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REACH-COMPLIANT KETAMINE EPOXY HARDENERS

A new generation of curing agents outperforms predecessors both during and after cure. By Paul Jones, Bitrez Ltd.

When it comes to searching for the ideal curing agent for epoxy resins, we're all after the holy trinity: long pot-life, reduced hazards and technical enhancement. Be it coatings, adhesives or composites, epoxy resins are used in a myriad of applications serving countless market needs. Whether formulated as single component high latency systems for elevated temperature cure or as multi-part systems offering a broad range of processing options, it's safe to say the versatility of this resin chemistry is unprecedented.

Whilst homo-polymerisation may be used as the means of transforming the epoxy functional material into a cured state, crosslinking with a co-reactant is more common. Co-reactants may include phenols, amino or anhydrides but amine and amine derivatives form the largest generic group. These amines are modified in many ways to improve technical, regulatory and commercial performance that encompass adduction, amido-amines and polyamides, Mannich bases, associated salts and other modifications.

KETAMINES

One other such alteration that has been used is the formation of a ketamine through the dehydration of a primary amine group with a ketone as depicted in *Figure 1*. The resultant ketamine demonstrates stability, if not exposed to atmospheric moisture, but as the reaction is reversible, when combined with the epoxy component and applied, the ketamine is hydrolysed, liberating the functional amine and ketone components. The regenerated ketone is a volatile released from the film and the original amine has active hydrogen groups that can react with the epoxy component in a conventional manner.

Ketamine curing agents are unusual insofar as they have non-linear reactivity profiles. This means they provide excellent pot-life whilst also having fast thin film cure speeds. Historically, conventional ketamine curing agents derived from short chain ethylene amines have offered desirable performance properties, but the liberated amines are generally of a low molecular weight with high vapour pressure and ensuing safety concerns. Indeed, resin manufacturers were recently forced to withdraw conventional ketamines from their product range in Europe because of REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) compliance.

A LEAP FORWARD

We have developed a new range of ketamines that offer the desirable pot-life/reactivity characteristics associated with this class of curing agent but liberate amines of a lower hazard classification. This series is offered as solvent-cut or solvent-free materials – meaning the solvent has not been added post production. Instead, the ketamine itself contains the inherent volatile that is to be liberated to allow the curing to occur.

RESULTS AT A GLANCE

New ketamine epoxy hardeners

- are REACH-compliant.
- technically outperform their conventional counterparts both during and after cure.
- offer long pot-life.
- offer reduced hazards.

Designed first and foremost for regulatory compliance, these new ketamine curing agents also reduce the hazard rating during application and some of the problems associated with free amines. Consideration was also given to residual free monomer levels. Although designed to function through reaction with atmospheric humidity, these new ketamine curing agents are less prone to problems associated with humidity during cure. When hydrolysing, conventional ketamines liberate ethylene amines that are prone to compatibility issues with conventional epoxy resins; this can lead to surface migration or exudation of free amine to the coating surface. Surface migration of amines can cause at best reduced gloss or in some cases tacky/greasy surfaces which in turn result in 'amine blush' or 'amine bloom'. These two phenomena are well documented but essentially consist of moisture condensing or water-soluble compounds migrating to the surface of the coating. The moisture can react with CO_2 and subsequently form ammonium carbamate by-products. Aside from the negative impact that this has on the aesthetic appearance of the film, these side reactions can alter the formulated stoichiometry resulting in an imbalance of the desired reaction. This in turn potentially reduces the mechanical properties and chemical resistance.

However, the new generation of ketamine grades offers enhanced epoxy compatibility. An added benefit is that some grades have been modified to enhance thin-film cure rate to further protect against the above problems.

To test conventional ketamine against the new generation ketamines, we carried out a number of laboratory tests. For comparative purposes we took a ketamine that has been commercially available from several sources, derived from diethylene triamine [DETA] and methyl isobutyl ketone [MIBK] and referenced it as K1 (*Figure 2*). This was bis[2-(1,3-dimethylbutylideneamino)ethyl] amine (CAS 10595-60-5).

The conventional ketamines that we used were an EDA [ethylene diamine], K2, and another DETA-based variant, K3. The new and novel ketamines were formulated to satisfy REACH regulations

and provide enhanced performance whilst eliminating the less attractive aspects of the conventional grades.

REGULATIONS AND LABELLING

Regulatory considerations include the registration requirements for the low poly-dispersity (PD) structured conventional ketamine and the hazard classification.
For conventional ketamine K1, we can detail the components as follows: ketamine K1 in its supply form has a free monomeric DETA level of around 2-5 % subject to the supplier specification, process used and subsequent storage conditions. With exposure to moisture the reaction liberates further DETA for reaction purposes. The ketamine reversal reaction liberates approximately 35 % monomeric DETA.
One version of the new ketamine epoxy curing agent range has been formulated so that the initial free amine level is <0.2 % as supplied; following the ketamine reversal reaction <2 % monomeric DETA is released, as analysed on hydrolysed product.
Labelling is a key issue (*Figure 3*). This reversal reaction means consumers and formulators may be left with technical and moral dilemmas regarding label requirements/advisory information as clearly the product supply label for a conventional ketamine is based on the free amine as supplied. However, knowing that on application the product hazard increases (albeit only until cross-linking occurs/completes), the label may warrant explanatory discussions with applicators who may become exposed to a product listed as potentially being fatal on inhalation.

The new ketamine curing agents have low free amine levels both upon supply and following hydration, so remain more consistent in terms of the hazards associated with corrosive amines. Of course, in either case the products liberate the solvent as a volatile component. With the introduction of GHS, the threshold limits and reporting requirements for free monomer levels were adjusted. The escalating hazard rating for free DETA is as shown in *Figure 3*.

THE NEXT GENERATION

From a technical perspective, the new ketamines offer significant performance improvement whilst maintaining desirable reactivity characteristics. For illustrative purposes *Figure 4* shows the relative reactivity of small-mass cure and thin-film cure rates using DETA and conventional Ketamine K1 as benchmark values against one of the new generation grades.
Figure 4 shows how the new generation of ketamine curing agents significantly improve working time/pot-life whilst maintaining desirable high thin-film reactivity. Alteration and extension to pot-life is the main design driver for this generic product group and the new ketamines satisfy that aspect as expected. Whilst they work just as well in this respect and in addition to the regulatory improvements outlined above, it is their technical performance, both during and after cure, that really sets them further apart from their analogous predecessors.
It is evident that poor compatibility, exudation and surface migration of free amine can result in blushing and blooming issues which offer

Figure 1: Ketamine formation. X = variable chain length and possibility of further functionality.

$$H_2N - [CH_2]_x - NH_2 \ + \ 2RR'\,C{=}O \ \underset{-2\,H_2O}{\rightleftharpoons} \ RR'\,C = N - [CH_2]_x - N = RR'$$

Figure 2: "K1" ketamine example.

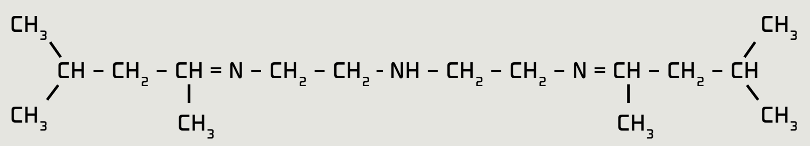

Figure 3: New ketamine label requirements [context: amines].

Labelling requirements for DETA-containing products			
Concentration range %		Labelling requirements	
Lower	Upper	Pictogram code[s] / Signal word	Hazard statements
00.00	< 00.10	None	None
00.10	< 00.20	None	EUH 208: contains 2,2 iminodiethylamine. May produce an allergic reaction.
00.20	< 02.00	None	EUH 208: contains 2,2 iminodiethylamine. May produce an allergic reaction.
02.00	< 05.00	 GHS 05/GHS06	H302 [Harmful if swallowed]
			H330 [Fatal if inhaled]
			H314 [Causes severe skin burns and eye damage]
			H317 [May cause an allergic skin reaction]
			H335 [May cause respiratory irritation]

aesthetic concerns, but the cosmetic defect is more an illustration of the fact that the intended or desired reaction hasn't fully occurred. These problems can also influence overcoatability and subsequent inter-coat adhesion which in turn can alter mechanical properties and chemical resistance. *Figure 5* shows surface films following the reactivity evaluation described here.
These new ketamine grades offer enhanced compatibility and vary in terms of their surface appearance from a moderate improvement to the surface film to a significant advance based on selected grades from within the range. The new ketamine grades are offered in several supply forms with some high solid content grades diluted with ketone and/or aromatic solvents or supplied free from any supplementary solvent – meaning they are supplied solvent-free but acknowledging the solvent inherently generated following hydration.
The stoichiometry differs from some of the conventional ketamine grades as do some of the viscosity values, but the resultant mixed viscosity tends to be similar. Increased active hydrogen equivalent weights [AHEW] call for increased curing agent addition. This in turn generally results in lower viscosity in the mixed system.
These grades can be used as curing agents in their own right or combined with other grades to formulate systems with bespoke reactivity and other process or cured performance attributes. For the coatings industry, the new kids in town really are a cut above.

Figure 4: Reactivity.

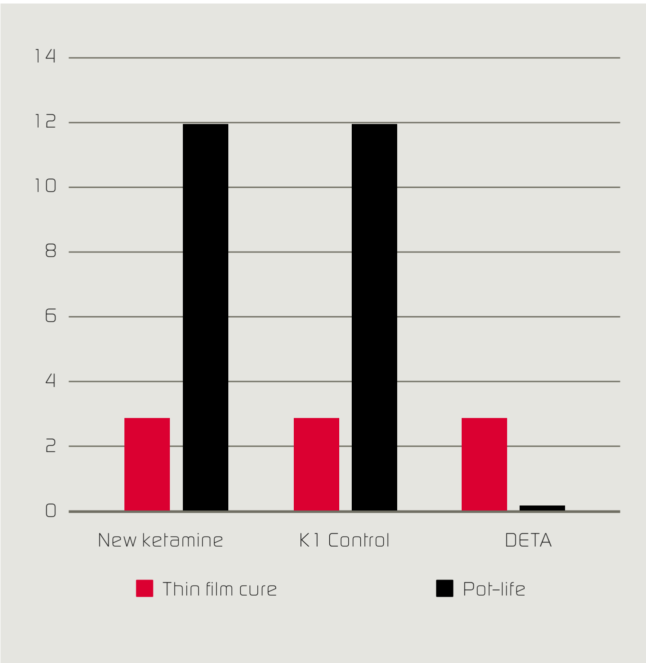

Figure 5: Surface films after reactivity evaluation

Grade	Comments
DETA	Greasy surface – susceptible to blushing issues
K1	Greasy surface – susceptible to blushing issues
New ketamine	Clear glossy surface

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"Limited to high solids."

3 questions to Paul Jones

Why have there been safety concerns regarding conventional ketamines? *They have high free amine content and on exposure to atmospheric moisture generate very high free amine levels [>2 % is fatal by inhalation.*

What is meant exactly by "enhanced epoxy compatibility"? *When mixed the old ketamines don't mix very well with epoxy and the surface has a "greasy" appearance whereas the new series is smooth and glossy.*

Can the new ketamine epoxy hardener be used for any application? *Where does it reach its limits? Many high solids coatings requiring longer open times and ketamines are perfect for this. They are limited to high solids [rather than solvent-free] systems and require >30 % atmospheric humidity to cure.*