

LOW VOC EPOXY COATINGS: PROBLEMS AND OPPORTUNITIES

CIOBANU DOMNICA, TULBURE MONICA, IONIȚĂ IRINA

University of Bacau, Marasesti Street, nr. 157, Bacau, cod - 600115
University of Iași, str, D. Mangeron no. 67, cod 700050

ABSTRACT: The modern refinements of these materials are much easier to apply and have found extensive use as tank linings, particularly for wine storage, and in food factories and chemical plants. The aromatic amine has been superseded largely by specially designed aliphatic and cycloaliphatic amine formulations and this trend is set to continue, particularly because of modern labelling requirements for DDM based hardeners. Some solvent-free coatings based on non-DDM hardeners, however, are limited by the inability to cure properly if the temperature is very low and humidity is high. The use of water-based epoxies may be unsuitable where chemical resistance is critical or where high humidity prevails during cure, especially when temperature and air movement are low.

KEYWORDS: adhesive, emissions, organic compounds, polymers, solvents, monitoring methods, VOC, epoxy.

1. INTRODUCTION

The 2-pack, cold curing epoxy coating market utilises mainly solid bisphenol A epoxy resins having an epoxy equivalent weight of approximately 500 (so-called Type 1 resins) and liquid bisphenol A or bisphenol F epoxy resins having an epoxy equivalent weight of about 200. The solid resins were the basis of the first epoxy paints because the basic drying mechanism is achieved by solvent evaporation to leave a dry but uncured film which later cross links to give full performance. For several decades, the pursuit of epoxy coatings with zero or near zero levels of organic solvent has been led by the suppliers of epoxy resins and hardeners; and, not surprisingly the paint manufacturers and paint users have sometimes been reluctant partners. The resistant to solvent-free (100 percent liquid epoxy) and water-based epoxy is readily appreciated because both are fundamentally more difficult to apply. A more acceptable concept is high solids, solvent-based coatings, but this introduces other difficulties which will be explained later.

In the 1950s, the embryonic 100 percent liquid systems, better known as "solvent-free epoxy coatings" were based on unmodified liquid bisphenol A epoxy and a solid aromatic amine hardener (DDM) which, incredibly, was bisolved or adducted at the site of application, mixed with the epoxy resin, and applied with a trowel. These crude products would certainly not have prospered or developed, had it not been for the desire of resin manufacturers to develop sales of liquid epoxy resins and reactive epoxy diluents to the coatings market, and also had it not been for the remarkable properties achieved. The first solvent-free epoxy coatings gave previously unachievable chemical resistance, exceptional hardness (resembling vitreous enamel), and no sensitivity to moisture. They could even cure normally under water.

In the 1960s, we saw the first water-based, 2-pack epoxy coating systems emerge. Again, these products were mainly developed by manufacturers of epoxy resins and hardeners, looking for growth from a broader product range. Essentially similar to solvent-free epoxies, they were based on liquid epoxy resins, but the hardeners were special polyaminoamide types, usually containing additions of organic acid. The hardeners were designed to confer water emulsification to the liquid epoxy. These early products were required to be mixed with the epoxy first; and then the water was added incrementally so that the mixture passed through a phase inversion step, after which more water could be added relatively easily. Careful design of the hardener created the correct rheology to achieve this.

Despite extraordinary excitement about these systems initially, market acceptance was much slower than for solvent-free coatings, probably because of the difficult mixing procedure. Modern improved derivatives of this technology, however, now meet an ever-growing demand and have been particularly successful for flooring and concrete coating.

Unlike solvent-free and water-based epoxies, high solids technology has not been driven by raw materials suppliers. The impetus comes largely from legislation that produced VOC regulations. Various VOC limits have been indicated and discussed⁴ and can be listed at breaks of 400 g/l, 340 g/l, and 250 g/l maximum. It is convenient for the purpose of this discussion to consider the long-term target for high solids epoxies to be 80 percent solids or higher.

It is sometimes assumed that solvent-free, water-based, and high solids epoxies are competing technologies seeking the same market. In the main, this is not completely accurate because the choice will be limited by the conditions of use.

Roy¹ has considered the selection of water-based epoxy versus high solids. Conventional, solvent-based epoxy may in some cases be or water-based but certainly not without constraints. Solvent-free epoxies may be unacceptable in the following situations: where special application equipment cannot be accommodated or justified, where there is a need for non-barrier type coatings containing anti-corrosive pigments; where very low temperatures prevail; where a short, usable pot life is problematic; where high build is not justified; where the viscosity cannot be tolerated; and where flexible coatings are required.

These fundamental limitations mean there is a continuing need for solvent-based, 2-pack epoxy coatings for a major proportion of the marine and maintenance market. The challenge imposed by VOC regulations is to raise the solids content, at application viscosity, from about 50 percent to 80 percent or higher. From an epoxy resin supplier's point of view, the creation of high solids technology is more challenging than was the creation of solvent-free or water-based technology. With high solids, no concessions in application techniques, performance, or drying time are accepted; whereas the market for solvent-free and water-based have developed through a willingness to trade off problems for advantages.

2. MATERIALS AND METHODS

All 3 technologies participate in the strengths and limitations of 2-component, ambient curing epoxy systems. The main challenge for all 3 systems is to overcome the problems of curing in cold and/or damp climates, but in each case, the reason is significantly different, as described below.

2.1. Solvent-free epoxies

Low temperatures can lead to "B stage cure," whereby the coating could be said to freeze solid in the partially cured state so that the lack of molecular mobility results in under cure, causing brittleness and lack of chemical resistance. Also, aliphatic amine hardeners can display amine blush at low temperatures (Fig. 1).

Both problems are largely solved by judicious formulation with cure accelerators and plasticisers. However, temperatures below 15 °C can still impair performance where the criteria are very demanding. The retardation of cure in solvent-free coatings is often resolved in practice because cure can resume once the temperature rises (in contrast to water-based emulsion).

epoxies are unacceptable. The response of high solids epoxies to cold curing at high humidity in this case is different yet again. Fundamentally the viscosity of the paint binder has been such that a 80 percent solid, content, the paint can be applied by conventional airless spray. In practice, the formulator finds the film formation by solvent evaporation alone is no longer possible because the required low viscosity of the resin system results in the paint film tending to remain liquid after the solvent has evaporated and must lower solid content epoxy paints, which are based largely on solid resins. Thus, the high solids formulation has to resemble a solvent-free coating to which 20 percent or less of organic solvent might be added. Speeding the cure of the epoxy to form a rapid setting film at low temperature is difficult and introduces the conflict of short usable pot life versus drying time. While this conflict is accepted as a trade-off against advantages in the case of solvent-free coatings, high solids coatings may be seen unfavourably by comparison with lower solids coatings, which can both dry quickly and after a long pot life.

3. RESULTS AND DISCUSSIONS

Solvent-free, 2-pack epoxy coatings are well developed in those markets where their use is appropriate. The limitations of short pot life and high viscosity are accepted as a trade-off against the strong advantages of performance, high build, and VOC compliance.

Currently the main challenges are to find safer alternatives to aromatic, amine-based hardeners and to accelerate cure at low temperature; otherwise, the market could be described as stable with no major changes either needed or anticipated. This subject will not be discussed further.

Water-based epoxies, on the other hand, are the subject of much ongoing development. Because the technology is complex, a basic understanding as given below should be beneficial to all potential users. Historically, there are several kinds of systems (Table no. 1).

Water emulsifiable epoxy (2 pack). Table 1

Epoxy Resin Types	
A. Liquid Epoxy 100% (Conventional)	Can pigment resin or hardener components
B. Liquid Epoxy 100% (Emulsifiable)	
C. Liquid Epoxy – Pre - emulsified	Must pigment resin or hardener components
D. Solid Epoxy – Pre - emulsified	
Hardener Types	
E. Polyamidoamines (aqueous)	
F. Polyamines (aqueous)	

The liquid resins A + B can be pigmented before emulsification. A, which is equatable with normal liquid unmodified epoxy resin, can be emulsified only after addition of a suitable hardener. The early systems worked this way, but while still technically very good, they no longer find favour because emulsifying the product on site is potentially problematic. Liquid resin B can be emulsified relatively easily by the paint manufacturer. Liquid epoxy C is supplied already dispersed in water by the epoxy resin manufacturer, allowing the manufacturer to control the maximum emulsion particle size, which is key to performance².

Resins D are solid epoxies carried in a small amount of organic solvent, and the emulsion is prepared by the epoxy supplier. D shows the same advantages as C but in addition has faster drying and much better film toughness. Emulsified types C and D, however, limit the scope for pigmentation. Pigmentation has to take place in the aqueous phase; and, therefore, only limited wetting of the pigments can be achieved, lowering gloss and film integrity. For this reason, C and D can usefully be combined with B types.

The hardeners E and F are selected for complex performance considerations. F-type polyamine adducts are distinguished particularly by better colour, lower viscosity, and faster drying.

The paint formulator needs to utilize or consider all these types to satisfactorily cover the full spectrum of coating needs.

To date, all commercial, water-based, 2-pack epoxy paints are based on I or more of these product types and, as such, are emulsified systems. There are 3 intrinsic problems with emulsion system that have to be understood and allowed for.

The emulsified resin component has to combine with the normally soluble hardener component during the mixing operation and film formation process (Fig. no. 2).

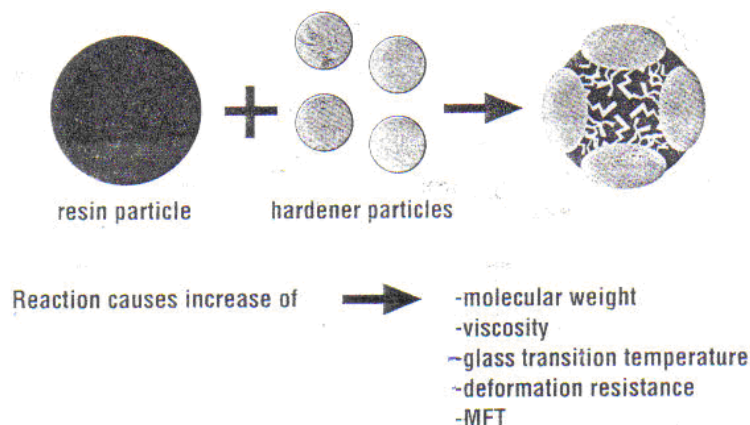


Fig. 2. Reaction of Ep – emulsified particles – with amine curing agents.

The emulsion particle size is crucial to achieving an acceptable level of mixing of the components. Even the best water-based epoxies tend to be less chemical-resistant than solution- or solvent-free types.

As the epoxy/hardener reaction proceeds, the molecular weight increases, driving up the MFT (Fig. no. 4). Satisfactory coatings can be formed only if the particles fuse together; this is possible only if the drying temperature is higher than the minimum film-forming temperature.

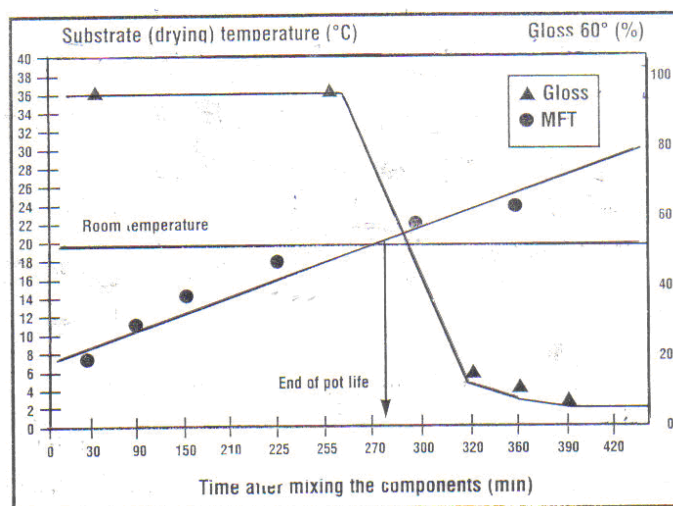


Fig. 3. Minimum film forming temperature of emulsified solid epoxy with amine adduct hardener

Failure of the particles to fuse together results in a discontinuous film (Fig. no.3).

The pursuit of fast drying encourages the use of emulsions based on dissolved solid epoxy resins, but these products have higher initial MFT and therefore may need modification with emulsified liquid epoxy to cope with low temperatures during cure.

The inevitable increase in MFT after mixing determines the usable pot life of a system. Whereas the paint film will normally lose water while the particles fuse, the paint in the can remains a low viscosity emulsion/dispersion long after the useable life has been exceeded.

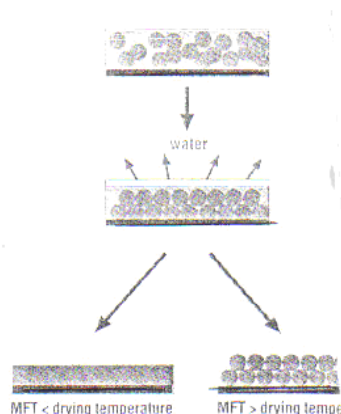


Fig. 4 Film forming of emulsions

Usable pot life ends when the MFT reaches or exceeds the substrate temperature. Paint used after usable pot life has ended will start to display poor gloss, indicative of a discontinuous film (Fig. 4). In unpigmented examples, a distinct opaque appearance may develop as the individual particles cure independently. Fig. 4 shows how the intersection of MFT with substrate temperature causes a sharp drop in gloss (and therefore termination of useable life). This effect requires careful management by both paint formulator and user. Safety factors must be built into the instructions on usable life to prevent operators from using the paint accidentally after expiration of the pot life. Unfortunately, there is no obvious change to the condition or the paint such as viscosity increase or gellation at the point when the pot life expires.

In situations where air space is confined and static, the atmosphere can become water-saturated, which prevents the paint film from drying, in extreme cases, this condition can totally prevent film formation and cure. Awareness of these 3 potential weaknesses and proper management to overcome them are essential if the benefits of the water-based systems are to be realized. In addition to the obvious environmental benefits, water-based epoxies bond exceptionally well to a number of difficult substrates, such as plastics, damp concrete, and old paint films. Also, water-based systems have been shown to be effective as tie coats for binding solvent-free epoxy flooring to wet concrete. When good film coalescence is achieved, the products form excellent anti-corrosive barrier coatings, especially a product based on a high functionality liquid epoxy (epoxy phenol novolac – EPN)². The emulsion particle size is key to film formation and stability^{2,3}, and typical particle size distribution curves are shown in Fig. no. 5.

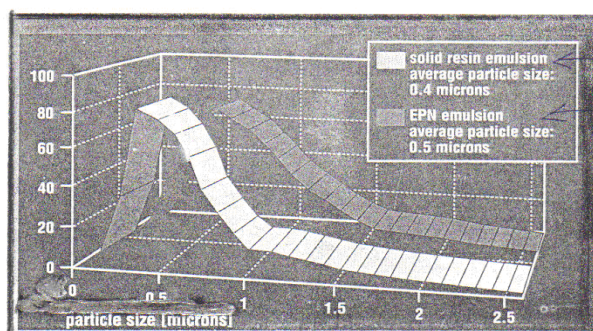


Fig. no. 5 Particle size distributions of epoxy resin emulsions

This quality of emulsion would normally be achievable only on high shear equipment and therefore from products sold as pre-dispersions (types found in Table I as C and D). Emulsified epoxies used in 2-pack systems

show some reduction in properties when compared to solvent-based systems. Nevertheless, the best products can be usefully substituted for convention solvent-based epoxy, except for use in strongly acid environments. The complexity of the technology is driven by the need to tailor formulations to give properties appropriate to the end use, as summarised in table no.2. It can be seen that a range of product types is required.

Applications. Table 2

Coatings on concrete	Very large floor and wall areas in: - warehouses - car park decks garages - shoppingcentres - electronic industry - fighway tunnel walls - sport stadiums airports - kitcnens - food processing plants - nuclear power plants	Preferred System Types Liquid epoxy/PAA or amine adduct Solid epoxy emulsion+liquid epoxy/PAA or amine adduct Solid epoxy emulsion/PAA or amine adduct EPN emulsion/PAA or amine adduct
Coatings on steel	Mostly primer coats: - beams for buildings - primers for passenger rail cars and busses - rail trucks and road tankers - ship enegine rooms - single coat for car springs and shock absorbers	Solid epoxy emulsion/PAA or amine adduct EPN emulsion/PAA or amine adduct
Coatings on plastic	Mostly primer coats: - various plastics	Solid epoxy emulsion/PAA or amine adduct
Coatings on wood	- floors in sports stadiums - floors in housing	Solid epoxy emulsion/PAA or amine adduct
Interlayer adhesion	- onto cured epoxy or polyurethane coatings	Solid epoxy emulsion/PAA or amine adduct For thick films liquid epoxy/PAA
Tile and parquet floor adhesives	- industry (tiles) - housing (parqued)	Liquid epoxy/special solvent-free hardener
Epoxy-modiffed concrete	Epoxy cement concrete (ECC) - repairs mortars - pourable grouts	Liquid epoxy/amine adduct (low reactivity, no organic co-solvent)

Ongoing development will be directed towards greater tolerance to ranges of temperature, humidity, and film thickness, as well as improved film coalescence. Improved visibility or pot life and weather resistance are also targets. The development of high solids, 2-pack epoxy has proved to be perhaps an even greater technical challenge than water-based.

4. CONCLUSIONS

Development has to date been led by the paint manufacturers rather than the epoxy suppliers, partly because it seems at first to be a technology requirement of formulation rather than resin design.

Systems that perform adequately for some situations are commercially available, but it is clear that much remains to be done.

The key problem arises in cold climates where a mechanism is needed to enable the low viscosity binders to form a solid film quickly. Conventional amine adduct and polyamide hardeners find use only where very low temperature cure is excluded and in any case tend to be viscous, making VOC reduction difficult to achieve.

Mannich bases (phenalkamines) offer some advantage, but a new chemistry is needed if the film formation problem is to be solved by rapid reaction only. Accelerators offer a feasible route, but traditional types are inadequate; a novel type has been proposed. Hardener and accelerator developments will, of course, always require a trade-off between drying time and pot life, and an additional complication may be that speeding the crosslinking at low temperatures (i.e., when the solvent evaporation is low) could cause problems of film contraction and possible loss of adhesion through internal stress.

The choice of the main component epoxy resin currently seems to lie between a basic low viscosity liquid epoxy resin (for which a fast curing mechanism must be found) or a film forming epoxy resin which has been: modified to reduce its solution viscosity. Other epoxy resins can be used as modifiers for the basic type-with some content of higher molecular species seeming to be desirable.

Multifunctional, epoxidised novolac can also be incorporated. They seem to have a potential role to play in combination with solid, film forming resins.

Developments are foreseen which provide further optimisation of film-forming epoxy resins with lower solution viscosity and improved hardeners and accelerators giving the exceptionally fast set-up times required.

BIBLIOGRAPHY

- [1] G.A. Roy, Rhone Poulenc, Louisville KY, US Coatings and Linings (November 1997).
- [2] A. Wegmann, "Novel Waterborne Epoxy Resin Emulsion," Journal of Coatings Technology (December 1998).
- [3] A. Wegmann, "Storage Stability of Epoxy Resin Emulsions," European Coatings Journal (7-8, 1999), 539-545.
- [4] E.Pratt, "VOC-Compliant Protective Coatings—The Way Forward," UK"Corrosion 93, Hammersmith, London.
- [5] C. Godau and B. Stengel-Rutkowski, Farbe & Lack (No. 4, 2000), 340-343.