Going from strength to strength

New additive improves performance in several key properties

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A new type of additive has been developed with the aim of enhancing several key properties of two-pack epoxies simultaneously. Flexibility, adhesion and corrosion resistance were all found to be improved. Some benefits could be obtained in the potlife to cure speed ratio.

Epoxy coatings are expected to have resistance to a wide variety of chemicals, outstanding corrosion resistance and adhesion to a wide range of substrates including poorly prepared metal surfaces and concrete. When developing new additives for the epoxy coatings market, it is important to keep in mind that any added ingredient can enhance performance in one area while detracting from performance in another. Also, current high performance products can be quite complex and adding a further new ingredient increases the complexity even more.

A good additive will target several aspects of an epoxy coating, seeking to improve two or three properties simultaneously in order to add value to the new raw material and reduce the complexity of existing formulations. But currently, separate raw materials are used to enhance adhesion to various substrates, improve corrosion resistance, aid in improving impact and bend properties, as well as improving gloss for aesthetic purposes.

These ingredients often do not complement each other. For example, adding low molecular weight low viscosity monofunctional epoxies can increase flexibility but reduce adhesion. Still other additives are used to lengthen potlife and shorten cure time, especially in cold weather, but this comes at the cost of colour and toxicity.

A current trend in the industry is to reduce VOC levels without impacting any other properties of a coating. In addition to this, the market requires thinner coats, while maintaining performance. Reducing VOCs in epoxy coatings is particularly challenging since the reduction of solvents generally leads to significant viscosity increases. This increase causes difficulty in mixing and application of these two-component systems.

In order to counteract this problem, lower viscosity, lower molecular weight resins are employed. These require more hardener to build molecular weight and cure, and the additional crosslinking in turn makes the cured coatings more brittle, reducing impact resistance and flexibility among other properties.

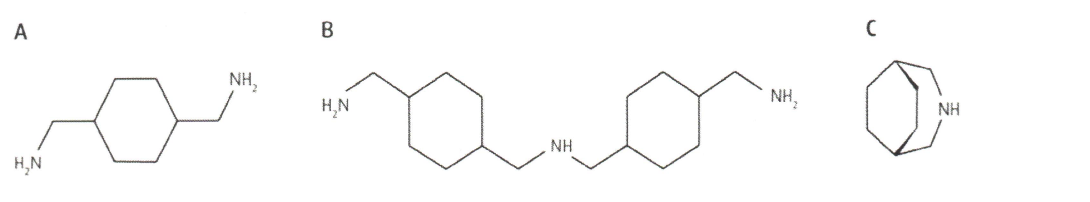
These epoxies also contain higher levels of functional groups requiring more of the costly hardener to cure. This not only increases costs but also increases the heat of reaction of the system, greatly reducing the workable potlife.

Table 1: Test formulations

Additive (g)	Solvent (g)	Epoxy (g)	Hardener (g)	Sample size (g)
0	10	74.6	15.4	100
15	10	62.2	12.9	100
30	10	49.7	10.3	100

Table 2: Cure times in hours for different solvents and additive levels

BA solvent	Control	15 % additive	30 % additive
Set to touch	2	1	1.5
Surface dry	3.5	3.0	3.5
Through dry	4.0	3.5	4.5
Xylene solvent			
Set to touch	4	4	4
Surface dry	6	6	5.5
Through dry	12	7	8
MEK solvent			
Set to touch	4	3	3
Surface dry	6	5	5
Through dry	24	6.5	6.5



1,4-bis (aminomenthyl) cyclohexane

Imino-bis (4-aminomethyl-4'cyclohexylmethyl) amine

3-azabicyclo [3.2.2] nonane

Figure 1: Components of "XTA 801" amine

Additive targets improvements in several properties

An ambitious project was therefore undertaken to develop a single multifunctional additive, allowing the removal of existing additives and enhancing final product performance. The base formulation was to be a simple low VOC system, consisting of a liquid epoxy resin and an adducted cycloaliphatic diamine. The following objectives were targeted:

» Develop chemistries to improve barrier properties to chloride ion migration, the key contributor to corrosion in harsh environments.
» Provide flexibility and impact resistance to a system that has neither of these.
» Maintain or improve adhesion.
» Introduce functionality that will improve potlife and cure time.
» The additive must also enhance aesthetics such as gloss or colour.
» No added VOCs.

Initial test results from this completely new additive are described below.

Experimental formulation details

A series of three mixtures was produced (*Table 1*). The level of additive was varied. Where applicable, the additive was added to the liquid epoxy resin. The solvent was then added and stirred for three minutes. Finally the hardener was added and stirred for an additional three minutes. The solvents employed in separate formulations were benzyl alcohol (BA), xylene and methyl ethyl ketone (MEK).

Amine adducts are widely used to cure epoxy resins. These adducts consist of amines reacted with an amount of epoxy sufficient to improve compatibility between the amine and the epoxy. The amine adduct used in the examples described below was composed of a mixture of four parts by weight of an amine ("XTA 801" from Huntsman, see *Figure 1*) and one part epoxy ("EPON 828" from Huntsman, see *Figure 2*).

The amine itself is a mixture of 1,4 bis-(aminomethyl) cyclohexane (60-100 %), imino-bis (4-aminomethyl-4'-cyclohexylmethyl) amine (13-30 %), and 3-azabicyclo[3.2.2] nonane (1-3 %), shown in *Figure 1* as A, B, and C respectively. The adduct was made by adding 600 g of amine to a large glass jar, followed by 150 g of the epoxy. This mixture was stirred for eight hours at room temperature. While this specific hardener composition was used for the examples below, this does not limit the types of adducts or other hardeners that can be employed.

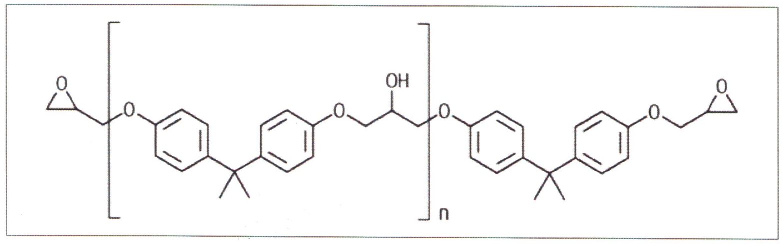


Figure 2: Bisphenol A epoxy based resin; n=0 for "Epon 828"

BA solvent	Direct impact (in. lb.)	Reverse (extrusion) (in. lb.)
Control	<5	<5
15 % additive	90	35
30 % additive	160	160
Xylene solvent		
Control	<5	<5
15 % additive	120	160
30 % additive	160	160

Table 3: Impact resistance of samples

BA solvent	Mandrel bend / inches / mm	
Control	1.5/38	fail
15 % additive	0	pass
30 % additive	0.25/6.5	Pass
Xylene		
Control	1.0/25	fail
15 % additive	0	pass
30 % additive	0	pass
MEK		
Control	1.0/25	fail
15 % additive	0	pass
30 % additive	0	pass

Table 4: Mandrel bend test results

	Crosshatch
Control	3B
15 % additive	5B
30 % additive	4B

Table 5: Crosshatch adhesion with BA as solvent

Results at a glance

››› Two-pack epoxy coatings are expected to meet high performance demands in many different applications. Reductions in VOC levels are increasingly demanded but pose difficulties because lower molecular weight and lower viscosity resins tend to produce brittle films.

››› Additives developed to enhance one set of properties may have adverse effects on other properties. A new type of additive has therefore been developed with the aim of enhancing several key properties simultaneously.

››› Experimental results are presented to show that flexibility, adhesion and corrosion resistance are all improved by use of the additive. In some cases, the additive increases potlife while providing slightly faster cure.

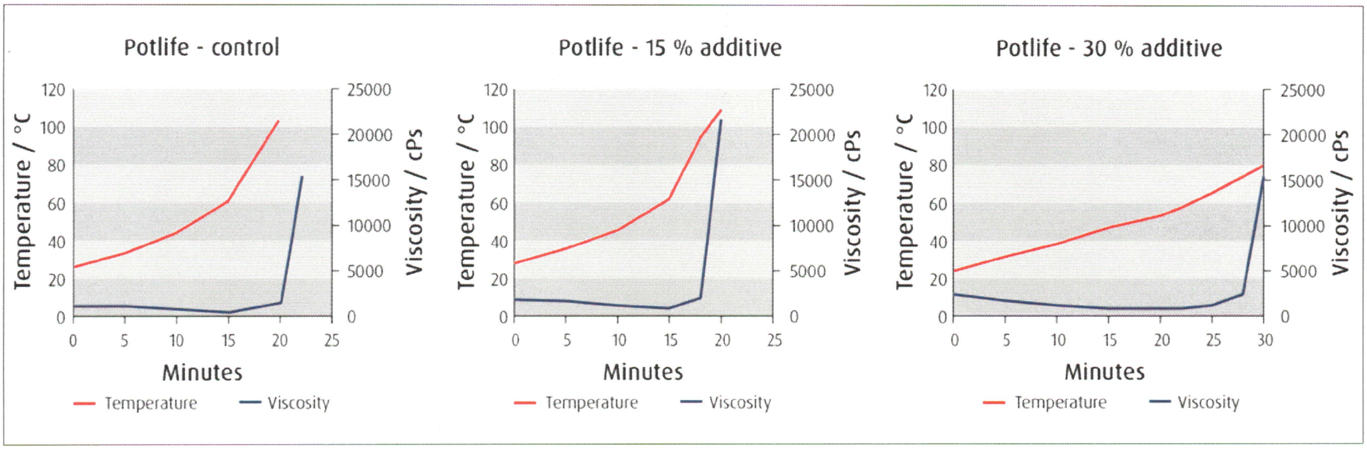


Figure 3: Potlife for formulations containing butyl acetate

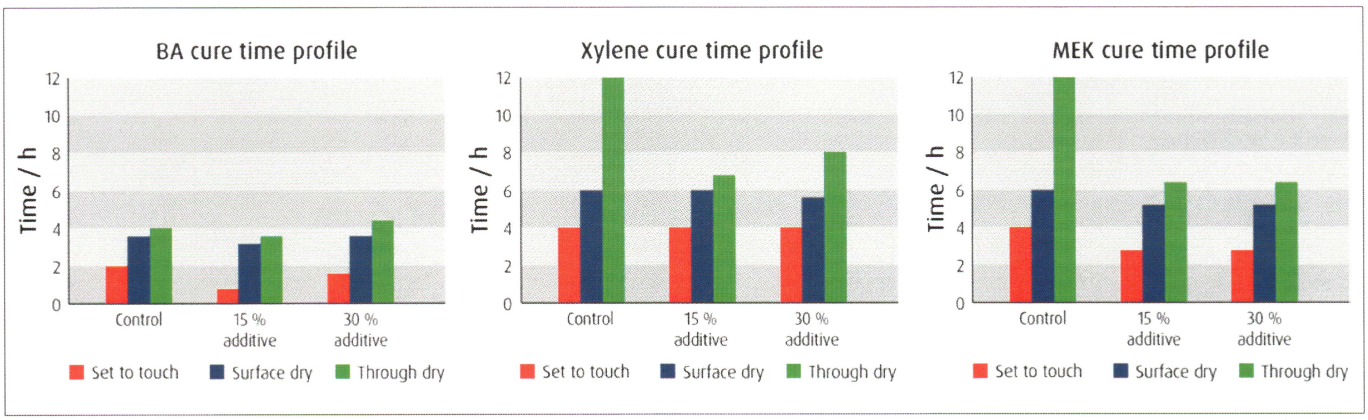


Figure 4: Cure time results with different solvents and additive levels

The generic epoxy formulations are shown in *Table 1*. The amine hydrogen equivalent weight (AHEW) for the hardener was 48.6 while the epoxy equivalent weight (EEW) for the epoxy was 188. The hardener to epoxy ratio (AHEW/EEW) was 0.8. The various solvents mentioned above were used as appropriate. Standard test panels were made by applying the epoxy mixture to a 0.8 x 76 x 127 mm cold rolled steel panel ("R35" test panel from Q-Lab) using a drawdown bar. They were then cured for seven days at 23 °C and 50 % relative humidity.

How potlife and curing rates were measured

The potlife of each system was measured as follows. The appropriate levels of epoxy and hardener were mixed for three minutes. The viscosity and temperature was recorded initially and then subsequently every two to five minutes. The potlife was defined as the time required for the temperature to reach 70 °C (though in some cases the temperature did not rise to 70 °C). The viscosity was measured using a "Brookfield RV" Digital Viscometer. The #6 spindle was used and set at 6 rpm to minimise any shear thinning effects. A digital thermocouple was used to measure the temperature.

Cure times were determined using a BK drying time recorder. The epoxy mixture was drawn down on an acrylic surface using a 150 µm drawdown cube. The recorder was set for 12 hours and samples were evaluated in duplicate. The needle sliding across the sample over the 12 hour period creates characteristic data for each sample. Explanation of the different phases is as follows:

Set to touch: When the tendency of the epoxy mixture to flow has ceased, the film may be considered set to touch.

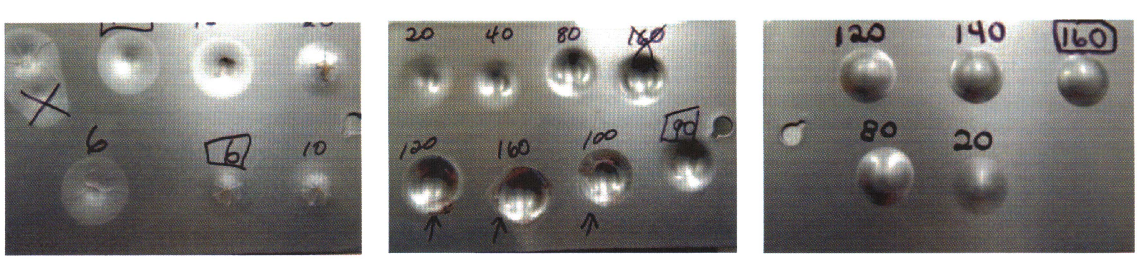


Figure 5: Impact resistance of sample containing BA solvent with test values shown in inch-pounds

A thumb print will show on the surface, but no epoxy will come off on the thumb.
Surface dry: As the drying process continues, a skin will form. Visually, this part of the film formation is seen when the stylus begins to tear the surface of the film. The film may be considered surface dry or dust free when the skin is no longer ruptured by the stylus.
Through dry: Coatings are considered through dry when the stylus rides above the film.

Impact and flexibility test methods summarised

The Conical Mandrel bend test is used to measure flexibility. This test was performed on the epoxy coated panels after seven days' cure according to ASTM D522-93a. The mandrel bend numbers are equivalent to the diameter of a rod around which the coated panel could be bent without cracking or delamination of the coating. Lower numbers thus indicate higher flexibility.
The panels were impact tested according to ASTM D2794-93. Cracking and delamination were recorded at the point of impact. Both forward (intrusion) and reverse (extrusion) indentations were evaluated. A coating was labelled as brittle if cracking or delamination was observed at less than 6 in.-lb.
The crosshatch adhesion was tested according to ASTM D3359-09. Coating samples were evaluated in duplicate. Adhesion was rated according to this ASTM method where 5B is no detachment, and 0B is almost complete detachment.

Corrosion resistance tested by salt spray exposure

Standard test panels were made by applying the epoxy mixture to the same cold rolled steel panels as for the other tests. For each mixture, duplicate 125 to 175 µm coatings were made on the test panel using a drawdown bar and allowed to cure for seven days at 23 °C and 50 % relative humidity.
Corrosion test panels were made by backing these test panels with white Rust-Oleum "Clean Metal Primer". The primer was allowed to dry for two days before the unprimed side of the test panel was coated with the epoxy/hardener mixture.
The corrosion resistance of each coating was tested after taping the edges of the coated samples with black electrical tape to prevent edge penetration of salt water. A single line was scribed vertically on the bottom half of the coated test sample with a razor blade.
The samples were placed into the salt fog box with the internal chamber temperature set at 35 °C and the saturator temperature at 47 °C with a spray rate according to ASTM B117-09. The samples were oriented with the test paint facing towards the atomiser and spraying was commenced. Salt spray was continued for 1056 hours (44 days).

Potlife extended, though cure can be faster

It is important to understand the effect of additives on potlife. Any additive that increases or at least maintains

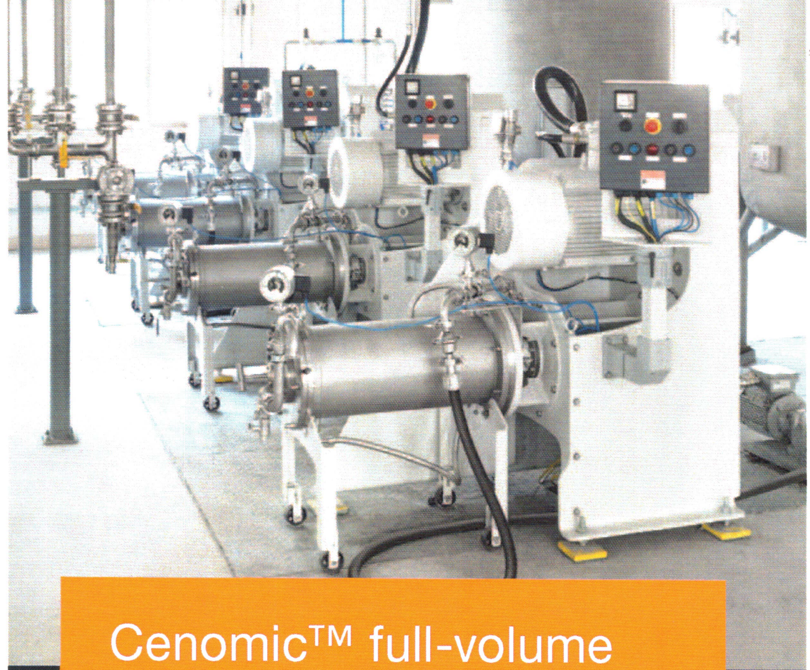


Table 6: Corrosion results at 1056 hours ASTM B117 using BA as solvent

	Blister at scribe	Frequency of blisters	Rust type	Surface coverage (%)	Scribe delamination (cm)
Control	4	medium dense	general	90	Complete delamination
15 % additive	4	medium	spot	5	1
30 % additive	none	none	spot	0.03	0.1

Table 7: Gloss with two different solvents

20 °gloss	BA	Xylene
Control	96	91
15 % additive	110	114
30 % additive	113	114

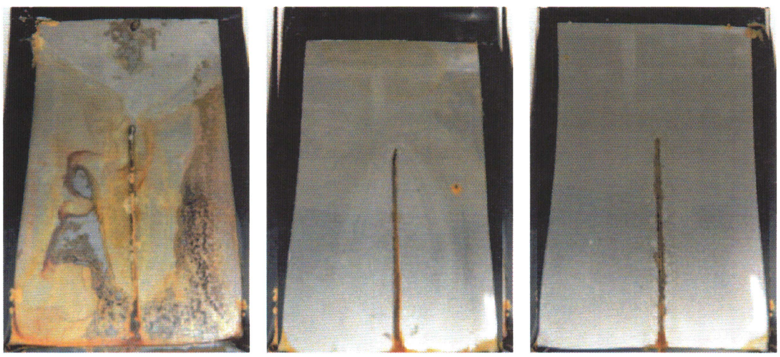


Figure 6: Salt spray corrosion testing results

potlife while simultaneously improving cure time properties is advantageous. The data shown in *Figure 3 (a,b,c)* indicate that the potlife for the control (no additive) and the formulation containing 15 % additive are similar.
The potlife for the formulation containing 30 % additive sample is considerably longer. A longer potlife allows the applicator more time to apply the coating before the epoxy becomes too viscous to flow. It is apparent based on the data in *Table 2* that the cure time is not significantly affected by the addition of any level of additive for the system with butyl acetate (BA) as solvent.
BA is known for its ability to compatibilise epoxy/amine systems, leading to consistent cure times (see *Table 2* and *Figure 4*. This is important since the cure time can affect productivity if it is increased significantly. For both the xylene and MEK systems, the addition of the additive greatly improves through dry time.

Flexibility and adhesion are improved

The results of the impact testing on samples using BA or xylene are shown in *Table 3*. Pictures of the BA impact test results are also shown in *Figure 5*. The maximum impact that can be recorded by this method is 160 inch-pounds. While the cured epoxy coating samples with no additive recorded less than 6 inch-pounds and are brittle, the samples with 15 % and 30 % additive had greatly increased impact resistance.
Mandrel bend flexibility is a function of the ability of the film to elongate as well as its ability to adhere to the substrate. The results of the mandrel bend test are shown in Table 4. Increasing the additive increased the flexibility dramatically while maintaining adhesion to the cold rolled steel substrate. This was made possible due to the unique functionality incorporated into the backbone of the additive molecule.
The results in *Table 5* show that the additive increased the adhesion of the coating. This is expected, since in both the impact resistance testing and the mandrel bend test, the adhesion of the coating to the substrate was enhanced as well.

Corrosion resistance and gloss also enhanced

The results of the corrosion testing are listed in *Table 6*. Note that the blister at the scribe is rated from 2 to 8 with the larger numbers indicating larger sizes. It is apparent from the table that the frequency of blister, the rust type, surface coverage, and scribe creep, all improve with increasing levels of additive. Pictures of the panels are also shown in *Figure 6*.
The gloss was measured at 20 ° on the coatings over cold rolled steel. It is apparent that the gloss is considerably enhanced with the addition of the additive (*Table 7*). While not measured, visual observation indicates that the composition of the additive is such that it significantly enhances the smoothness of the surface, dramatically increasing the Distinctness of Image (DOI).

Additive provides high flexibility in formulation

The objectives for the project were exceeded. An additive that improved potlife and cure time was obtained. The same product also provides greatly enhanced flexibility, impact resistance and outstanding corrosion resistance with excellent adhesion. It also provides significantly improved gloss, and enhances clarity or DOI.
The product can be added to the A and/or B side of a coating formulation, allowing for adjustment in the relative size of A and B sides for better mixing ratios. It is easy to formulate and improves the performance of 'poor' solvents such as xylene or MEK.

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