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SOLUTIONS FOR POLYURETHANE CAN COATINGS

By Dr Guido Streukens, Dr Marcel Inhestern, Dennis Menne and Dr Dörte Wessels, Evonik Operations.

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SOLUTIONS FOR POLYURETHANE CAN COATINGS

PU coating solutions for direct food contact and cosmetic packaging applications. By Dr Guido Streukens, Dr Marcel Inhestern, Dennis Menne and Dr Dörte Wessels, Evonik Operations.

Can coatings ensure zero interaction between a metal container and its contents and market the product with an appealing external appearance. Add regulatory requirements and to reduce solvent-borne systems and efficient processing demands into the mix and the options become limited. A new range of innovative hardeners for PUR powder and liquid coatings present a viable solution and the resulting coatings offer performance to compete epoxy-based systems.

Metal cans are a useful companion in our daily lives. Whether it is our daily use of deodorant, hairspray or the quick preparation of food or a refreshing drink, it's normally some kind of metal can we're holding in our hands. We are now so used to this everyday handling that we don't usually worry about the demands placed on the metal can and its wide range of uses. This starts with the variety of items that need to be stored safely inside the can – from deodorants to foods or drinks. Also, the material of the can differs from tin-plated steel (for food) to aluminium (for cosmetics). In addition, spray cans are pressurised with a propellant, whereas food cans often need to withstand aggressive chemicals for years while maintaining the quality and safety of the food.

Apart from these basic needs, most cans usually contain consumer goods and so also need to look appealing on the shelf and stand out against rival products, so the design and outer coating is also important. But even more important is the internal coating which is absolutely essential to ensure the safety of the product for human application or consumption. In both the cosmetic and food industries, this internal coating plays a vital role by helping to prevent any interaction between the metal container and the actual contents to be used. Nobody wants to enjoy foods that have taken on the taste of metal. And no metal can will survive the exposure to the acidic ingredients in some soft drinks for a prolonged period. So, a protective barrier between containment and can is crucial (*Figure 1*).

Not many chemistries can combine all these requirements, making the options for can coatings fairly limited. Today, there are stringent regulatory requirements, company commitments to reduce the use of potentially harmful materials, as well as intensified public discussion and awareness of these issues and recycling. These have all resulted in a steady decline in the options available for using traditional crosslinking technologies for food and body contact.

EFFICIENT PROCESSING REQUIRES FAST CURING SPEEDS

Over the past decades epoxy-based systems have been the established industry standard in this sector as they offer drying times of seconds and an impressive performance. They enable very high crosslinking densities which ensures high chemical resistance and provides a reliable barrier between the contained liquid and the metal can.

Nevertheless, in recent years, many consumers have been avoiding plastic products containing the chemical BPA, increasing the public pressure to use alternative chemistries to epox-

RESULTS AT A GLANCE

- Food can coatings need to withstand aggressive chemicals and heat treatment, offer flexibility, and comply with stringent regulations.
- A novel crosslinker is using a novel blocking mechanism that enables faster cure speed and lower curing temperatures.
- Powder coatings present a solvent-free solution for manufacturers and now formulators have developed a PUR powder crosslinker with enhanced functionality.
- The newly developed crosslinker for powder coatings meets all the stability and regualtory requirements of the food industry.

ies. Consequently, today's cans use a variety of different coating chemistries, each tailored to the specific application. Apart from the final properties of the coating in terms of flexibility or resistance, the application performance also plays an important role. Due to the required production throughput, often very high curing speeds are required.
For instance, in beverage cans – probably the application with the highest production rates, efficient processing is key, and epoxy-based coatings are still widely used. In cosmetic aerosol cans, good compatibility with the propellent and high flexibility make polyamide-imide systems (PAM) a good alternative. Flexibility is important as all forming steps, i.e. the rolling of the neck, take place after the actual coating of the can and so the coating needs to withstand severe mechanical stresses during production.

IMPROVED PROCESSABILITY WITH NOVEL HARDENER

In food cans, the most challenging requirement is the need for high resistance to all kinds of foods. This means withstanding different acids or oils and other foods for a long period of time. Typical canned food products often require a shelf life in excess of 5 years. In addition, heat treatment during the preservation process adds to the resistance requirements of food can coatings. In this area, polyurethane-based coatings have gained more and more importance in recent years. A range of innovative hardeners for such coatings may present the solution.
Polyurethanes for can coatings are normally applied in a solvent-borne process and employ a chemically blocked crosslinker to allow for storage stable 1K coating formulations. "Vestanat B 1186 A" can be regarded as a standard curing agent for these applications, but we also present newer developments to further improve the processability or the carbon footprint of the product. With alternative blocking mechanisms, much higher reactivy and thus much lower curing times can be achieved.
Also, with "Vestagon EP-B1190" we present a food-contact compliant PUR powder coating hardener for the use in interior cans.

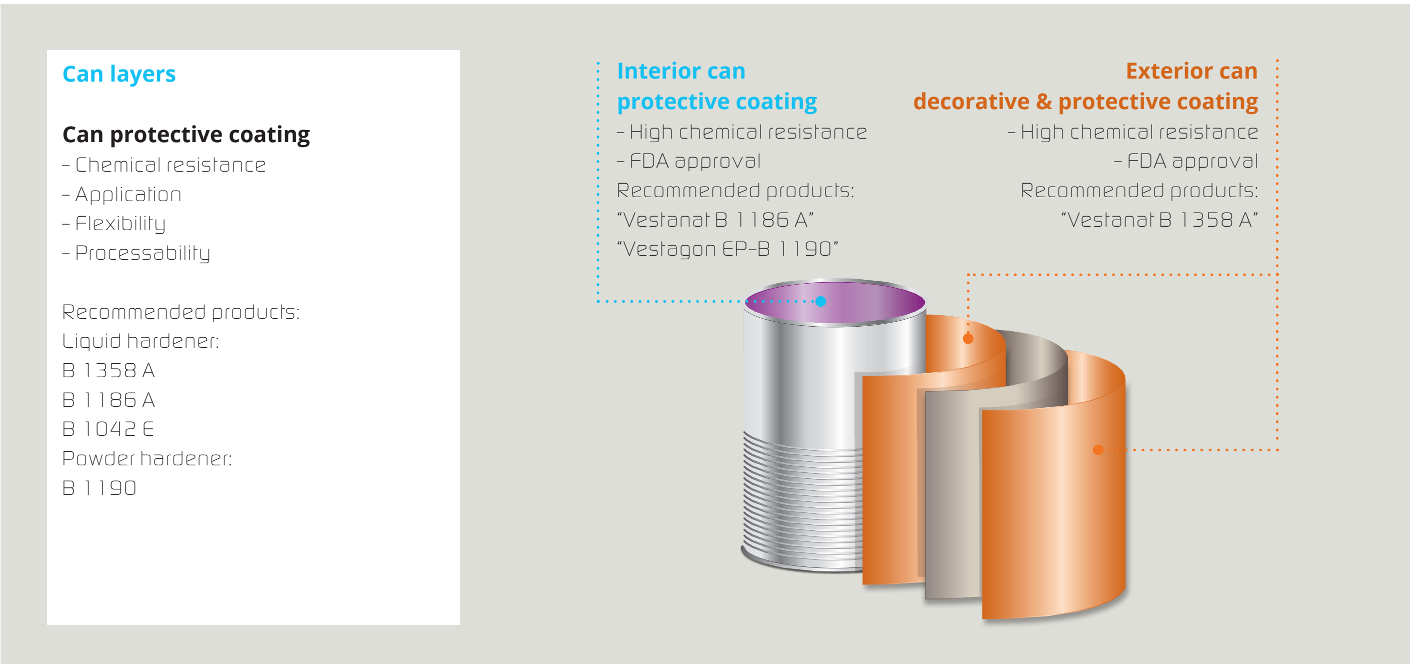
LIQUID 1K PUR CAN COATINGS

A high chemical resistance in coatings is usually induced by a very densely crosslinked network, but this can interfere with the requirements of providing a flexible coating.
The advantage of PUR coatings is that they offer a unique combination of both, chemical resistance, and flexibility. This is a unique property of polyurethanes in general. The urethane groups build up hydrogen bonds between the individual polymer chains. This allows for a less dense chemical network and thus higher flexibility while keeping a higher level of chemical resistance.
To prepare a typical PUR coating, e.g. for a can or a coil application, a hydroxy-functional polyester resin is crosslinked by an isocyanate containing hardener. Novel polyester resins allow for high coating flexibilities and are approved for the use in direct food contact. Optimum chemical resistance is provided using crosslinkers based on IPDI isocyanurates. In these grades, the use of blocking agents enables the formulation of storage-stable, heat-curable hardeners for 1K systems. The different blocking agents presented in the following differ for example in reactivity and food contact compliance.

BLOCKING AGENTS AND FOOD COMPLIANCE

Methylethyl ketone oxime (MEKO) is currently the most widely used blocking agent. MEKO offers a high reactivity regarding curing time and temperature (see purple line in *Figure 2*). Due to its toxicological profile, MEKO is not a preferred option for interior ➔

Figure 1: Layers of different can coatings.



can coatings but is widely used on exterior can coatings.

In contrast, e-caprolactam is a blocking agent suitable for food contact compliant crosslinkers. Coatings with hardeners that contain ε-caprolactam need higher curing temperatures and/or times compared to MEKO (see orange line in *Figure 2*). A novel FDA compliant hardener that is widely used for interior can coatings offers high chemical resistance and meets demanding sterilisation requirements. To obtain a coating with high chemical resistance requires a relatively high crosslink density. The crosslink density can then be adjusted by the amount of crosslinker used. *Table 2* gives an example of a recipe based on the novel polyester resin and a novel ε-caprolactam-blocked polyisocyanate crosslinker using excess crosslinker (OH: NCO stoichiometry: 1:4). This results partly in allophanate structures via self-crosslinking and, thus, to higher crosslinking density and improved chemical resistance.

A less commonly used blocking agent is diethyl malonate (DEM). Compared with systems using ε-caprolactam or even MEKO blocked hardeners, coatings using DEM-blocked hardeners are characterised by significantly lower curing temperatures and times (see turquoise line in *Figure 2*). However, an alternative curing mechanism applies compared to typical blocked crosslinkers. DEM does not deblock upon heat but the blocking agent itself reacts with the resin's hydroxy group. During this transesterification process ethanol is released and evaporated. Thus, the ethanol leaving the system drives the equilibrium towards the cured system.

Due to these ester networks, coatings based on DEM-blocked hardeners cannot be expected to offer the same high chemical resistance compared to coatings prepared using MEKO or ε-caprolactam-blocked hardeners. However, due to the low curing temperatures, a variety of new applications are feasible, i.e. for plastic substrates which cannot withstand high temperature exposure. Furthermore, as there is no release of blocking agent except for ethanol, an approval for food contact applications seems highly conceivable in the future.

Figure 2: Blocking agent related curing settings.

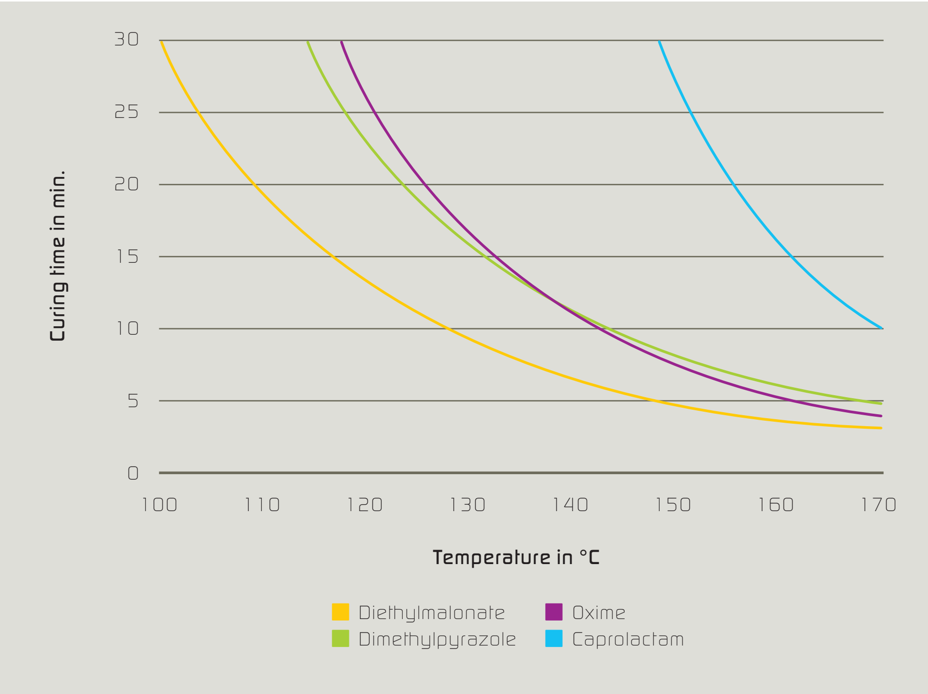
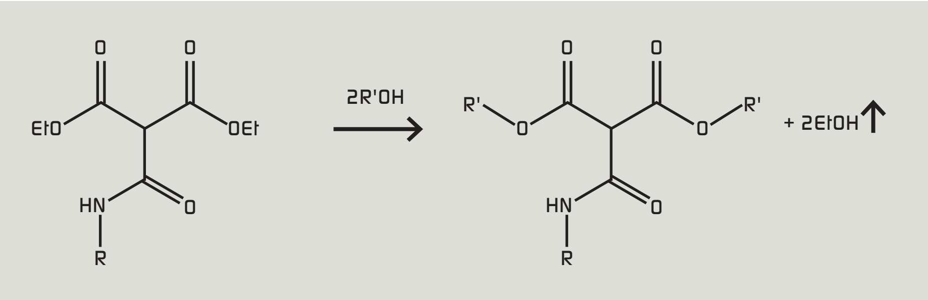


Figure 3: Reaction mechanism of curing with DEM-blocked crosslinkers.



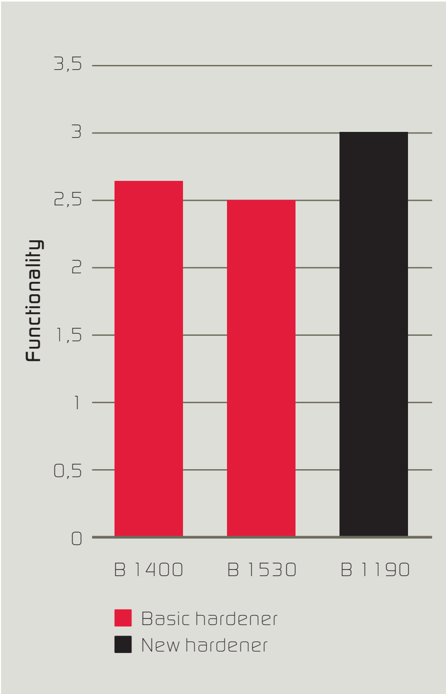
PUR POWDER COATINGS FOR CAN COATINGS

Because of increasingly strict regulations regarding VOC emissions, coating manufacturers are steadily being forced to search for new alternative coatings. The most obvious next step would be to move away from solvent-borne systems towards powder coatings.

In the world of polyurethanes, powder coatings have been established for quite some time now and are widely used, i.e. for automotive applications, household appliances or in construction. Powder coatings offer a multitude of advantages, the absence of solvent emissions being just one of them.

First, with powder coatings, much higher film thicknesses – up to 150 µm – can be achieved in a single applied layer. Additionally, due to electrostatic charging of substrate and coating material, overspray is drastically reduced, and the small amount of overspray that accumulates, is recycled, and can be sprayed again. This leads to a yield of >95 % of coating on the substrate, which reduces waste and improves the efficiency of the entire process. Another advantage of powder coatings is the extended shelf life. Since all ingredients are solid and stable up to a certain temperature, powder coatings can be stored for many years without any loss in quality.

Figure 4: Functionality of blocked PUR crosslinkers for powder coatings.



On the other hand, powder coatings do have certain limitations. Metals are the only possible substrates because they need to be chargeable and heat cured. The use of curing ovens also limits the size of the substrate. For the relatively small and metal-based cans, none of these limitations play a major role – here powder coatings can achieve their full advantages.

INCREASED CROSSLINK DENSITY FOR GREATER RESISTANCE

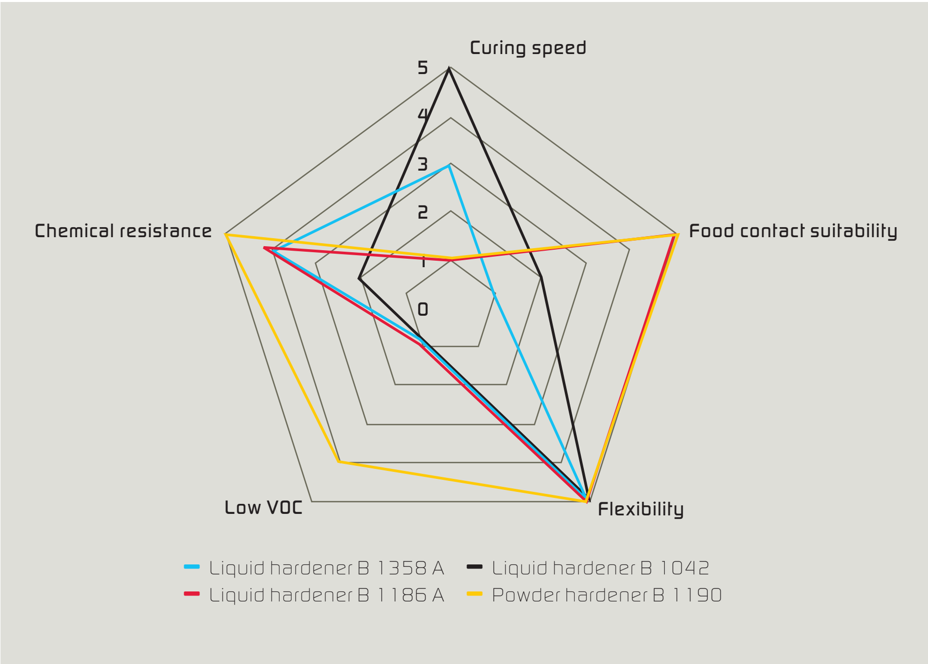
The novel polyurethane powder crosslinker is especially designed for the use in direct food contact application. It is an ε-caprolactam blocked crosslinker and compliant with FCN-No. 1268 and 21 CFR 176.170.

Similarly to liquid coatings, a high crosslink density is also desirable for powder coatings to achieve a high chemical resistance. Typical crosslinkers for powder coatings exhibit an average functionality of 2.5. Since increasing the crosslink density by overdosing the crosslinker does not work in powder coatings, the design of a new crosslinker with higher functionality was required to increase crosslink density and to meet chemical resistance requirements for food or cosmetic cans.
Figure 4 shows the enhanced functionality of the novel polyurethane powder crosslinked over typical powder coating hardeners.
Figure 5 compares the relative performance of powder coatings prepared with the novel PUR crosslinker and coatings prepared with the liquid hardeners mentioned in the above section. Powder coatings using the novel crosslinker score very high in terms of low VOC without compromising on the coating performance. Flexibility is at the same high level as for comparable liquid PUR systems. Chemical resistance is even slightly higher, since this functionality reduces the need for allophanate bonds created by overdosing the crosslinker in liquid applications.

STABLE AND REGULATION-COMPLIANT SOLUTION

Polyurethane systems have continued to gain more importance, especially in the food can coating sector. The outstanding resistance to most chemicals, also under heat treatment, combined with the superior flexibility allows for a wide range of applications. Recent developments in the blocking mechanism now allow for much lower curing temperatures or significantly reduced curing times. This affects the overall process efficiency and improves productivity of metal can manufacturing.
The newly developed curing agent for PU powder coatings combines all the stability and regulatory requirements of the food industry and provides a BPA-NI (non-intended BPA) coating solution that end consumers demand on the basis of a solvent-free powder coating process.

Figure 5: Liquid hardeners versus PUR powder hardener.



Dr Guido Streukens
Evonik Operations
guido.streukens@evonik.com

Table 1: The basic needs for can coatings can be summarised into four general categories.

Chemical resistance	Coating must withstand a wide variety of contents including acids	Prevent metal can from corrosion and contamination of the contents
Application	Coating must be applied and cured at high speed	Higher application speeds result in increased productivity
Flexibility	Coating must be flexible enough to withstand the forming process of the can and any impacts during transportation/storage	High design freedom of the can to reduce metal thickness. High flexibility also helps to prevent defects of the coating which leads to corrosion, i.e. when a can is dropped during use
Processability	Coating must withstand high temperatures and pressure during sterilisation	Necessary to ensure safety of the contents (e.g. food)

Table 2: Coating formulation for interior food packaging.

p.b.w.	Product
65.0	Polyester resin 30% in SN 100/SN 200 4:1
28.0	TiO_2 pigment
3.8	Curing agent
0.12	Tin catalyst
2.08	Butylglycol
1.0	Butyldiglycolacetate