ELSEVIER

Progress in Organic Coatings 59 (2007) 76–80

PROGRESS IN ORGANIC COATINGS

www.elsevier.com/locate/porgcoat

Anticorrosive properties of the epoxy–cardanol resin based paints

L.K. Aggarwal *, P.C. Thapliyal, S.R. Karade

Central Building Research Institute, Roorkee 247667, India

Received 22 September 2006; accepted 16 January 2007

Abstract

An epoxy–cardanol resin was developed using epichlorohydrin, bisphenol-A and cardanol. On evaluation it was found that epoxy–cardanol resin exhibits better properties as compared to epoxy resin in terms of increase in tensile strength, elongation, bond with steel and lowering of water vapour transmission of the film. The improvement in these properties indicated that the paints based on modified resin would be more durable than the epoxy based paints. Accordingly, paints were formulated using the developed resin and their performance were compared with their counterparts made with unmodified epoxy resin. Zinc powder, zinc phosphate, micaceous iron oxide and synthetic iron oxide were used as pigments along with fillers, additives and an aromatic polyamine adduct hardener. For both types of paints similar doses of pigments and additives were used. Physico-mechanical properties, chemical resistance and corrosion protection efficiency of the formulated paints were determined. It was found that the anticorrosive properties of epoxy–cardanol resin based paints are superior to that of the paints formulated with the unmodified epoxy resin. Micaceous iron oxide based paints in epoxy–cardanol resin showed the best performance followed by zinc phosphate based paints. It is concluded that the developed resin is a better binder media for the formulation of paints.

Keywords: Epoxy; Cardanol; Pigments; Paints; Permeability; Corrosion; Chemical resistance

1. Introduction

The surveys of corrosion damage in the early 1990s showed that in an industrialized country, 4% of the gross national product (GNP) is lost as a result of corrosion. This figure includes both direct and indirect costs [1]. The survey on causes of corrosion failures has shown that over 40% of the failures are due to improper selection of materials, ineffective design measures and non-use of efficient and durable protective coatings. All these causes of corrosion failure could be avoided. For this purpose newer corrosion resistant materials, better monitoring and detection techniques and technologies for repair and rehabilitation are the need of the hour. To meet these requirements, present investigations are directed towards the development of highly resistant coating system for the protection of steel structures exposed to aggressive environment.

In anti-corrosion coatings, use of epoxy resin dominates over other synthetic resins due to its superior strength, low shrinkage, better bonding with different substrates, good dimensional stability and long term corrosion and chemical resistance [2,3]. These properties have prime importance in the construction and building applications. The ambient curing epoxy systems generally consist of two components—a base component and a curing agent or hardener. The base component is epoxy resin, which is normally a standard liquid epoxy resin DGEBA, diglycidyl ether of bisphenol-A (a condensation product of bisphenol-A and epichlorohydrin). The room temperature curing agents that are generally used with epoxy resin to initiate the cross linking are polyamines, polyamides and their adducts [4,5]. One problem with the coatings made with epoxy resin is that they are rigid and have limited deformability. It does not help in stress relaxation during their service life and may fail due to cracking. To overcome this problem and to achieve other desired properties epoxy resin is often modified with different other polymeric compounds, such as coal tar [6,7], cashew nut shell liquid [8–11], phenolic and other resins [12–14].

In this study, an attempt has been made to modify an epoxy resin with a cardanol resin for improving its physical properties and chemical resistance. The modified resin was synthesized using epichlorohydrin, cardanol and bisphenol-A and designated as epoxy–cardanol resin. Properties of the two resins, epoxy–cardanol and unmodified epoxy, were evaluated by determining their physico-mechanical and chemical resistance properties. Paints were formulated using the developed

* Corresponding author. Tel.: +91 1332 283354; fax: +91 1332 272272.
E-mail address: lka_cbri@rediffmail.com (L.K. Aggarwal).

0300-9440/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2007.01.010

epoxy–cardanol and the unmodified epoxy resins with pigments, additives and aromatic polyamine adduct as a hardener. The developed paints were evaluated for their physico-mechanical properties, chemical resistance and corrosion protection efficiency.

The paper reports the outcome of the study in two parts. The first part relates to the synthesis and evaluation of the modified epoxy resin and the second deals with the formulation and evaluation of the formulated anticorrosion paints.

2. Synthesis and evaluation of resins

2.1. Synthesis of resins

A modified epoxy resin was synthesized using epichlorohydrin, bisphenol-A and cardanol as main raw materials. Glycidyl ether of cardanol was obtained by reacting epichlorohydrin and cardanol, and a prepolymer of epoxy resin DGEBA by reacting epichlorohydrin and bisphenol-A. The reactions were carried out in an inert atmosphere at about 150 °C. The two resins thus obtained were mixed in a predetermined ratio and heated at about 60 °C under controlled conditions. The resin so obtained was designated as epoxy–cardanol resin.

The epoxy equivalent weight of the epoxy–cardanol resin was 210–230, viscosity 5000–6000 mPa S at 25 °C and density 1.05 g/cm^3. The unmodified epoxy resin had an epoxy equivalent weight of 180–200, viscosity 8000–10,000 mPa S at 25 °C and density 1.15 g/cm^3. An aromatic polyamine adduct based hardener was used with these resins. This hardener had an amine value of 320–340, viscosity 3000–5000 mPa S at 25 °C and density 1.10 g/cm^3.

2.2. Preparation of test samples

Mild steel and glass panels of 150 mm × 100 mm size were used and prepared according to the method given in IS: 101 Part 1/Sec. 3: 2001 [15]. The steel panels were made free from oil and grease by cleaning them with xylene and then brushed uniformly with an emery cloth of IS Grit No. 180. Traces of emery dust were removed by wiping with a linen rag and swapped with a linen rag pre-soaked in a hydrocarbon solvent to degrease the panels. Then the panels were dried to remove the traces of condensed moisture. The glass panels were degreased and dried in a similar way. Two coats of each resin were applied on the thoroughly cleaned steel and glass panels using a paintbrush. The coated panels were left in the laboratory for 7 days to ensure full drying and curing of the films. The edges of the steel panels were then sealed with wax to prevent attack from the edges. At least three steel panels were prepared for each chemical resistance and humidity cabinet test. To obtain free film properties, the films were carefully removed from the coated glass panels.

2.3. Testing of the coatings

Free film properties of the coatings, such as tensile strength, elongation and water vapour transmission were measured as per ASTM-D-2370-1992 [16] and ASTM-D-1653-1993 [17]. Bond strength was measured by the pull out method as per BS: 3900-E-10-1979 [18] using a Dyna Proceq adhesion tester, while scratch hardness and adhesion and flexibility were determined using the coated steel panels according to the method given in IS: 101 Part 5/Secs. 1 and 2: 1988 [19].

Table 1
Properties of the epoxy and the epoxy–cardanol coatings

Property	Epoxy–cardanol	Epoxy
Tensile strength (N/mm^2)	21.5	16.4
Elongation (%)	16.5	7.2
Specific permeability (mg/(cm^2 mm 24 h))	0.140	0.214
Hardness, Shore D	83.0	85.0
Shear strength (N/mm^2)	7.70	5.86
Vicat softening point (°C)	64.0	43.0
Adhesion (bond strength) with steel (N/mm^2)	3.2	2.5
Scratch hardness, 1500 g load	No failure	No failure
Coefficient of thermal expansion (10^{-6} per °C)	8.8	17.1
Scrub resistance, 10,000 cycles	No failure	No failure
Salt spray, 1000 h	No corrosion spots	Few corrosion spots

2.4. Results

Results of the above studies show that the modification of the traditional epoxy resin with a cardanol resin improves properties of the film. For example, tensile strength and elongation are increased while water vapour transmission decreased (Table 1). The coefficient of thermal expansion became comparable with that of the concrete, which is 6.1×10^{-6} to 12.2×10^{-6} per °C [20]. These results indicate that the coating based on the modified resin would be more effective and durable as compared to the epoxy based coating. It means that the modified resin could be a better binder for paints.

3. Formulation and evaluation of paints

3.1. Formulation of paints

Paints were formulated using pigments like synthetic iron oxide, zinc phosphate (ZnP), zinc powder, micaceous iron oxide (MIO), blank fixe, calcite, magnesium silicate and titanium dioxide along with other additives and solvents. Epoxy–cardanol resin with the aromatic polyamine adduct based hardener and unmodified epoxy resin with the same hardener were used as binders. The pigment volume concentration of the paints was kept at about 25% except that of the zinc powder based paints for which it was 70%. The compositions of various paint formulations used are given in Table 2.

3.2. Preparation of the test samples

Mild steel and glass panels were prepared as discussed in Section 2.2 above. The panels thus prepared were coated with the developed paints for carrying out laboratory tests. Two coats

Table 2
Composition of the paints

Composition		Paint designation	
Pigment	PVC (%)	Epoxy–cardanol resin	Epoxy resin
Zinc powder	70	Z_1	Z_2
Zinc phosphate + iron oxide	25	Z_3	Z_4
Micaceous iron oxide	25	M_1	M_2
Micaceous iron oxide + blank fixe	25	M_3	M_4

of each paint were applied on the steel and glass panels using a paintbrush. The coated steel panels were used for determination of resistance of coatings against various exposure conditions, whilst the glass panels were used to obtain free films for different tests. The coated panels were left in laboratory for 7 days to ensure full drying and the curing of the paint films. The edges of the steel panels were sealed with wax to prevent the ingress of chemicals from the edges. At least three panels were prepared for each test. The properties like coverage, drying time and film thickness of different paints are given in Table 3.

3.3. Testing of the paints

3.3.1. Physico-mechanical properties of the paints

Physico-mechanical properties of the paints were determined following the procedure mentioned in Section 2.3.

3.3.2. Immersion test

The chemical resistance behaviour of the paints was studied by an immersion test, in which the painted steel panels were placed vertically in 3000 ml glass beakers containing different reagents such as water, 5% sodium chloride (NaCl), saturated solution of urea and di-ammonium phosphate (DAP) for 180 days. The panels were examined at regular intervals to evaluate the degree of attack on the paint films and on the substrate. For this purpose, the panels were taken out at different intervals, washed with water and visually examined for the film integrity, overall appearance and any paint failure.

Table 3
Properties of different paints

Paint system	Coverage (m^2/l)	Dry film thickness (μm)	Drying time	
			Touch dry (min)	Hard dry (h)
Z_1	4.5–5.0	85 ± 5	30	48
Z_2	4.5–5.0	85 ± 5	30	48
Z_3	5.0–5.5	85 ± 5	28	45
Z_4	5.0–5.5	85 ± 5	28	45
M_1	4.5–5.0	85 ± 5	35	55
M_2	5.0–5.5	85 ± 5	35	55
M_3	4.5–5.0	85 ± 5	34	52
M_4	5.0–5.5	85 ± 5	34	52

Table 4
Free film properties[a]

Paint sample	Tensile strength (N/mm^2)	Elongation (%)	WVT (mg/(cm^2 mm 24 h))
Z_3	16.78	18.26	0.20
Z_4	13.09	13.51	0.28
M_1	18.28	20.13	0.18
M_2	14.10	16.50	0.30
M_3	16.71	21.01	0.24
M_4	13.98	14.47	0.32

[a] All values are the mean of five observations.

3.3.3. Humidity cabinet test

The steel panels coated with different paints were kept in a corrosion cabinet maintained at about 100% relative humidity and temperature in the range of 42–48 °C as per IS: 101 Part 6/Sec. 1: 2000 [21]. Observations were recorded at regular intervals for any sign of deterioration of paint films during the 180 days of exposure. The panels were taken out of the cabinet, washed with the water and visually examined for any paint failure.

3.4. Results and discussion

The results of the tensile strength, elongation, water vapour transmission of the free films and the bond strength, scratch hardness and flexibility, and adhesion are given in Tables 4 and 5, respectively. Chemical resistance results are given in Tables 6 and 7, while the humidity cabinet test results are given in Table 8.

3.4.1. Physico-mechanical properties of the paints

Physical properties of the paints like drying time, coverage and film thickness are given in Table 3. It can be noted that the panels were coated with a similar thickness of the paints as dry film thickness of all the paints was 85 ± 5 μm. The touch dry time for different paints varied from 28 to 35 min, while hard dry time varied from 45 to 55 h. Broadly the covering capacity of the paints varies from 4.5 to 5.5 m^2/l.

Tensile strength, elongation and water vapour transmission data is given in Table 4. The tensile test data for paints Z_1 and Z_2 could not be recorded, because these paint films were very

Table 5
Properties after application on the steel substrate

Paint sample	Bond strength[a] (N/mm^2)	Adhesion and flexibility, 3.2 mm diameter mandrel	Scratch hardness, 1500 g weight
Z_1	2.32	No failure	No failure
Z_2	1.98	No failure	No failure
Z_3	2.79	No failure	No failure
Z_4	2.41	No failure	No failure
M_1	2.77	No failure	No failure
M_2	2.29	No failure	No failure
M_3	2.86	No failure	No failure
M_4	2.37	No failure	No failure

[a] All values are the mean of five observations.

Table 6
Results of the water and sodium chloride immersion tests—180 days

Paint sample	Water immersion	Sodium chloride (5%) solution immersion
Z_1	Blisters throughout the panels	Blisters through out the panels
Z_2	Blisters throughout the panels	Blisters through out and corrosion
Z_3	Small blisters (10% area)	Small blisters (15% area)
Z_4	Blisters through out and corrosion	Blisters, throughout
M_1	No signs of paint failure	No signs of paint failure
M_2	Blisters (15–20% area)	Blisters, through out the panels
M_3	Few small blisters	Few small blisters
M_4	Small blisters through out the panels	Blisters through out the panels

Table 7
Results of the urea and di-ammonium phosphate immersion tests—180 days

Paint sample	Urea solution immersion	Di-ammonium phosphate solution immersion
Z_1	Small blisters in 10% area	Blisters through out the panels
Z_2	Blisters and few corrosion spots	Small blisters through out the panels
Z_3	Few small blisters	No signs of paint failure
Z_4	Blisters in 25% area	Small blisters through out the panels
M_1	No signs of paint failure	No signs of paint failure
M_2	Small blisters in 20% area	Blisters in 50% area
M_3	No signs of paint failure	Few small blisters
M_4	Blisters in 75% area	De-bonding of film after 30 days

brittle and failed without significant elongation during the test. From Table 4 it can be noted that the tensile strength for the coatings Z_3, M_1 and M_3, which were formulated using the modified resin are in the range of 16.71–18.28 N/mm^2, while the tensile strength values for unmodified resin based paints, Z_4, M_2 and M_4 vary between 13.09 and 14.1 N/mm^2. It shows that the modified resin based paints exhibit about 25% higher tensile strength than the paints made with unmodified resin. Similarly elongation for the epoxy–cardanol resin based paints is about 15% more than that of unmodified resin based paints indicating more flexibility. The values of water vapour transmission (WVT) of modified resin based paints is about 20% lower than that of unmodified resin based paints (Table 4). The above-mentioned results show that the free film properties of modified resin based paints are superior to that of unmodified resin based paints. Furthermore, paint films based on micaceous iron oxide and zinc phosphate show the highest tensile strength and minimum water vapour transmission, so these paints should have better performance as compared to the other formulated paints.

Table 8
Results of the humidity cabinet test—180 days exposure

Paint sample	Observations
Z_1	Small blisters (25% area)
Z_2	Small blisters through out and few corrosion spots
Z_3	No signs of paint failure
Z_4	Small blisters
M_1	No signs of paint failure
M_2	Small blisters (50% area)
M_3	Small blisters (10% area)
M_4	Small blisters throughout and few corrosion spots

3.4.2. Properties of the paints after the application on the substrate

Bond strength values of different paints are given in Table 5. The bond strength of the modified resin based paints are in the range of 2.32–2.86 N/mm^2 and for epoxy resin it is in the range of 1.98–2.41 N/mm^2, i.e. the bond strength for the modified resin is about 15% higher. During the test, it was observed that the paint based on the modified resin failed cohesively (failure in the paint film) while it was adhesive bond failure (failure between the paint film and substrate) in case of unmodified resin based paint films, at relatively low stress level. Amongst the formulated paints, MIO and zinc phosphate based paints show better adhesion properties as compared to zinc powder based paints and the bond strength of MIO based paints in modified resin is the highest followed by zinc phosphate based paint (Table 5).

In adhesion and flexibility test the coated panels were subjected to bending using a mandrel of 3.2 mm diameter and the results obtained for the different paints are given in Table 5. The paint films showed no signs of damage, detachment or cracking after the test indicating good flexibility, the elongation of the paint films is about 28% as per ASTM D 522-93 [22]. Therefore, the elongation values for the attached paint film were higher as compared to the elongation of the free films of the paints, 13.51–21.01% (Table 4). All the paints pass the scratch hardness test when tested using a weight of 1500 g (Table 5) showing good abrasion resistance.

3.4.3. Chemical resistance tests

Chemical resistance test results are reported in Tables 6 and 7. In water immersion test, paint M_1 showed no sign of disintegration while M_3 and Z_3 showed few small blisters. Paints, Z_2, Z_4 and M_4 showed medium dense blisters of average size and presence of corrosion. Z_4 showed maximum corroded area of about 10%. These results show that the performance of the micaceous iron oxide based paints in modified resin is the best followed by zinc phosphate based paint in the same resin. Similar trend is observed when the painted panels were immersed in a 5% sodium chloride solution for 180 days, i.e. M_1 and M_3 paints showed the best performance followed by Z_3. Panel coated with M_1 paint is not affected while others show signs of failure of paints.

In urea and di-ammonium phosphate solution immersion tests, paint M_1 showed the best performance followed by Z_3 and M_3 paints. Other paints showed considerable blistering and/or corrosion (Table 7). In these tests also micaceous iron oxide and zinc phosphate based paints in modified resin, i.e. the paints

based on the modified epoxy resin showed superior performance. Big size blisters appeared in the paint M_4 within 15 days and the coating completely peeled off after 30 days of exposure. On the basis of the above results, it can be inferred that the performance of the modified resin based paints is superior to the unmodified epoxy resin based paints.

3.4.4. Humidity cabinet test

Results of the humidity cabinet exposure test are given in Table 8. In this test, Z_3 and M_1 paints showed the best results, as no signs of failure was observed in these paint films up to 180 days of exposure, followed by M_3 with few small blisters on the panels. Paints Z_2 and M_4 showed small blisters throughout the panels along with few corrosion spots, while Z_1 and Z_4 paints showed small blisters.

Strength and permeability of the paints film are important factors for the anticorrosive efficiency of the paints. In the present investigations paint M_1 with the highest strength and the lowest permeability amongst the formulated paints showed minimum blistering in immersion and humidity cabinet tests, i.e. the best film integrity and appearance, while the paint M_4 having the lowest strength and highest permeability showed maximum blistering. The corrosion of the substrate is minimum in M_1 and maximum in M_4, with the exception of Z_4 in the water immersion test. Hence, the anticorrosive behaviour of the paints has some relation to their strength and permeability properties.

4. Conclusions

The results of the above studies show that the modification of epoxy resin with a cardanol resin has resulted into improvement in its properties. Anticorrosive properties of the epoxy–cardanol resin based paints are superior to that of paints formulated using the unmodified epoxy resin, irrespective of the pigments, fillers and the additives used. Therefore, the developed resin is a better binder media for the formulation of anticorrosion paints than the unmodified epoxy resin. Amongst the formulated paints, paint M_1 exhibited excellent properties with respect to film integrity and overall appearance.

Acknowledgement

The authors are thankful to the Director, Central Building Research Institute, Roorkee, India for granting permission to publish the paper.

References

[1] S. Kadaria, R. Bahri, Industrial corrosion and mitigation, in: CORCON, NACE International, India Section, Mumbai, 2000, pp. iii–iv.
[2] A.C. Giudice, J.C. Benitez, Optimising the corrosion protective abilities of lamellar micaceous iron oxide containing primers, Anti-Corros. Methods Mater. 47 (4) (2000) 226.
[3] P.S. Kshirsager, R. Menon, Epoxy resins for use in construction industry, Pop. Plast. 32 (12) (1987) 27.
[4] C.A. May, Epoxy Resins—Chemistry & Technology, Marcel Dekker Inc., New York, NY, 1988, p. 465.
[5] S. Paul, Surface Coatings—Science and Technology, vol. 2, John Wiley and Sons, New York, NY, 1983, p. 3.
[6] N.S. Moss, The parameters affecting the performance of coal tar/epoxy coating, J. Oil Colour Chem. Assoc. 56 (1972) 34.
[7] S.M. Singh, Studies on tar–epoxy systems and their resistance to chemicals, Paintindia 34 (7) (1984) 23.
[8] M.K. Trivedi, P.R. Shah, Epoxy resins from cashew nut shell liquid, Paintindia 33 (10) (1983) 13.
[9] L.K. Aggarwal, IPN protective coating for enhancing the durability of concrete structures, Indian Concrete J. 70 (7) (1996) 367.
[10] L.K. Aggarwal, K.K. Asthana, R. Lakhani, Epoxy-phenolic IPN coating for concrete and reinforcing steel, Indian Concrete J. 69 (5) (1995) 269.
[11] K.K. Asthana, L.K. Aggarwal, R. Lakhani, A novel interpenetrating polymer network coating for the protection of steel reinforcement in concrete, Cement Concrete Res. 29 (10) (1999) 1541.
[12] L.K. Aggarwal, P.C. Thapliyal, S.R. Karade, Anti corrosive paints for the protection of steel structures, in: International Conference on Corrosion (CORCON 2004), NACE, New Delhi, December 2–4, 2004, pp. 1–11 (Paper No. 101).
[13] N.S. Pradhan, Paints for ships, Paintindia 56 (5) (2006) 91.
[14] E.P. De Silva, E.A. Alvarenga, Castro MMR & Lins VFC. Atmospheric corrosion of materials used in the civil construction industry, Anti-Corros. Methods Mater. 53 (1) (2006) 43.
[15] IS: 101, Indian standard for sampling & test for paints, varnishes and related products, Part 1, Test on liquid paints, Sec. 3, Preparation of panels, 2001, p. 1.
[16] ASTM-D 2370, Standard test method for elongation and tensile strength of free films of paint, varnish, lacquer and related products with tensile testing properties, 1973, p. 472.
[17] ASTM-D 1653, Method of test for moisture vapor permeability of organic coating films, 1993.
[18] BS-3900, British standard methods of test for paints, E-10, Pull off test for adhesion, 1979, p. 1.
[19] IS: 101, Indian standard methods of sampling and test for paints, varnishes and related products, Part 5, Mechanical test on paints films, Sec. 1, Hardness test, 1988, p. 1.
[20] A.M. Neville, Properties of Concrete, 4th ed., Longman, London, 1995.
[21] IS: 101, Indian standard method of sampling and test for paints, varnishes and related products, Part 6, Durability tests, Sec. 1, Resistance to humidity under conditions of condensation, 2000, p. 1.
[22] ASTM D 522, Standard test methods for Mandrel Bend test of attached organic coatings, 1993, p. 420.