A NEW EPOXY RESIN BASED EMULSION PRIMER

E. V. Shynkarova and V. D. Koshevar

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Metal structures are easily destroyed under the environmental influence. A new protective material, an anticorrosive primer based on an emulsion resin ED-20 dispersed in water has been developed and tested.

* Corresponding Authors
Fax: 8017 284 27 34
E-Mail: schinkarova@igic.bas-net.by
[a] Institute of General and Inorganic Chemistry, National Academy of Sciences of Belarus, Republic of Belarus, Surganova Street, 9/1, Minsk, 220072.

Introduction

Epoxy resins- the most important film-forming materials for paints and varnishes – are widely used for corrosion protection because of their unique properties which are: high adhesion of epoxy coatings (PC) to the most of construction materials, good physical and mechanical properties, low shrinkage during curing and resistance to hydrolysis due to absence of easily saponifiable group in their molecules. In addition, liquid epoxy resins have low toxicity and relatively low energy consumption is needed to emulsify them in an aqueous medium.

The epoxy resin based compositions are the most promising and environmentally friendly for coatings.[1] Further, the developments in the production of epoxy resins and their use for coatings comply with both ecological (Directive 2004/42/EC of the European Parliament) and the economical considerations.

Recently, a number of companies including Russians are engaged in manufacturing the industrial coatings based on various resins (alkyd, epoxy, polyurethane) emulsified in water.[2,3] Benefits of coatings formed from aqueous emulsions of epoxy: excellent resistance to corrosion, high adhesion to various surfaces.

The technologies for developing industrial resin (epoxy, alkyd, polyurethane) emulsions is getting attention in the Republic of Belarus because allnecessary conditions such as raw materials, equipment and the market are easily available. JSC "Lakokraska" (Lida) now manufactures the equipment for emulsification of resins. One of the limiting factors for the application of aqueous emulsions of resins in Belarus is the lack of domestic development of coatings based on it.

The purpose of this study is to report on import replacement of protective material in an epoxy emulsion primer which protects the metal from corrosion.

Experiments

In developing highly corrosion reistant primer one has to ensure high protective properties and environmental safety. The pigment based on a mixture ferrite of calcium and zinc obtained from the galvanic waste from Belarusian enterprises is environmentally friendly.

There are two components of the primer which are mixed immediately prior to use. One part includes an anticorrosive pigment, filler, processing aids (wetting agent, defoamer, corrosion inhibitor, thickener) and hardener. This part of the primer was prepared by grinding the componentson a bead mill at a shaft speed 1200 min^{-1} for 1 h

The second part is a 60 % emulsion of epoxy resin obtained by the direct emulsification of the epoxy resin.[4] The epoxy resin ED-20 consisting of 21.3 % of epoxy groups with epoxy equivalent weight equal to 202 g $equiv^{-1}$ is used. The emulsifier (GOST 10587-84), surface-active substance Emulsogen LCN-287, and polymer microparticles were used for stabilizer . The emulsion was prepared by NDG-10 disperser with a peripheral speed of 20 m s^{-1}. Physical and technological characteristics of the epoxy emulsion are shown in Table. 1.

It should be noted that epoxy emulsion can only be used in coatings with special hardeners, which in most cases is the aqueous amine-containing composition. The chemical composition and structure of the hardener affects the properties of the coatings.

Early it was found[5] that the optimum cross-linking agent for this system is aminoadduktovy water-based hardener Epilink 701 (Netherlands), whose properties are shown in Table. 2.

Table 1. Physical and technical characteristics of the epoxy emulsion

Appearance	milky-white liquid
Dry residue	56.0±1 %
Dynamic viscosity at 20 ° C	0.8 Pa s
pH	7.5
Droplet size, microns	0.1-7

Table 2. Physico-chemical properties of hardener

Appearance	White emulsion
Dynamical viscosity at 25 ° C	5-10 mPa s
Amine value	130-165 mg KOH/g
Hydrogen equlvalent	250-350 g/mol

Before applying the primer its two parts are mixed together. The primer is applied by spraying on the steel. Metal samples were degreased with white spirit. Coatings cured at a temperature (20±2)º C "cold cure" for 2, 5, 7, 10 days. and (80±2)ºC "hot set" for 1 and 2 hours.

The following technical and technological properties of primers and coatings were studied:

Dynamical viscosity was measured by a VZ-246 viscosimeter with a nozzle diameter of 4 mm at temperature of 20±2 °C according to the GOST 8420 standard; Mass fraction of non-volatile substances at 105±2°C according to the GOST 17537 standard; Hardness of the coating according to the GOST 5233 standard; Adhesion by method of parallel cuts in accordance with GOST 15140 standard; Thickness of dry coating layer was determined by the GOST 6-10-403-77 standard; Resistance to static exposure of 20 % and a 3% solution of sodium chloride, water and engine oil in accordance with GOST 9.403; Impact strength of the coating according to GOST 4765-73.

Appearance of the coating after tests carried out in hostile environments was evaluated according to GOST 9.407 standard. Kinetics of curing was studied of coatings to modify the content gel fractions (insoluble fraction after crosslinking). Gel content was determined by extracting the soluble fraction of acetone in a Soxhlet apparatus for 24 hours.

Results and Discussion

The volume content of each component determines certain properties of the coating. Thus, for example, coatings of fillers or pigments in the coating characterize a pigment volume concentration (*PVC*) above which the quality of the coating deteriorates.[6]

PVC is given by:

$$PVC = \frac{\sum\left(\frac{m_p}{\rho_p}\right)_i}{\sum\left(\frac{m_p}{\rho_p}\right)_i + \sum\left(\frac{m_b}{\rho_b}\right)K}$$

where

m_p, m_b– weight, respectively, pigment and binder;

i – the amount of excipients;

ρ_p, ρ_b -the densities, respectively, of pigment and binder;

K – constant (dry residue of a binder).

We calculated the PVC of the primer on the above formula. The calculation is made of the ratio of 100 wt. parts hardener. The optimum composition was proved to be 38 %.

The kinetics of curing primer coatings have shown that there is slow growth of gel fraction in the "cold curing". The quantity of the insoluble fraction after 2 days crosslinking is 80 % after 5 days 87 % and after 7-10 days it is 94 %. The insoluble fraction after curing at 80 º C for 1.2 h is 96 %. It can be assumed that the gelation process is largely completed in "hot" curing PC for 1-2 hours..

The data obtained are in good agreement with the results of measuring the hardness of the investigated coatings. Hardness of the coating cured at (20±2)°C for 2 days equalled to 13 rel. units, the solidification is significantly increased with increasing cure . The greatest hardness acquired after curing for 7-10 days is *H*=0.3 rel. units. As a result of the "hot" curing of coatings, the hardness reached 0.5 rel. u

Key performance primers and coatings based on it are shown in Table. 3.

Table 3. Properties of epoxy primer and coatings based on it

Data	Values
Volume solids,%	50
Working viscosity VZ-4 primer, sec	25-30
Opacity, g m^{-2}	72
Drying time to degree 3 (20±2)ºC, h	3
Viability after mixing at temperatures (20±2)ºC, h, not less	1
Coating thickness, micron	
monolayer	30
two-layer	60
The time prior to application of subsequent layers at a temperature of (20±2)ºC, day	1
Color coating	brown
Adhesion of the coating to the substrate, pts	1
The coating hardness conv. and:	
after drying (20±2)ºC for 7 days.	0,3
after drying (80±2)ºC for 2 h	0,5
Conditional lightfastness, h	24
Impact strength of the coating cm, not less than	50
Resistance to static two-layer coating to water at (20±2)ºC, d, not less	30
Resistance to the effects of engine oil (20±2)ºC, not less	40
Resistance of the coating in a 20% sodium chloride solution at (20±2)ºC, h, not less	150
Resistance of the coating in a 3% sodium chloride solution at (20±2)ºC, h, not less	150

It is established that during the tests, listed in Table. 3, the environment preserved integrity of the coatings, there are no signs of cracking and blistering. After removal of coatings on metal, the traces of underfilm corrosion is not observed..

The coatings were tested for resistance to variable temperature, high humidity, salt spray and UV rays. Laboratory cyclic tests were carried out for 30 cycles (2880 h). Methods for carrying out one set of tests is presented in Table. 4.

Table 4. Technique one test cycle

№	Test equipment	Test conditions	Time
1	Salt spray chamber, mode A (salt spray test)	T =35±2 ºC, Solution: NaCl, c =50±5 g dm^{-3}, pH = 6.5-7.2	8 hour
2	Exposure to air	T = 15±30ºC Humidity not more than 80 %	16 hour
3	Salt spray chamber, mode B (test condensate)	T = 40±2 ºC Humidity in 100 %	8 hour
4	Exposure to air	T = 15±30 ºC Humidity not more than 80 %	16 hour
5	The apparatus of artificial weather	T = 40±2 ºC Ultraviolet radiation	8 hour
6	Exposure to air	T = 15±30 ºC Humidity not more than 80 %	16 hour
7	Camera cold	T =-20±2 ºC	8 hour
8	Exposure to air	T = 15±30 ºC Humidity not more than 80 %	16 hour

Dry film thickness was 80-90 μ. Sample test results are shown in Table. 5. The Table 5 shows that the coatings have high resistance to the variable temperatures, high humidity, salt spray and UV.

Table 5. The test results of samples

№	Data	Document	Value of the index according to GOST	The actual value of the index
1 2	Decorative properties of the coating	GOST 9.407-84 p. 2.2	No changes	Nochanges
3 4	Protective properties of the coating	GOST 9.407-84 p. 2.3	Lack of destruction	Coating damage is not observed

Conclusion

The developed primer is a new modern material. It provides excellent protection against corrosion of metallic structures in corrosive saline environments, and increases ecologically friendly and improved sanitary conditions.

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