# **Colloidal Aspects of Waterborne Epoxy Paints**

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# INTRODUCTION

L iquid epoxy resins or an aqueous dispersion thereof in combination with a water-reducible curing agent (aminoamides, polyamidoamines, or epoxy adducts) represent the state-of-the-art in waterborne epoxy technology.<sup>1-3</sup> This technology emerged a few decades ago in the course of a trend towards environmentally friendly coating compositions. Current commercial waterborne epoxy paints are generally competitive with their conventional solvent-based counterparts in a number of important application fields including the construction industry, building engineering, and corrosion protection.

Whether the performance of waterborne formulations approaches that of their solvent-based counterparts in each sphere of utility is still debatable. In particular, waterborne epoxy paints are considered to suffer a few drawbacks:<sup>4,5</sup> shorter pot life, lower chemical resistance (especially to organic acids), and poorer protective properties (anticorrosive coatings).

Nevertheless, waterborne epoxy paints are still one of the most convenient classes of ambient cured coatings. They provide outstanding decorative, mechanical, and protective properties, combined with inflammability and lower toxicity.<sup>4-7</sup> Relatively poor weather, light, and thermal stability are drawbacks of both water and solvent-based epoxy coatings, which in turn limit their outdoors application. These drawbacks can be at least partly overcome by modification with a suitable film forming resin—acrylic, vinyl, etc.<sup>8</sup>

Two principal technologies are used for producing waterborne epoxy paints: (1) so-called "self-emulsifying technology," in which one component is liquid epoxy resin, and the other is an aqueous composition based on a water-thinnable epoxy hardener; and (2) "emulsion technology," in which a pre-made epoxy emulsion of liquid or (more frequently) solid polyfunctional epoxy resin is mixed with an aqueous hardener solution prior to application.<sup>4</sup>

This paper summarizes some results and observations obtained in the course of development of a series of waterborne epoxy paints (Tambour Ltd.). An attempt has been made to give a deeper look into selected colloid aspects of the "liquid epoxy resin plus water-thinnable hardener" approach. This could give a better understanding of the means to control and improve coating properties through proper selection of epoxy resin, hardener, and colloid-affiliated additives (co-solvents, co-emulsifier) and circumstances of film formation. WaterThe colloidal aspects of formulating two-part ambient cured waterborne epoxy paints which utilize so-called self-emulsifying technology (liquid epoxy resin plus water-thinnable hardener) are discussed. Experimental data are presented for commercial amine-type water-thinnable hardeners on dilution behavior, co-emulsification with liquid epoxy resins, and performance of paint compositions. Approaches are offered for the selection of key components and some additives (in particular, of co-solvents and co-emulsifiers) for epoxy waterborne film forming compositions.

borne epoxy paints based on epoxy emulsions will not be discussed in this paper.

### **EXPERIMENTAL**

Commercial water-thinnable hardeners (*Table* 1) and liquid epoxy resins (*Table* 2) were used in this work for model experiments and formulation of epoxy emulsions and paint compositions.

Rheological measurements were performed using a rotortype viscometer (Sheen Rotothinner). Surface tension measurements used a ring tensiometer (Torsion Balance, White Elec. Inst. Co. Ltd.). Particle size distribution was determined using a laser analyzer Galai CIS-1 (diluent: aq. solution of Triton X 100, 0.05%). Molecular weight characteristics were measured with GPC assembled instrument [RI Waters 410, IP SP 8810, column by Polymer Laboratory 2 MIXE (3 µm)].

### **Components and Compositions**

**PAINT COMPOSITION:** Guide formulations for two-part, ambient cured epoxy waterborne paints, which contain all necessary functional components, are available from suppliers of water-thinnable hardeners (curing agents) or liquid epoxy

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Table 1—Liquid Epoxy Resins (Commercial)

Sample	Viscosity at 25°C m Pa s	EEW° g/Eq
R1 R2 R3 R4	870 11000 570 7200	195 188 187 178
(a) Epoxy equivalent weight		

resins.<sup>9-13</sup> Basically, these formulations can be presented in two versions, comprising the following components (% wt):

#### Version 1

Part W (Water-Based):	
Water-thinnable epoxy hardeners, 50-80% solids	
Co-solvent-1	
Rheology additives	0.5-1
Co-emulsifier (lower molecular weight)	0.2-0.5
Wetting agent	0.6-1.2
Pigments and extenders	
Other functional additives	0-1
Water	
Part R (Epoxy Resin-Based):	
Liquid epoxy resin	14-15
Plasticizer, modifier	
$C_{1} = 1$ and $2$	0.2

W/R weight ratio ca. 4:1

#### Version 2

Part W:	
Water-thinnable epoxy hardener, 50-80% solids	
Water	
Co-solvent-1	0.5-1
Wetting agent	0.5-1
Pigments and extenders	
Other functional additives	0-1.5
Part R:	
Liquid epoxy resin	14-16
Emulsifier (higher molecular weight)	
Active diluent or co-solvent-2	

Water			 5-7
	W/R weight	ratio ca. 4:1	

These versions differ in their approach to the use of additives affecting colloid properties and the emulsification process. In the first version, the emulsifying capacity of the hardener is enhanced, while in the second version, the resin phase is transformed into a more easily emulsifiable state.

HARDENER: Water-thinnable hardener is the first component to be selected for epoxy waterborne paints.

The macromolecular composition and molecular structure of amino-type hardeners designed for waterborne epoxy paints is quite specific and resembles amphiphilic emulsifiers. For example, amido-amines, synthesized by condensation of polyamines with fatty acids or their dimers, consist of a hydrophobic (fatty) part and a hydrophilic part. The latter carries amine groups or their salts with a volatile organic acid, which makes the hardener molecule partially ionic, thereby increasing its affinity to water. So, their properties are characteristically amphiphilic.<sup>17</sup>

Therefore, a water-thinnable epoxy hardener, in addition to being a polyfunctional curing agent, performs an emulsifying function. It provides a film forming emulsion during the mixing of the hardener and resin components in the case of "liquid epoxy resin plus aqueous hardener solution" technology, or maintains colloid stability of a previously prepared epoxy emulsion in the case of "epoxy emulsion plus aqueous hardener solution" technology.

For example, let us estimate an emulsion particle size that can be obtained with a standard liquid epoxy/water-thinnable hardener combination (Araldite PY 340-2 plus Hardener HZ 340, Ciba Geigy).<sup>9</sup>

From the standpoint of the emulsifier/resin ratio (3-10%) that has been used to obtain direct emulsions of resins,4,14,15 the recommended resin/hardener ratio 1.67/1 of solids by weight (or 1.52/1 of solids by volume) for the PY 340-2/HZ 340 combination is excessive. Let us assume that the emulsification proceeds until the full quantity of the hardener is adsorbed on the water/resin interface.

The maximum interfacial area S developed with 1 cm<sup>3</sup> of the hardener can be calculated from the following formula:

$$S = \frac{\rho}{M} \cdot S_{o} \cdot A \tag{1}$$

where S<sub>o</sub> is the surface area per one adsorbed hardener molecule,  $\rho$  and M are the density, and the molecular weight of the hardener, A is the Avogadro number.

The number average molecular weight of HZ 340 is 212 (GPC evaluation). For the magnitude of  $S_0$ , one may assume  $40\text{\AA}^2$ /molecule (in the range of the surface-active molecules of higher molecular volume),<sup>16</sup> and  $\rho = 1.08$  g/cm<sup>3</sup>. Calculation according to equation (1) gives  $S = 1.22 \times 10^7 \text{ cm}^2 \text{ per } 1$  $cm^3$  of the hardener or, for the resin/hardener ratio,  $1.85 \times 10^7$  $cm^2 per l cm^3 of epoxy resin.$ 

The specific interfacial area of emulsions  $(S_{sp})$  correlates<sup>17</sup> with their particle radius (r):

$$S_{sp} = \frac{3}{r}$$
(2)

Using the resin-bound value of S, the calculation according to equation (2) gives  $r = 1.62 \ 10^{-7}$  cm (or 1.62 nm, and particle volume 17.8 nm<sup>3</sup>). Correspondingly, each particle contains ca. 42 of epoxy molecules and 49 hardener molecules. The calculated r value is a few order less than the radius of regular liophobic emulsions, and corresponds to the particle size of microemulsions and solubilizates.<sup>18</sup> This means that the stoichiometric hardener/resin ratio is sufficient for formation of an epoxy emulsion even of high dispersity.

Viscosity and surface tension of the hardeners listed in Table 2 are compared in Figure 1. A somewhat sharper drop in viscosity on dilution with water and somewhat higher values of surface tension are characteristic for epoxy adduct-type hardeners (H3, H4, and H5) in comparison to amido-amine H1. Polyamino-amide H2 exhibits a flatter dilution profile, with substantial viscosity dropping below 10% solids.

#### Table 2—Commercial Water-Thinnable Hardeners (Curing Agents)

Sample	Hardener Type	Viscosity at 25°C m Pa s	Solids, %	AHWª g/Eq
Н1и	Amido-amine	9000	55	175
H2 F	Polyamidoamine	22000	50	150
H3 I	Modified amino-adduct	25000	70	200
H4 F	Polyamine adduct	2300	80	200
H5 F	Polyamine adduct	20000	80	115

(a) Active equivalent weight hydrogen

All tested hardeners only reach a state of cloudy solution when diluted with water in the concentration range of 6-25% solids (so-called cloud-point). As for any solutions of partially soluble polymers and oligomers, the cloud-point reflects their transformation from the state of a true solution into a state of microemulsion.<sup>19</sup> Addition of 2-5% water-miscible co-solvents (ethyl alcohol, methoxy propyl acetate, propylene glycol ethers, etc.) causes substantial improvement in dilution profile of these hardeners, decreasing viscosity and shifting the cloud-point concentrations to more dilute solutions.

Continuing dilution of hardener solutions below their cloudpoints did not result in an inflection in the surface tension versus concentration dependence; such an inflection would be attributed to the critical concentration of micelle formation (CCMF). For example, a solution of hardener H2, upon dilution below the cloud-point concentration range of 7-10% solids, yields a dispersion with particle size of 210-230 nm.

Therefore, these hardeners should be referred to as "noncolloid" (i.e. nonmicellar) surfactants, as is characteristic for water-soluble polymers and oligomers having a nonregular molecular structure. Correspondingly, they can be effective in emulsification processes at elevated concentrations compared to typical micellar emulsifiers (soaps).<sup>20</sup>

LIQUID EPOXY RESIN: The major criterion for selection of epoxy resins for waterborne paints is their performance in coatings. Their emulsifiability is another important factor. Special grades of liquid epoxy resins, hydrophilized and having reduced viscosity, have been offered for commercial use [for example, see references (9) and 10)]. General purpose liquid epoxy resins can also be used if their viscosity and hydrophobicity are reduced by addition of a co-solvent, active diluent, or emulsifier.

VOLATILE ADDITIVES (CO-SOLVENTS): Waterborne epoxy paint formulations may contain one or more volatile organic liquids to perform the following functions:

—Improve compatibility between the hardener and water,

Table 3—Functions	of Volatile Additives	(Co-Solvents)
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providing a better dilution profile and a later cloud-point;

--Promote the emulsifying process (as a component of the water phase);

—Promote the emulsifying process (as a diluent of the resin phase);

-Extend the colloid stability of the paint (influencing its pot life);

				Example <sup>a</sup>		
Function	with Water	Volatility	δ	SW	ER	
Improvement in dilutability for a hardener	Medium	Medium	N N	Propylene glycol lethyl Ether Aceta 18 5	te 34	
Emulsification promoter (in water phase)	haro) High Modium		Propy	lene glycol methy	l ether	
	ingri	Modian	10.4	Unlimited	68	
Emulsification promoter (in resin phase)	Medium	Medium	Methoxy Propyl Acetate			
			9.4	20	—	
Colloid stabilizer	High	Medium		Butyl glycol		
			9.9	Unlimited	6	
Promoter for drving	High	Low		Propylene glycol		
		2011	14.9	Unlimited	<1	
Water-releaser	High	High	Methyl alcohol			
			14.5	Unlimited	610	
Coalescina agent	Low	Low	Bu	utyl carbitol aceta	te	
0.0			9.1	6.5	<1	



—Keep the structure of the drying film "open," allowing complete release of water and promoting a coherent film;

—Ease the removal of water from a drying film; and

-Act as a coalescing agent.

When selected to perform each of these functions, the cosolvent needs to be considered according to its volatility and polarity, which indicates its affinity to key components (water, hardener, epoxy resin) and its distribution between the phases on emulsification and film forming processes. Since no commercially available solvents are capable of performing all functions simultaneously, the use of more than one co-solvent (2-5% volume total) may be recommended. *Table 3* provides examples of co-solvents and their volatility and miscibility with water.

When a stable emulsion is produced, any surface active component in the composition will be distributed between the interface and solution, and any nonsurface active component, for example, a co-solvent, will be distributed between the water and resin phases.

# Table 4—Particle Size of Emulsions, Obtained in Different Regimes

		Mean Particle Size, nm			
Regime	2 min of Intense Stirring	After 0.5 hr	After 1 hr	After 2 hr	
		R1/H1	Emulsion		
Stirring	1010	849	1000	984	
Resting	1010	742	1210	1170	
		R1/H2	Emulsion		
Stirring	000	296	831	2440	
Resting	828	431	639	2670	

As the hardener, which stabilizes the emulsion, becomes more involved in the reactions with epoxy resin, a shift in the distribution of a co-solvent toward the water phase will be stimulated. This improves the solubility of the hardener in the aqueous phase and maintains its effectiveness as a surfactant, while resisting early aggregation and loss of application characteristics.

**CO-EMULSIFIERS:** Two types of emulsifiers are offered to promote emulsification of liquid epoxy resins: lower molecular weight emulsifiers (having a higher diffusion mobility and surface activity from aqueous phase) and higher molecular weight surfactants. Both are nonionic and, having HLB > 12, enable direct emulsions formation.

Correspondingly, emulsifiers of the first group are to be introduced into the aqueous phase, serving simultaneously as wetting agents and temporary emulsifiers during the emulsification process (Surfynol 104 [Air Products] as an example). The higher molecular weight emulsifiers (Atlas G 1350 [ICI], etc.) are more suitable for the resin phase.

**OTHER COLLOID ADDITIVES:** Functions of a few other additives are conventional, particularly:

—Defoamer and antifoam agents. Water-thinnable hardeners are different in their foam-build properties (which tend to be more expressed in a diluted state), and defoamers tend to show substantial selectivity.

—*Pigment wetting agent.* As a regular process, pigments and extenders are dispersed in a moderately diluted hardener solution. Except in some special cases, no additional dispersant is needed.

—Substrate wetting agent. A few substrate wetting agents (Borchigol VL 73 S is an example) are recommended to reduce surface tension of aqueous hardener solutions. Sometimes, especially for amino-adducts without an additional surfactant, the surface tension of the hardener solution falls in

the range of 36-40 dynes/cm, i.e., 2-6 units higher than is needed for architectural and industrial substrates.

—*Rheology additives* should also be viewed as colloid modifiers, since they act to modify inter-particle interaction. Just as for regular water-based paints, molecular thickeners and inter-particle bridgers (associative thickeners, particularly) and disperse structure-formers (e.g. selected brands of bentones) can be utilized.

## **EMULSIFICATION PROCESS**

The standard procedure to prepare two-part waterborne paints for application is hand mixing or mechanical stirring (severe stirring is not obligatory) and dilution with water if necessary. A rest period of 20-30 min (induction period) is allowed between mixing and use.

The mixing of the two parts of a waterborne epoxy paint prior to application initiates two spontaneous processes: (1) a mass transfer across the water/resin interface (thus providing conditions for self-emulsification); and (2) a chemical reaction between epoxy resin and a hardener. These processes proceed simultaneously and, to a certain extent, are mutually dependent. Both affect all the technological properties of the paint: flow behavior, drying time, stability of the coating properties during the pot life, the pot life limit, etc.

**EMULSION TYPE**: Waterborne epoxy paint technology is based on direct emulsions (epoxy-in-water); otherwise the binder is not water-dilutable.

The hydrophilic-lipophilic balance number (HLB), the critical packing parameter, and some other criteria<sup>21</sup> stand for the emulsion type. An illustrative criterion to predict the type of emulsion, which utilizes a classical colloid approach,<sup>22</sup> was suggested in terms of viscosity ( $\eta$ ), surface activity of corresponding components in both phases ( $\Delta$ ), and their concentrations (c) on condition of equality of volumes of the coemulsifying phases ( $V_w = V_r$ ):

$$\mathsf{D} = \frac{\eta_{\mathsf{r}}}{\eta_{\mathsf{w}}} \cdot \frac{\Delta_{\mathsf{w}}}{\Delta_{\mathsf{r}}} \cdot \frac{\mathsf{c}_{\mathsf{w}}}{\mathsf{c}_{\mathsf{r}}} \tag{3}$$

where r indicates the resin and w the aqueous phases. Condition D > 1 refers to oil-in-water (resin-in-water, r/w) emulsions, and D < 1 to inverse emulsions (w/r).

Taking into account the well-known influence of phase volume ratio on direction of emulsification process,<sup>23</sup> equation (3) can be rewritten as:

$$\mathsf{D} = \frac{\eta_{\mathsf{r}}}{\eta_{\mathsf{w}}} \cdot \frac{\Delta_{\mathsf{w}}}{\Delta_{\mathsf{r}}} \cdot \frac{\mathsf{c}_{\mathsf{w}}}{\mathsf{c}_{\mathsf{r}}} \left(\frac{\mathsf{V}_{\mathsf{w}}}{\mathsf{V}_{\mathsf{r}}}\right)^{\eta} \tag{4}$$

where n > 1.

So, adding a water phase gradually to a resin phase, we are in a condition of  $V_w < V_r$ . Having a co-emulsifier in the resin phase, we provide  $\Delta_w$ ,  $\Delta_r$ , and  $D_{r/w} < 1$  and, correspondingly, observe formation of an inverse emulsion in the first step of the emulsification process. In the next step, when  $V_w$  becomes larger than  $V_r$ , the emulsion transforms into a direct emulsion in excess of hardener solution through the phase inversion point (PIP-technology). This technology demands that the viscosity of epoxy resin be as low as possible.

According to a more widely distributed technology, a resin phase is added to a water phase, providing  $V_w > V_r$  and higher

surface activity from the water phase. Therefore, this technology from the beginning stands for the emulsion "resin-inwater" (direct emulsion technology).

It is to be noted that any waterborne epoxy emulsion or paint is in a nonequilibrium state from the moment of its formation up to the cured state. So, any predictive calculations based on equilibrium characteristics (solubility parameter, surface tension, surface activity, etc.) should be viewed as approximate.

Nevertheless, the design of commercial water-thinnable hardeners finally provides the formation of resin-in-water emulsion at any order of mixing, when the stoichiometric of somewhat higher resin/hardener ratio is used along with a moderate dilution of a hardener with water.

Wegmann<sup>4</sup> considers inverse emulsification more effective. In our experience, a well-formulated composition has to allow both consequences for mixing parts W and R, giving finally in both cases a resin-in-water emulsion with close particle size, application characteristics, and coating performances.

FORCED AND SELF EMULSIFICATION: Description of the technology as "self-emulsifying" is quite conventional. This term is based on the experience that the mode and intensity of coemulsification W and R parts have little influence on the flow behavior, other technological characteristics, and coating performance, if the composition is well-balanced. Practically, it is enough if these parts are properly mixed during a few minutes and allowed a stand-by period of 20-30 min before application.

*Figure 2* and *Table 4* provide a comparison of particle sizes for emulsions obtained with or without agitation. Conditions for this experiment, which illustrates the contribution of self-emulsification, are described in the following:

Parts W and R were mixed (room conditions, stoichiometric resin/hardener ratio) and stirred rapidly for two minutes. Then the emulsion was separated into two portions. One was stirred continuously (half as intensively, 500 rpm), and the other was kept resting in a separate container.



Table 5—The Formation of Cured Films on Epoxy Resin/Hardener Interfaces (Hardener H2, 10% Solids, 48 hr for Interfacial Contact)

Resin	Weight of Cured Films g/m <sup>2</sup>	Film Thickness µm
R1 R2 R3 R4		347 57 207 147

Immediately after intensive agitation, the emulsion obtained from R4/H2 system shows unimodal particle size distribution. In 30 min of rest it becomes bimodal due to appearance of a finer fraction of 155 nm (*Figure* 2a). Emulsion R1/ H2 shows bimodal particle size distribution from the very beginning (*Figure* 2b). In 30 min without agitation this emulsion forms a fraction of highly dispersed particles (460 nm), whereas its rough fraction decreases.

As seen from the data in *Table* 4, both agitated and nonagitated emulsions are characterized by rather similar particle size distributions 30 min after mixing. In time, both emulsions of R1/H2 exhibit the same character of change in particle size, since self-emulsifying process soon becomes overlapped with coagulation. Both emulsions of R1/H2 remained practically unchanged over the two hour observation period, thus exhibiting greater stability in comparison to emulsions R1/H2.

These data show that emulsification of liquid epoxy resins in water-thinnable hardeners proceeds as a conjunction and overlapping in time of two processes: forced emulsification (controlled by supply with an external energy) and self-emulsification (controlled by spontaneous internal processes).

Self-emulsification phenomena are caused by mass transfer across the resin/water interface. Two possible mechanisms are shown schematically in *Figure 3*: depending on circumstances, mass transfer across an interface can produce a new disperse phase when proceeding in either direction.

Mechanism A is more characteristic for epoxy emulsions, since it demands conditions that can be satisfied easily in technical compositions: high enough concentration of an emulsifier (the functionof which is performed by the hardener) and low viscosity of the resin. According to this mechanism,<sup>24</sup> self-emulsification of liquid epoxy resin proceeds through the following steps: (1) penetration of aqueous hardener solution into the resin phase (with the help of fluctuations of its density and viscosity, which co-solvents and coemulsifiers introduced into the resin phase intensify); (2) formation of pre-shaped particles (especially with the help of microphase separation); and (3) detachment of the pre-shaped particles under the action of osmotic-type forces.

In particular, higher molecular weight emulsifiers incorporated into the resin phase may cause microseparation and formation of a hydrophilic network of nuclei for self-emulsification<sup>25</sup> due to their incomplete (nonmolecular) compatibility with liquid epoxy resins. Such micro separation is stimulated when even a small amount of water is added to the resin phase.

Mechanism B demands that a substantial amount of watermiscible co-solvent be introduced into the oil phase (which has to be nonviscous), and that a stabilizer be present in the water phase. The latter function can be performed by the hardener molecules. Compared to the previous mechanism, this mechanism has been claimed to generate finer ultramicroemulsions.<sup>24</sup> In our experiments, however, no direct evidence was obtained that this mechanism generates a new and more disperse phase in the presence of a reasonable (5-10%) amount of water-miscible co-solvents in the liquid epoxy resin.

The agitation applied during the first step of emulsification probably (1) advances the resin/hardener interface, forming a rough emulsion, and (2) promotes detachment of self-emulsified fine particles from the resin surface, which is restricted due to relatively high viscosity of the aqueous phase. Such agitation is needed immediately after mixing, but then the self-emulsification processes mainly contribute to disperseness of the emulsion.

According to Rehbinder,<sup>26</sup> self-emulsification may only occur when the interfacial tension is less than 0.1 dynes/cm (25°C), which is well below the accuracy of a regular instrumental interfacial tension measurement. But this consideration was developed for homophase liquids. Any subphase or phase nonuniformity of the resin phase should be viewed as a factor promoting emulsification processes and self-emulsification particularly.<sup>25</sup>

Simple experiments with undisturbed resin/hardener interface can illustrate the intensity of self-emulsifying and the other affiliated processes on the interface.

When a layer of hardener solution is spread over a liquid epoxy resin surface (in a regular Petri-dish, with layers of aqueous and resin phases of 3-7 mm thick), within 6-20 hr a crosslinked polymer film will be formed that is durable enough to be collected, washed out with appropriate solvent, dried, and weighed. Then one can calculate the amount of cured resin per unit area. *Table* 4 exhibits some typical results.

When this experiment is carried out with a nonviscous liquid epoxy resin, which is suitable for self-emulsifying technology, or with a more viscous species, modified with a solvent, active diluent, or an emulsifier, a milky-white interfacial layer appears in one to two hours. This layer remains redispersible in a hardener solution for a few hours as an emulsion of partially cured epoxy resin. Then, in another four to six hours, an interfacial reaction terminates with coagulation of the previously formed emulsion and with formation of a coherent cured film, insoluble in epoxy solvents.

A few liquid epoxy resins are compared in *Table 5* in respect to their ability to form a cured film on the resin/hardener interface, showing a qualitative correlation between the resin viscosity and quantity of the cured polymer film.

Assuming for these polymer films that density is 1.0, solids content and conversion is 50%, their weight per unit area was recalculated into film thickness. The data, which is represented in *Table* 5, ranges between 60 and 350 microns. In order to produce, for instance, a film of 200  $\mu$ m thickness by the Fickian diffusion<sup>27</sup> of one oligomer (hardener) into the other (epoxy resin) with a diffusion coefficient<sup>28</sup> D = 10<sup>-12</sup> cm<sup>2</sup>/s in place of self-emulsification mechanism, the system needs, according to approximate calculation, ca. 230 days.

**STABILIZATION:** In order to produce a stable emulsion, the process of emulsification has to consist of two steps, partially overlapped with time: emulsification and stabilization. When the self-emulsifying step is over, the system needs either the hardener, possessing sufficient stabilizing functions, or an additional higher molecular weight surface active component as

a stabilizer in order to maintain its dispersity and associated properties.

Commercial water-thinnable hardeners normally manifest a sufficient stabilizing function during the emulsification process and later on. But this function becomes gradually depleted during the pot life in the course of hardener consumption in the curing process. Higher molecular weight surfactant or polymer dispersant can promote colloid stabilization for a longer period, thereby extending the pot life.

**MACROCONDITIONS FOR EMULSIFICATION:** According to the previous analyses and practical experience,<sup>9-14</sup> the conditions for effective emulsification by mixing and stirring parts W (aqueous pigmented phase, hardener-based) and R (liquid resin-based) include:

—volume W/R ratio well > 1;

—viscosity  $\eta_r/\eta_w$  ratio > 1;

—surface tension (W part) < 38 dynes/cm (substrate-tolerant application demands < 34 dynes/cm); and

—solids content—above cloud-point: amido-amines > 6-8%, amine adducts > 10-12%.

# FILM FORMING PROCESS AND POTLIFE

Film formation from waterborne epoxy paints was studied extensively.<sup>29</sup> It was pointed out that when the chemical reaction starts between the epoxy resin and the hardener, the minimum film forming temperature (MFFT) of the emulsion rises gradually, therefore putting a time limit on the ability of full coalescence of resin particles. So, in the case of waterborne epoxy paints, it is more appropriate to determine its pot life according to the coating performance, rather than rheology (the latter approach is accepted for epoxy solvent-based paints). Here it is worthwhile to discuss a few features of film forming processes associated with colloid behavior of the binder.

From experiments with synthetic latices and film forming emulsions it was shown<sup>30</sup> that the MFFT depends on  $T_g$  of the latex polymer as well as on the colloid stability of the polymer dispersion. So, each measure that helps to elevate or maintain colloid stability of epoxy/hardener emulsion can extend its pot life.

The phase inversion point (PIP) is desired to be as late as possible. In case of early phase inversion, microdrops of water will be locked in the curing film, causing porosity. From the colloid standpoint, this may be avoided by the use of cosolvents and a co-emulsifier that lower the chemical reaction rate.

Four types of co-solvents (see *Table 3*) can improve the drying process: a water-releaser (highly volatile water-miscible liquid), and those which are retained in a drying layer: coalescents, capable to maintain the ability for coalescence in spite of the development of curing reactions, promoter of drying and colloid stabilizer, which maintains solubility of the hardener in water.

*Figures* 4 and 5 exhibit a typical situation for the time dependence of paint viscosity, surface tension, dry time, and coating gloss (experimental paints I and II).

Paint I, whose behavior is shown in *Figure 5*, becomes a gel in five hours after mixing W and R parts. Surface tension remains unchanged and as low as 32.5 dynes/cm during the



whole period of experiments (4.5 hr). The later the composition is applied to a substrate, the shorter its drying time. Coating gloss remains almost unchanged during two hours (paint 1, *Figure* 5) or three hours (paint II, *Figure* 6) and then drops rather fast.

For high gloss epoxy waterborne paints, the pot life limit is relatively short and sharp. According to the data presented in *Figure 5*, the following approximate formula is applicable to these paints:

$$t_a + t_{td} = Const$$
 (5)

where  $t_a$  is the period between the W + R mix and application and  $t_{td}$  is the touch-dry time.

So, the total time, including the stand-by period and the drying time, is a characteristic for each glossy paint. Hence, the faster curing the paint one wants to prepare, the shorter the pot life will be. For instance, when the demand for touch-





dry time is no longer than five hours, paint II can be practically used for 1.5-2 hr after mixing W and R parts. Well balanced formulation of a gloss decorative paint allows pot life >2 hr (without losing gloss with time) and touch-dry time two to four hours.

As a continuation of *Figure* 3, a scheme of colloid transformations during the pot life and film forming processes is represented in *Figure* 6. This scheme outlines considerations regarding various components of waterborne epoxy paints.

# PAINTS

Based on liquid epoxy resin/water-thinnable curing agent combinations, epoxy waterborne paints expand their application in building engineering, for maintenance, in anticorrosive coatings and more. Aminoamide and polyamidoamine hardeners are more suitable for architectural coatings, whereas adduct-type hardeners should be preferred for anticorrosive and chemical resistant coatings.<sup>31</sup> An incomplete list of their technological applications is as follows:

**BUILDING PAINTS:** Waterborne epoxy paints, due to their excellent adhesion to building substrates, including damp concrete, easy washability, chemical, solvent, and wear resistance of coatings, are exploited successfully and increasingly:

—for sealing, healing, and priming concrete and similar building substrates;

—as intercoats between old paints and new topcoats, especially in case the latter contains some active solvents (thereby preventing lifting); and

—as topcoats for indoor and limited for outdoor application, mainly for laundries, kitchens, hospitals, and other special compartments, that demand easy decontamination and chemical resistance of the coatings.

**FLOORING PAINTS:** Compositions with elevated solid content (>70% in W + R mixture), and thereby having relatively low volume shrinkage, are useful for industrial flooring, but mainly for toppings.

Figure 6—Colloid processes during pot life and film formation (schematic representation):

(1) Epoxy emulsion, fine particle (secondary particle, formed due to the self-emulsification process) and big particles (primary particle, formed by the forced emulsification); (2) fine particle, stabilized with adsorbed molecules of a hardener; (3) fine particle, stabilized with hardener molecules, partially consumed in curing reaction; (4) aggregate of the secondary particles; (5) applied to a substrate emulsion or emulsion paint; (6) phase inversion point; and (7) coherent coating.

**PLASTIC PAINTS:** Having very low VOC, waterborne epoxy paints do not damage polymer substrates, even thermoplastics. At the same time, they have a high potential for adhesion. Thereby, the paints with surface tension <32 dynes/cm are convenient for application directly to plastics.

ANTICORROSIVE PRIMERS: With suitable anticorrosive pigments, which here are key components and as important as resin and hardener, properly formulated waterborne epoxy metal primers provide corrosion resistance comparable to solvent-based counterparts.

**MAINTENANCE PAINTS:** This type resembles the building topcoat, but contains more volatile co-solvents, adhesion promoter, polymer modifier, and sometimes an anticorrosive pigment.

# CONCLUSION

Selected colloid properties of five commercial water-thinnable epoxy hardeners (as representing various types of amine-type curing agents, particularly amido-amine, polyamidoamine, and polyamine adduct) were studied to provide a better foundation for their use in epoxy waterborne paints.

Their viscosity/dilution (with water) profiles are substantially different, as are their cloud-point concentrations (in a range of 6-25% solids). Surface tension ranged between 33 and 40 dynes/cm for different hardeners, remaining practically unchanged on moderate dilution below the cloud-point. Above the cloud-point their aqueous solutions can provide effective emulsification of liquid epoxy resins when the stoichiometrical epoxy/hardener ratio has been used (which is near the technically recommended ratio).

By measurement of particle size in emulsions obtained in different regimes (with and without continuous stirring), two characteristic sizes of disperse particles were found in liquid epoxy/waterborne hardener emulsions: "secondary" particles (200-400 nm), produced due to a self-emulsification process from the rough primary particles, produced by the forced emulsification, and aggregates of the secondary particles (ca. 3000 nm).

A simple method was used to evaluate the result of interfacial processes: formation of a cured epoxy film on an undisturbed interface. A thicker interfacial layer of emulsion is a reflectance of effective self emulsification, and the thickness of an insoluble film is a proof of well-balanced emulsifiability.

Functions of co-solvents and co-emulsifiers are discussed to promote their well-grounded selection for paint compositions. A well-known effect of performance deterioration for the gloss waterborne epoxy paints after a few hours of standby before application (particularly, reduction of their gloss) that normally occurs well before the paint gels, should be explained as a result of reduction in colloid stability, early aggregation, and restricted particle coalescence.

A properly selected liquid epoxy resin, water-thinnable hardener, amount of additives (particularly co-solvents and co-emulsifiers), and a properly timed application are needed to provide a reliable emulsification of liquid epoxy resins, an acceptable pot life, and a stable performance for epoxy waterborne coatings.

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