIO (P3) formula, 61.84%, and 66.82%, respectively.

Comparing the three protective elements in water-borne paints formulations, it was clear that all of them could inhibit corrosion of steel by different mechanisms and to different extends. $ZnCrO_4$ could be adsorbed and converted to hydroxylated Cr_3^+ and this inhibited electron transfer reaction.[33] MIO could inhibit corrosion by purely physical mechanism due to its lamellar structure, which was responsible for decreasing permeability of paint and retarding movement of aggressive molecules to steel surface.[2] MTDT adduct could be adsorbed and formed monolayer on the steel surface via the lone pairs of electrons on the sulfur and oxygen atoms. More over the hydrophobic tail of adduct could form hydrophobic network to protect steel from water and aggressive molecules, so the adhesion of the film was improved.[15,16,34,35] Economically it was clear that MTDT adduct could protect steel with very small concentration, 0.09 g per 100 g paint formulation, so it was considered as the lowest cost protective element compared with $ZnCrO_4$ and MIO which should be added with high concentration. From environmental point of view, it was well known that $ZnCrO_4$ is carcinogenic, while MIO and MTDT adduct were friends to environment. Also MTDT adduct could be colored by any color due to its transparency, while this advantage was not found in both $ZnCrO_4$ and MIO.

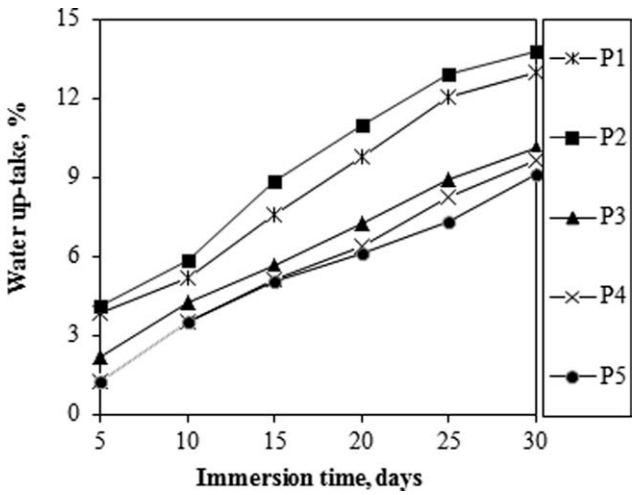

Figure 3 Water up-take (%) against time of immersion of zero VOC paints.

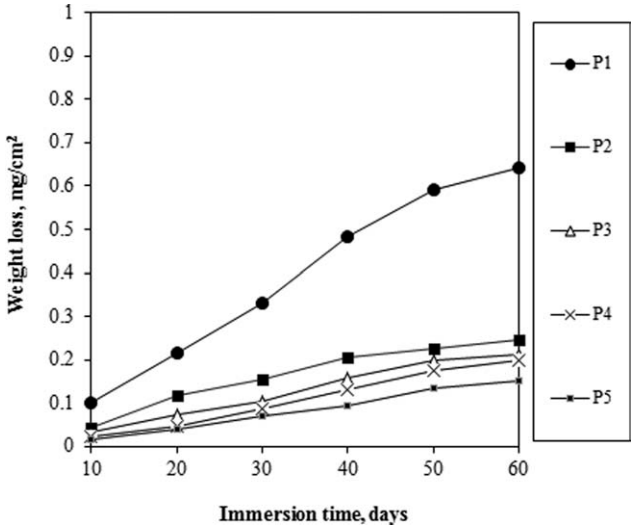

Figure 4 Weight loss of coated steel panels against immersion time.

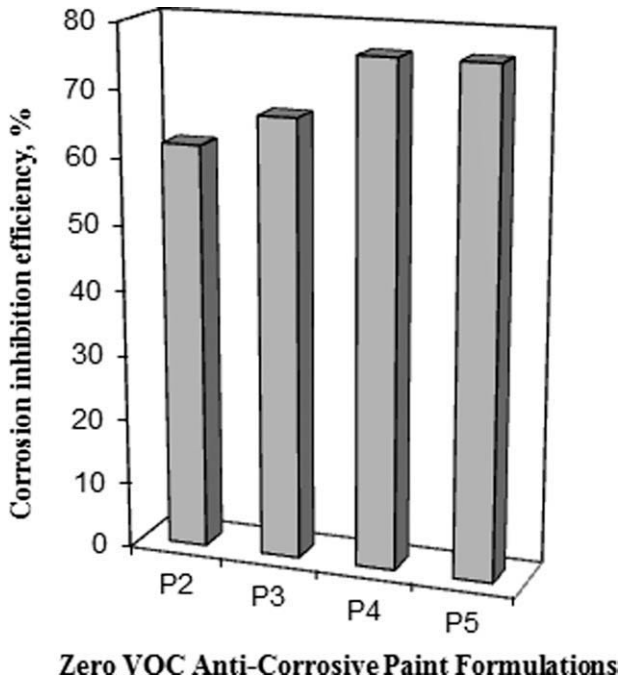

Figure 5 Corrosion inhibition efficiency (%) of anti-corrosive paint formulations.

CONCLUSION

Finally it can be concluded that:

1. Zero VOC MTDT adduct was prepared successfully and miscible with the prepared water-borne paints.
2. MIO, MTDT adduct, and their blend were considered as environmentally friendly anticorrosive elements and could replace unfavorable carcinogenic $ZnCrO_4$.
3. The prepared water-borne MTDT adduct gave excellent corrosion protection for mild steel with very small concentration, low cost, and variable colors.
4. MTDT adduct/ MIO blend showed superior corrosion inhibition efficiency of mild steel. It is safe and has excellent performance.
5. The corrosion inhibition efficiency of anticorrosive water-borne paints could be arranged in the descending order: MTDT adduct/MIO blend formula (P5) > MTDT adduct formula (P4) > MIO formula (P3) > $ZnCrO_4$ formula (P2) > control formula (P1).

References

1. Schmitt, G. Br Corros J 1984, 19, 165.
2. Brock, T.; Groteklaes, M.; Zoril, U. In European Coatings Handbook; Curt, R.; Vincentz Verlag: Hanover, 2000, p 150.
3. Giúdice, C. A.; Benítez, J. C. Anti-Corrosion Methods Mater 2000, 47, 226.
4. Liu, B.; Li, Y.; Lin, H.; Cao, C. Corros Sci 2002, 44, 2657.
5. Mahdavian, M.; Attar, M. M. Prog Org Coat 2005, 53, 191–194.
6. Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettinger, J. C.; Long, G. J.; Power, P. P. Science 2005, 310, 844.
7. Mohamed, H. A.; Badran, B. M.; Aglan, H. A. J Appl Polym Sci 2001, 80, 286.
8. Badran, B. M.; Mohamed, H. A.; Aglan, H. A. J Appl Polym Sci 2002, 85, 879.
9. Mohamed, H. A., Badran, B. M. J Appl Polym Sci 2010, 115, 174.
10. Luo, H., Guan, Y. C.; Han, K. N. J Corros 1998, 54, 721.
11. Stoyanova, A. E.; Sokolova, E. I.; Raicheva, S. N. J Corros Sci 1997, 39, 1595.
12. Beccaria, A. M.; Bertolotto, C. J Electrochem Acta 1997, 42, 1361.
13. Kertit, S.; Hammouti, B. J Appl Surface Sci 1996, 93, 59.
14. Mohamed, H. A.; Farag, A. A.; Badran, B. M. Eurasian Chemico-Technological J 2006, 8, 225.
15. Mohamed, H. A. Corros Eng Sci Technol 2010, 45, 262.
16. Quraishi, M. A.; Sharma, H. K. Mater Chem Phys 2002, 78, 18.
17. Abdennabi, A. M. S.; Abdulhadi, A. I.; Abu-Orabi, S. Anti-Corros Methods Mater 1998, 45, 103.
18. Khaled, K. F. Electrochim Acta 2003, 48, 2493.
19. Almeida, E.; Santos, D.; Uruchurtu, J. Prog Org Coat 1999, 37, 131.
20. Geurts, J.; Bouman, J.; Overbeek, A. J. Coat Technol Res 2008, 5, 57.
21. Mohamed, H. A.; Farag, A. A.; Badran, B. M. Eurasian Chemico-Technological J 2008, 10, 67.
22. Mohamed, H. A.; Badran, B. M.; Farag, A. A. J Appl Polym Sci 2010, 117, 1270.
23. Mohamed, H. A. J Coat Technol Res 2010, 7, 85.
24. Galgocci, E. C.; Weinmann, D. J.; Proc. XXII Waterborne, "High Solids and Powder Coatings Symposium 1995, 119.
25. Bennett, H.; Bishop, J. L.; Wulfinghoff M. L. Practical Emulsions; Chemical Publishing: New York, 1968, p 64.
26. Gotsis, C.; Sofokleous, K. Metallurgical Mater Transact B 1998, 29, 17.
27. Reck, E.; Wilford, J. Eur Coat J 1998, 1, 28.
28. Ivan, P. Modern Paint Coat 1998, 88, 45.
29. Bastidas, J. M.; Morcillo, M. F.; Rodríguez, J. J Coat Technol 1998, 70, 61.
30. Schwartz, M.; Kossmann, H. Eur Coat J 1998, 3, 134.
31. Ivanov, I. B.; Dimitrov, D. S. In Thin Liquid Films; Ivanov, I. B., Ed.; Marcel Dekker: New York, 1988; Chapter 7.
32. Ivanov, I. B. J Pure Appl Chem 1980, 52, 1241.
33. Buchheit, R. G.; Guan, H.; Laget, V. N. US Patent, US 7,135,075 B2, Nov. 14, 2006.
34. Bouklah, M.; Attayibat, A.; Kertit, S.; Ramdani, A.; Hammouti, B. Appl Surface Sci 2005, 242, 399.
35. Quraishi, M. A.; Jamal, D. Mater Chem Phys 2001, 71, 202.