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HARDENER FOR ULTRA-FAST CURING EPOXY COATINGS

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HARDENER FOR ULTRA-FAST CURING EPOXY COATINGS

Meeting market demand for high-performance and EH&S-compliant curing agents. By Dr Asli Capan, Evonik Operations.

Changes to the classification of raw materials have led to developments in hardener technology to meet evolving market needs. An ultra-fast curing agent with robust performance provides comparable or superior properties for multi-component epoxy coatings. The technology was developed to provide rapid curing at low temperatures, avoid substances of high concern and enhance the protective properties of the final coating.

In recent years, the demand for EH&S-friendly (EH&S = Environment, Health & Safety) solutions in the coatings industry has surged, driven by stringent regulatory requirements. The market is now more focused on adopting technologies that not only deliver superior performance but also have minimal toxicity impact. This shift is particularly evident in the development of curing agents for epoxy coatings, where innovations in curing technologies are being driven by market demands for eco-friendly solutions with high solids content and superior EH&S profile. These advancements are crucial for enhancing productivity and efficiency, especially in industrial applications where quick turnaround times are essential. Furthermore, the ability to achieve fast curing at lower temperatures without compromising performance is a significant advantage, reducing energy consumption and operational costs. There is also a significant push for technological advancements that deliver superior performance through improved corrosion resistance and improved productivity with an emphasis on minimising downtime and achieving faster cure rates, especially at low temperatures. This paper explores the innovative solutions developed to meet these market demands, focusing on new high-solid amine curing agent technology designed for ultra-fast curing in multi-component applications.

PROTECTIVE COATINGS SUBJECT TO COMPLEX REGULATION

For protective coatings, there is a growing need for high-performance hardeners that not only offer rapid curing speeds but also conform to environmental standards. Shortening the application time boosts manufacturing productivity, leading to greater efficiency and profitability, especially in industrial applications where quick turnaround times are necessary. Employing systems with shorter curing times can also cut down on energy consumption. The capability to use epoxy systems with fast-curing properties enables their application in scenarios where time is a critical factor.

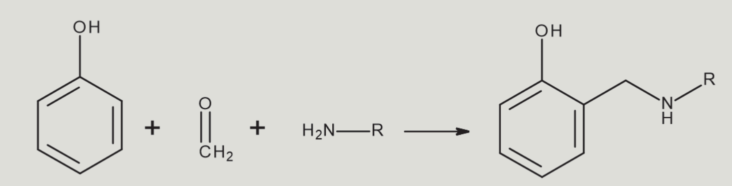
RESULTS AT A GLANCE

- → Stringent regulatory requirements are driving the demand for high-performance eco-friendly, health and safety-compliant solutions, particularly in curing technology for epoxy coatings.
- → A new high-solid curing agent for multi-component spray applications provides ultra-fast curing.
- → It also provides excellent hardness development at low temperature and resistance to carbamation, corrosion and chemicals.
- → The novel curing agent prioritises environmental responsibility while offering enhanced performance without compromising functionality or protection.

Table 1: Typical properties of the new high-solid curing agent.

	23 °C	5 °C
Loading (PHR for EEW 190)	40	
Solid content in %	80	
Viscosity in mPa.s	2000	
Gel time in min	13	
Thin film set time in h	2	4.5
Carbamation resistance water drop 1h / wet patch 1d	5/5	5/5
Pore resistance in Ohm	10^9	

Figure 1: General representation of a Mannich base synthesis.



Typically, Mannich bases or accelerators are used to ensure fast cure in epoxy systems, and although this can improve curing speed, these systems also bring some disadvantages. Mannich bases are obtained via the reaction of a phenol derivative (phenol, cresol, nonylphenol, t-butylphenol...etc) with formaldehyde and an amine (*Figure 1*). Because of the acidic hydroxyl group on the phenol ring, they have fast curing properties at low temperatures down to 0-5 °C. However, Mannich bases often show low blush and carbamation resistance, as well as suffering from exudate and low flexibility. Moreover, these products contain differentiating portions of free phenols, either as impurity or intentionally kept in order to remain liquid at room temperature. Additionally, phenol is a toxic material so products that contain phenol require special personal protective equipment, careful disposal and exhibit an unfavourable EH&S profile [1].

Several chemicals can be used to accelerate the crosslinking reaction between epoxy and amine. Widely known examples are tertiary amines, alcohols, organic acids like salicylic and benzoic acid, phenols and water [2]. Although this approach can be beneficial in terms of cure speed, using accelerators can cause higher costs, solubility problems and regulatory concerns because of the toxicity.

Besides fast cure speed, EH&S-friendly solutions are increasingly required in the protective coatings market. The classification, labelling and packaging of substances and mixtures (CLP regulation) is updated regularly through an "Adaptation to Technical Progress" (ATP). In 2018, ATP 13 was published, introducing new regulatory classifications for chemical substances. Salicylic acid, a widely recognised organic acid accelerator phenol derivative, was one of the substances classified as suspected of causing harm to the unborn child [3]. With this new CMR (carcinogenic, mutagenic, or reproductive toxicant) classification, salicylic acid is considered to be a substance of high concern due to its low EH&S profile for the consumers, and this imposes restrictions on its use as a raw material in epoxy hardener technologies.

Every country uses regulatory rules to identify hazardous chemicals and substances of concern to inform users about their health and environmental impact. In recent years, regulations affecting the chemicals that can be used in the marine and protective coatings industry have became more restrictive worldwide. Since awareness has increased, especially regarding the negative health effects, formulators now avoid using substances of high concern in new product developments.

Therefore, there is a market need for ultra-fast curing agents with robust performance, and a good EH&S profile, which also offers a good balance of viscosity and corrosion resistance. To address these needs, we developed a new high-solid amine curing agent for ultra-fast curing in multi-component or 'twin feed' applications. Crucially, this technology doesn't contain any substances of high concern and can be globally registered.

UNIQUE COMBINATION OF BENEFICIAL PROPERTIES

The new high-solid curing agent ("Ancamine 2844") for multi-component spray applications provides an ultra-fast curing property with very good hardness development at ambient temperature and 5 °C with excellent carbamation resistance, as well as corrosion resistance of up to 3000 h in salt spray (*Table 1*).

The new curing agent has been designed to provide a 40 PHR loading with a standard liquid epoxy resin (LER). The product offers superior performance with low consumption level, not only with fast curing properties but also with good barrier properties and corrosion resistance. We investigated the barrier properties of the clear coat using electrochemical impedance spectroscopy (EIS), where the pore resistance (Rp) was above 10^9 Ω, obtained following 24 h of exposure to an aqueous salt solution, indicating excellent all-round corrosion resistance.

HARDNESS DEVELOPMENT AND DRYING SPEED

A pendulum hardness test was performed according to the ISO 1522 test method. *Figure 2* shows the results at different temperatures. As an indication of fast property development, at 23 °C an epoxy resin mixture containing the new hardener reaches a high level of hardening (360 Persoz) in 24 hours which corresponds to full through cure. When measured at 5 °C, the mixture hardens to 170 Persoz within 24 hours, then increases gradually and continues to full hardening within 7 days (*Figure 2*).
We evaluated drying speed at 23 °C and 5 °C using the thin film set time (TFST) method. The results indicated a drying time of 2 hours at 23 °C and 4.5 hours at 5 °C. Additionally, the thumb twist test, another method for determining drying speed was employed in accordance with ASTM D1640 standards. The test revealed that the film surface did not retain any fingerprint marks when tested after two hours of drying at room temperauture (*Figure 3*).

RESISTANCE TO CARBAMATION, CHEMICALS AND CORROSION

The carbamation resistance test was conducted according to the ISO 2812-3 wet patch method. Films of a Type 1 liquid epoxy resin (LER) mixed with the new high-solid curing agent cured in 24 hours at 60 % relative humidity before the wet patch was put on and no carbamation was observed on transparent film.
We also tested the chemical resistance of the novel curing agent against the standard modified cycloaliphatic amine hardener via immersion test according to the ISO 2812 method. 10 g pucks of 5.5 cm diameter were prepared with the Type 1 LER–new curing agent mixture, cured at 23 °C for 7 days, and then immersed in different chemicals for 28 days. The chosen chemicals were polar and apolar organic solvents, acidic and basic solutions. We also measured the reduction or uptake in weight (*Figure 4*), and the change in Shore-D hardness.
When measured as % weight uptake, the novel curing agent showed only a slight change in weight in most of the chemicals that were used for immersion, with comparable results to a modified cycloaliphatic amine hardener, with the exception of alcohols. In ethanol, the novel curing agent demonstrated bet-

Figure 2: Hardness development of LER-curing agent mixture at 23 °C and 5 °C.

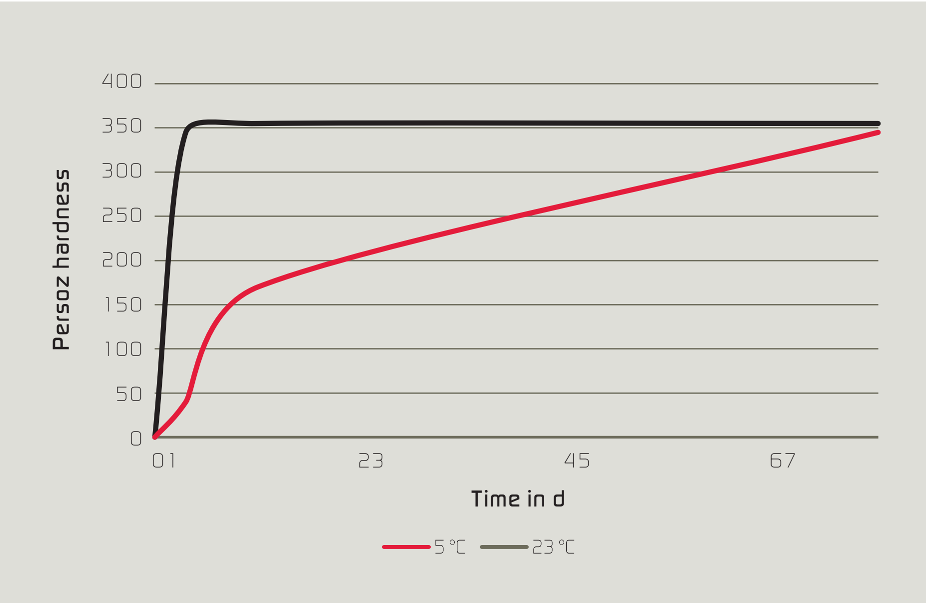
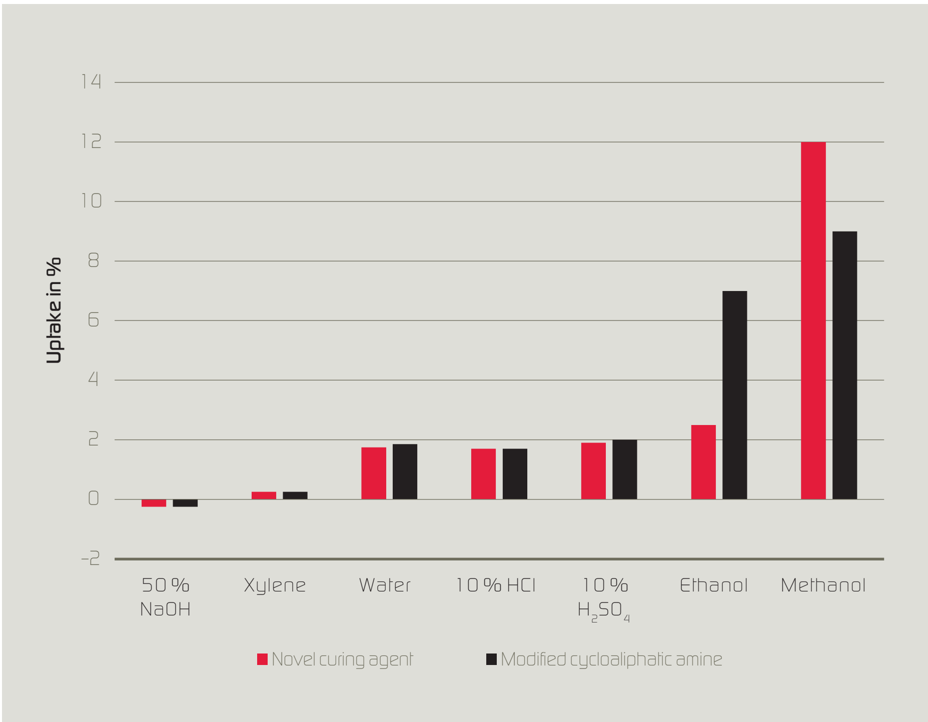


Figure 3: Thumb twist test after 1.5 h and 2 h respectively.

Figure 4: Novel curing agent vs. modified cycloaliphatic amine comparison for % uptake hardness change after 28 d chemical immersion.



ter chemical resistance than the comparison while both resistances drop significantly in methanol.
Chemical resistance results were similar when prepared pucks of the new curing technology with Type 1 LER were checked for Shore-D hardness after 28 days of immersion. While the Shore-D values of the pucks with the new hardener changed by less than 5.5 %, pucks of cycloaliphatic amine hardener showed a drastic decrease of hardness, with the exception of methanol, which affected both systems negatively.
We tested the corrosion resistance of the new curing agent using a mixture of formulated epoxy coating for corrosion resistant applications in salt spray chamber tests according to the ASTM B117 method. We used a coating recipe containing 33 % Type1 liquid epoxy resin, 3.7 % monofunctional reactive diluent, 6 % zinc phospate anticorrosive pigment, 6 % iron oxide red pigment, 29 % fillers, 18.8 % solvents and 3.5 % performance additives for coatings. The proportion of the new curing agent used was 13.2 g in a 100 g A+B mixture. No blisters or rust were observed after 3000 hours of testing, proving a very high corrosion resistance when used for an anticorrosive coating (*Figure 5*).

USE AS AN ACCELERATOR

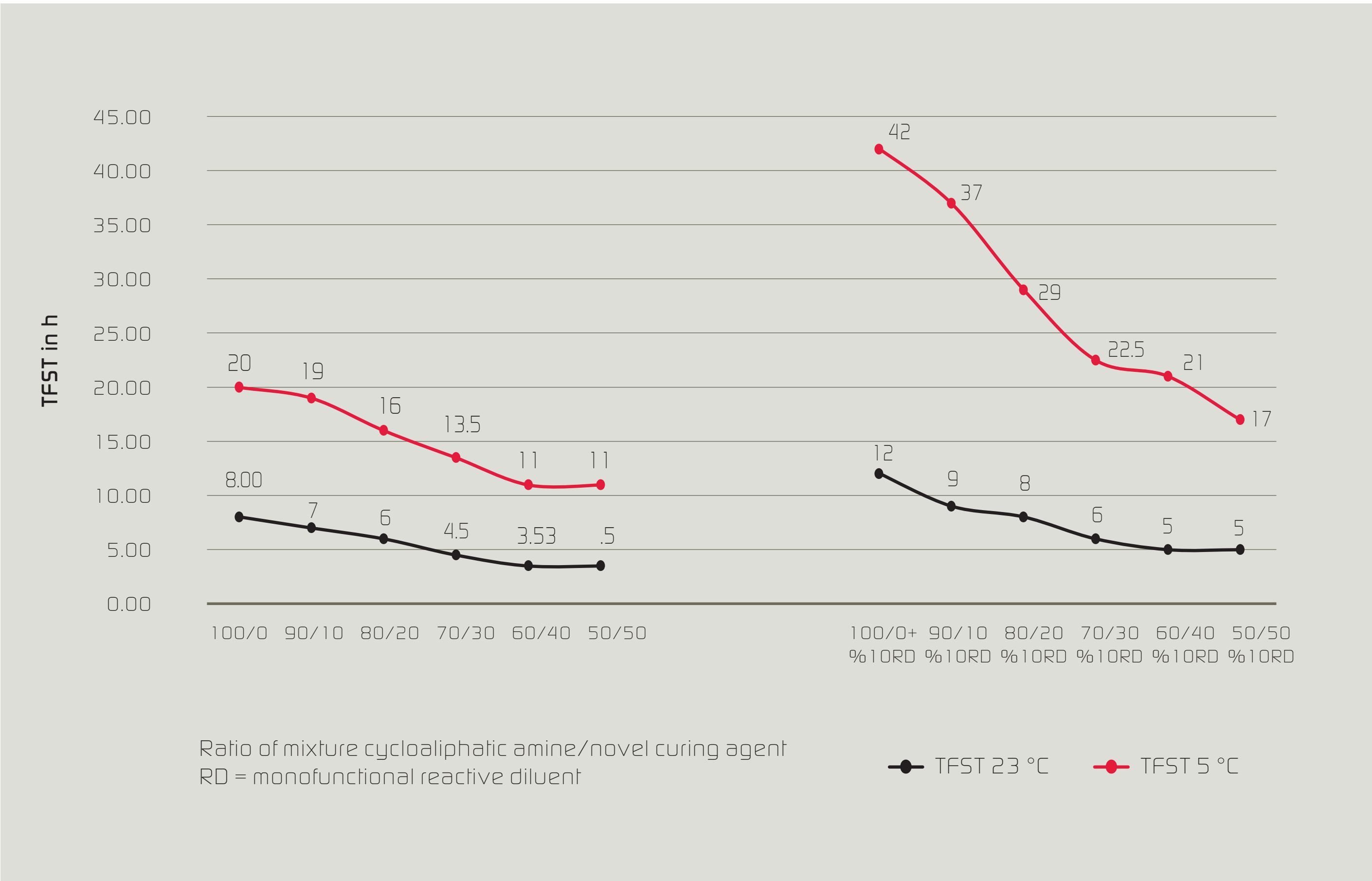
When used in a hardener mixture as an accelerator, the new hardener is effective starting from just 10 % addition (*Figure 6*). It can decrease the drying time of a standard cycloaliphatic amine from 8 hours to 3.5 hours at 23 °C, and from 20 hours to 11 hours at 5 °C with an addition of 40 %. An acceleration effect occurs without any negative impact on carbamation resistance, impact resistance or hardness development. The same test was conducted in a diluted system with a monofunctional reactive diluent at 10 %. Similar results were obtained with a decrease in the drying time from 12 hours to 5 hours at 23 °C, and from 42 hours to 11 hours at 5 °C with a 40 % addition. For each case, it is important to check the compatibility and long-term stability with the respective hardener.

COMPARATIVE ASSESSMENT VS EXISTING HARDENERS

The novel curing agent offers properties and performance that are comparable to typical fast-curing hardeners based on aliphatic amines. *Figure 7* highlights a performance

Figure 5: Salt spray test panel after 3000 h.

Figure 6: Acceleration effect of the new hardener when used in different ratio mixtures with a standard cycloaliphatic amine hardener (w/ & w/o reactive diluent, mixed with LER).

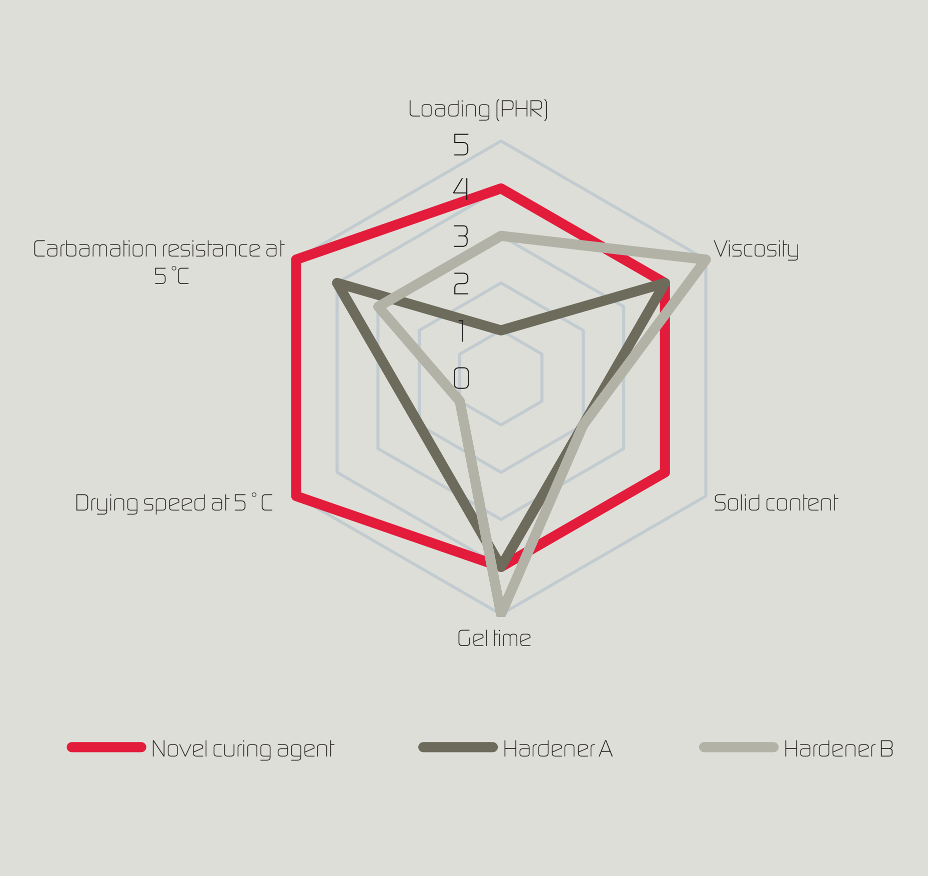


comparison with other fast-curing aliphatic polyamines. The innovative technology has the highest solids content at 80 % and offers a similar gel time and viscosity compared with the given examples, while the drying speed and carbamation resistance at 5 °C is distinctively enhanced with lower PHR, enabling low loading with the same amount of epoxy resin.

RAPID CURING WITHOUT SACRIFICING FUNCTIONAL AND PROTECTIVE QUALITIES

The novel high-solid curing agent was developed to align with the evolving market demand for ultra-fast curing epoxy systems that are suitable for multi-component applications. It boasts an impressive EH&S profile and high solids content, ensuring good overall performance properties. In particular, it provides robust corrosion and chemical resistance, along with excellent hardness development, even at low temperatures. As a versatile technology, it is capable of acting as both a primary curing agent and as an accelerator when mixed with other hardener systems to boost curing times without compromising the system's performance properties, enhancing productivity and efficiency across different applications. With its high solids content and robust EH&S profile, the new curing agent provides excellent hardness development and resistance to carbamation, corrosion, and chemicals. For optimal results, its suitability as a co-hardener for acceleration depends on compatibility with the respective hardener, gel time, and long-term stability.
This new product epitomises the industry's drive towards innovation in curing technologies that prioritise environmental responsibility, enhanced performance, and productivity, particularly in the realm of rapid curing at lower temperatures, without sacrificing the functional and protective qualities of epoxy coatings.

Figure 7: Comparison of novel curing agent with fast-curing epoxy hardeners.



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REFERENCES

[1] Walker F. H., Vedage G.A., Cook M.I., Rasing R.M.T., Air Products and Chemicals, Inc., Curing agent for low temperature cure applications, EP 2 108 668 A1, 14.10.2009.
[2] Lee H., Neville K., Handbook of epoxy resins, 1967.
[3] Annex VI to the 13th Adaptation to Technical Progress (ATP) to the CLP Regulation (Commission Regulation (EU) No. 2018/1480).