Technical **ARTICLE**

Bright prospects

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Polyurethane-based Powder Coatings have long been known for their high crosslinking density combined with very good mechanical properties in the coating. They are therefore ideally suited for anti-graffiti applications and coatings for heat transfer printing. In addition to these classical applications, this review article describes new developments in the area of polyurethane powder coatings. These include optimization of matting and food contact applications, as well as challenges in the area of low-temperature curing.

The development of coating formulations is strongly influenced by legislation, and the VOC Directive is particularly relevant for the coatings industry. The explicit goal is to reduce, or even altogether eliminate, solvents as major components of a coating formulation or as a vehicle for uptake of essential components. This trend has significantly accelerated the development of, for example, water-borne coatings and high-solid systems. Of these environmentally compatible technologies, powder coatings are among the fastest growing coating systems.

Regulations and cost efficiency

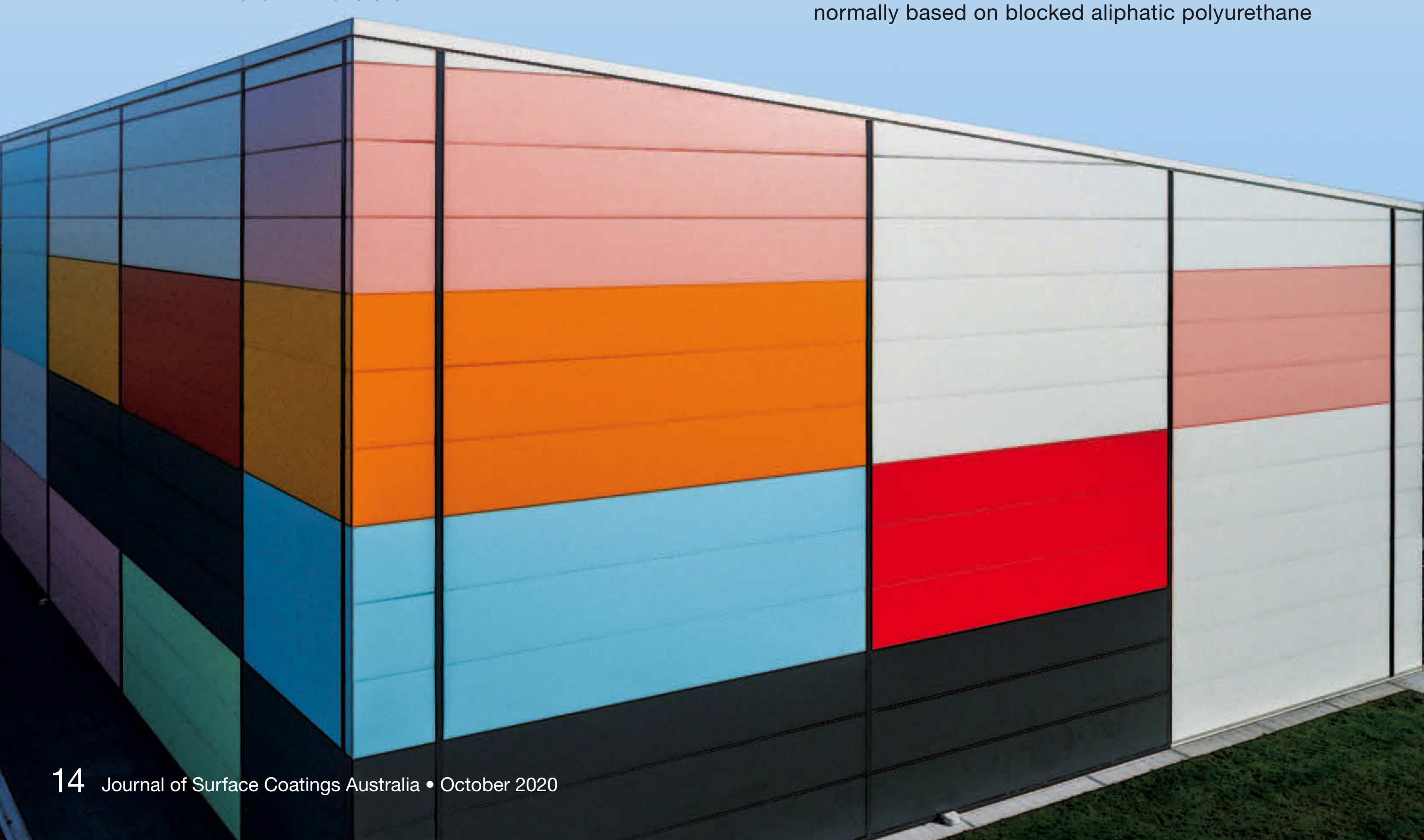
Powder coatings are already a widely used and well accepted alternative to classical solvent-borne coating systems, due to increasingly strict emission regulations, among other reasons. Continuing improvements in the area of crosslinker chemistry and coatings development are factors that will promote more widespread use of powder systems, even in the future.

But the use of powder is advantageous not only for ecological and regulatory reasons: Economic factors are also causing producers as well as downstream users to switch from conventional liquid systems to powders. When the use of powder technologies is technically feasible, this is often the most efficient option, for a number of reasons:

- raw-material costs are lower;
- waste costs are lower due to recycling of overspray;
- high film thicknesses are obtained in a single step;
- solvents are avoided;
- often, no primer is needed.

Global differences in powder technologies

Although powder coatings are now well established worldwide, clear regional differences are observed in the propagation of the various technologies: PU powder coatings that are normally based on blocked aliphatic polyurethane



crosslinkers are very widely used in North America and Japan whereas in Europe, where crosslinkers without blocking agents are preferred, their market share is significantly lower.

Despite these differences, global use of PU powder coatings shows clear and continuous growth. This is attributed to their versatile formulation options and particularly well-balanced performance characteristics. PUR powder surfaces are found in many applications including automotive construction, household gadgets, facade elements, gardening tools, and even metal profiles for the construction sector.

Externally blocked crosslinkers

Crosslinkers for commercially available PU powders can be divided into two categories: externally blocked crosslinkers, in which the isocyanate group is reversibly protected by a blocking agent, and internally blocked crosslinkers, where two isocyanate groups block each other by dimerization with the formation of a uretdione ring.

Up to the present time, PU powder coatings have for the most part used externally blocked crosslinkers. The blocking of the highly reactive isocyanate group is based on the formation of a chemically inert urea bond. The crosslinker can thus be formulated together with hydroxylated resins so as to be stable in storage. The isocyanate is released again only by thermal cleavage of the urea bond, which allows, by reaction with the hydroxyl group, the formation of the considerably more stable urethane group. Most externally blocked PU crosslinkers for powder coatings are ε-caprolactam-blocked adducts based on isophorone diisocyanate (IPDI). Thermal cleavage of the ε-caprolactam occurs at temperatures above 160°C. In formulations with hydroxylated polyesters, the polyaddition reaction leads to highly crosslinked films and offers a wide range of performance characteristics in no way inferior to those for liquid two-component solutions. It must be noted, however, that ε-caprolactam is a volatile component that does not remain in the coating and must therefore be regarded as a VOC.

Internally blocked crosslinkers

Internally blocked polyurethane crosslinkers are produced by dimerization with the formation of a uretdione ring, which is cleaved on heating into two reactive isocyanate groups. The absence of any volatile blocking agent results in significantly lower emission values for such systems. The cleavage occurs at temperatures above 160°C, so that uretdione-based crosslinkers are stable during extrusion and in the formulated powder. Although the active content of reactive groups in these products is similar to that for ε-caprolactam blocked crosslinkers, their functionality is somewhat lower. It is possible to compensate for this by using polyester resins with a higher degree of branching. In contrast to externally blocked adducts based on oligomeric substances of low molecular weight, uretdione-based crosslinkers have a linear polymeric structure that results in a slightly higher melt viscosity. The extrusion temperature should therefore not lie below 120°C.

Results at a glance

- Powder coating have significant environmental advantages, particularly in terms of the recycling of overspray and their low to zero VOC content.
- Polyurethane powders offer particularly high performance. PU powder technology and market developments are reviewed.
- PU powders are particularly useful in antigraffiti applications, where high crosslinking density can be obtained, giving resistance to repeated cleaning. Their high Tg is useful in heat transfer printing, where woodgrain and other effects are applied to the cured powder.
- Ways to optimise the matting of PU powders are discussed.
- PU crosslinkers can also be added to hybrid powder formulations to improve their performance by crosslinking the OH groups formed during cure.
- Future prospects include the development of better lowtemperature cure formulations and PU powders suitable for food contact.

High performance in anti-graffiti applications

PU powder coatings display their strengths to the full when used as anti-graffiti coatings: They show especially high resistance to the graffiti paints used and, most importantly, also to the cleaning agents employed. The key to this high resistance is the very high crosslinking density of the coatings, as is evidenced, for example, by the high glass transition temperature (Tg). By using polyester resins of high hydroxyl content, Tgs of up to 140°C can be attained. Due to the special properties of the urethane group, these have the required flexibility even in such highly crosslinked systems. The preferred choice for highly crosslinked polyurethane powder is Vestagon B 1530, due to its high functionality. Although these anti-graffiti coatings have high crosslinking densities, they have good mechanical properties.

Fig. 1 illustrates the advantages of polyurethane powders over other crosslinking technologies and shows clearly that cleaning of the coating (in the lower part in each case) without residue is possible only with PU powders.

Heat-transfer printing

Sublimation printing is another application where high crosslinking density of the cured coatings is an absolute must. Sublimation (or heat transfer) technology is a process where, after the actual powder coating, a printing ink is applied to generate a pattern on the component.

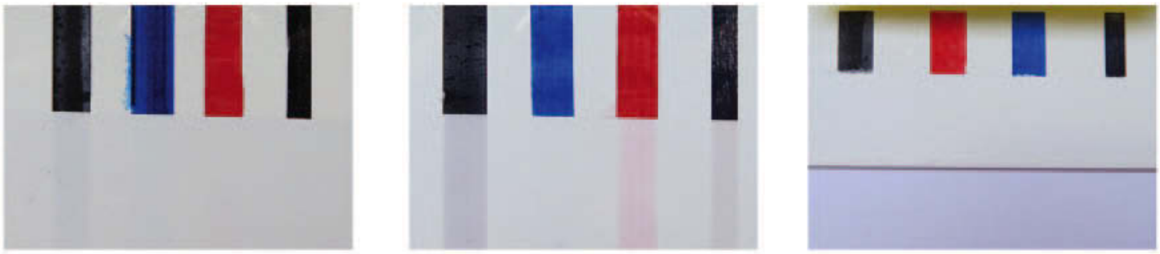


Fig 1: Graffiti cleaning test. Apply 3 graffiti paints and black permanent markers to coated metal sheets. After 24 hours, wipe half of the sheet with a cotton wool pad soaked in ethanol and rate on a scale of 0 (no residue) to 5 (clear residue).

The ink must be thermally fixed for the sublimation process to function. The underlying coating must therefore be heat-resistant without softening or changing its morphology in the process; this is why polyurethanes with high glass transition temperature Tg are particularly suitable for the purpose. In addition, a high crosslinking density is helpful in preventing the paper or film (for transfer of the ink) from sticking to the coating.

This technology greatly improves the visual appearance of facade elements, particularly for aluminum components such as window frames, front doors, garage doors, office furniture, and kitchen cabinets with, for example, a realistic wood finish look.

Optimizing and controlling matting

More than half of all powder-coated surfaces are matt. With liquid coatings, this effect is achieved by the addition of fairly large amounts of fillers or matting agents.

However, addition of similar amounts in powder coatings would mean that the coating could no longer be easily extruded. Moreover, the effect of matting agents is much less pronounced in powder coatings.

For this reason, various alternative approaches have been used in the past for matting of powder coatings; these are differentiated on the basis of the crosslinking chemistry.

For PU powder coatings the use of resins of different reactivities has proven to be a simple and efficient method of generating matt surfaces.

A mixture of different polyesters is used here with the appropriate PU crosslinker; the polyesters should in one case have a high (260–300 mg KOH/g) and in another case a low (30–50 mg KOH/g) hydroxyl number.

Because the two resins have different reactivities with the crosslinking agent, this use of two resins generates microscopically small domains that cure faster than other domains. This prevents perfect flow behavior and thus produces the matting effect. However, each combination of binder and crosslinker leads to a specific gloss value that can vary between low and high gloss, even if the resins have the necessary hydroxyl content and have been tested with a particular crosslinking agent.

This means that every polyester combination must be tested empirically for its matting effect with the respective crosslinking agent.

In addition, care should be taken in the development phase not only that the desired gloss region is attained, but also that this is insensitive to small changes in proportions, because slight fluctuations in production cannot be ruled out. The curves in Fig. 2 and Fig. 3 indicate how the proportions of the polyester resins and PU crosslinkers can be set so that even with small fluctuations in composition the influence on the gloss level is as low as possible.

Fig. 2 shows the gloss level as a function of the ratio of the two polyester resins used (3115 and 3225). The polyesters are mixed in ratios varying between 20:80 and 30:70. BF 1321 was used as hardener (NCO : OH = 1:1). At a ratio of 25:75 (the lowest point of the curve) the gloss is least sensitive to slight fluctuations of the polyester ratio in both directions.

Fig. 3 shows the gloss level for the above formulation as a function of the stoichiometric ratio between OH-functional resin and PU crosslinker for a constant ratio (75:25) of the two polyesters. The stoichiometric ratio of NCO to OH was varied between 0.7:1.0 and 1.1:1.0. If the amount of crosslinker is substoichiometric, the gloss level is significantly less sensitive to small fluctuations in composition that when it is used in or above the stoichiometric quantity.

Polyurethane-enhanced hybrid powder coatings

The most commonly used powder systems are hybrid powders. These are lower priced but are known to have low resistance to yellowing; their chemical resistance is also relatively poor, due to their low crosslinking density.

One option for improving the chemical resistance of hybrid powders is to mix in PU crosslinkers. During the cure reaction, hybrid powders form a certain number of OH groups by reaction of the epoxy resin with carboxyl groups. These hydroxyl groups can then be reacted with PU crosslinkers to increase the crosslinking density. This leads to significant improvement of chemical resistance, surface hardness, weathering resistance, and glass transition temperature Tg in these coatings. Coating developers thus have the possibility of adapting their hybrid powders to specific market requirements, particularly where high chemical resistance is necessary, as for example in household gadgets.

Fig. 4 shows the relationship between crosslinker content and gloss reduction after treatment with sodium hydroxide solution. The best properties are

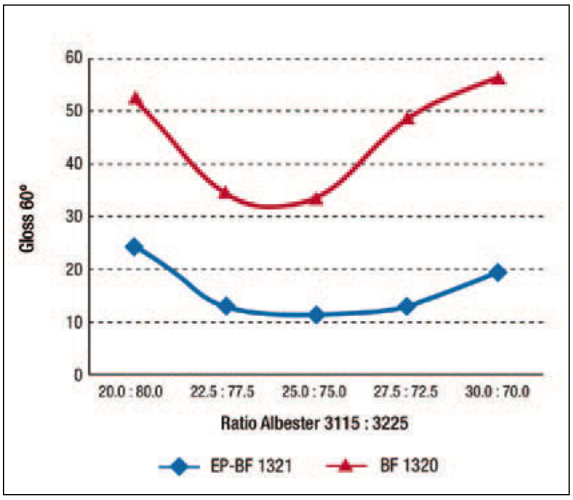


Fig 2: The lowest point of the curve shows that the gloss least for fluctuations in the ratio of the two polyester resins is sensitive.

achieved with an NCO : OH stoichiometric ratio of 1:1 in the crosslinking agent, obtained in the present example by addition of 6.8% crosslinker.

Curing at lower temperatures

Crosslinking of powder coatings at even lower temperatures is a development being demanded also of PU-based systems, because current systems require curing times of up to one hour at 170°C.

Very recent results have shown that the uretdione ring of internally blocked PU crosslinkers can be cleaved to give back the isocyanates at temperatures as low as about 130°C, if appropriate catalyst systems are used. At these low curing temperatures, however, allophanates and isocyanurates may also be formed in addition to the desired urethane bond. This means, ultimately, that such coatings must be crosslinked with an overstoichiometric ratio of about 1.4:1 (NCO : OH), because more isocyanate groups are needed for curing.

A further disadvantage of these high-reactivity coatings is their limited storage stability and the need to store these powder coatings under refrigeration.

Much more convenient here is a catalysis using diazabicyclononene (DBN). With this type of catalysis the usual 1:1 stoichiometry for PU can be retained and the powder coatings have a storage stability that is in the usual range for PU powders. Crosslinking is possible at temperatures above 150°C, which is regarded as entirely adequate for many applications. To ensure satisfactory flow behavior under these conditions special crosslinkers must be used, which are now well established on the market.

Apart from the obvious advantages of energy and time savings, this technology extends the range of applications for PU powder coatings. For example, even temperature-sensitive substrates and very heavy metal parts with low heating rates can be coated.

Polyurethane powders for food contact

Coatings in direct contact with food are subject to very strict regulations. The requirements of regulatory authorities and institutions, voluntary commitments, and also intensified public discussion have all resulted in a steady reduction in

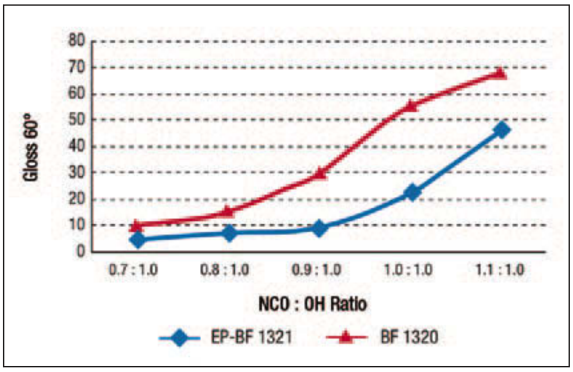


Fig 3: Relationship between stoichiometry and gloss level after curing. The gloss is very good with a stoichiometric ratio of approximately 0.8:1.0 least sensitive to change.

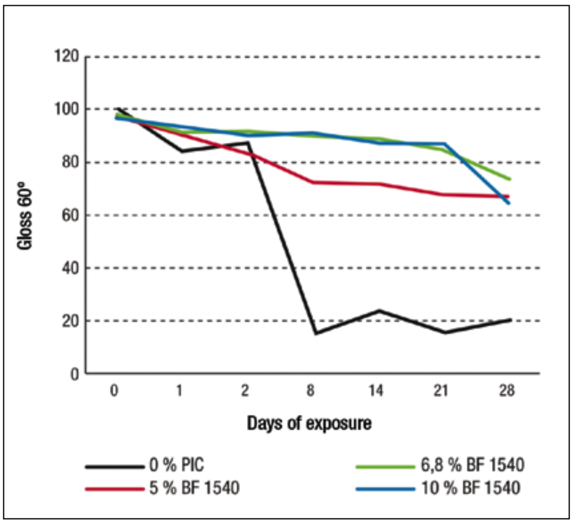


Fig. 4: Effect of the cross-linking agent content on gloss and resistance to a sodium hydroxide solution.

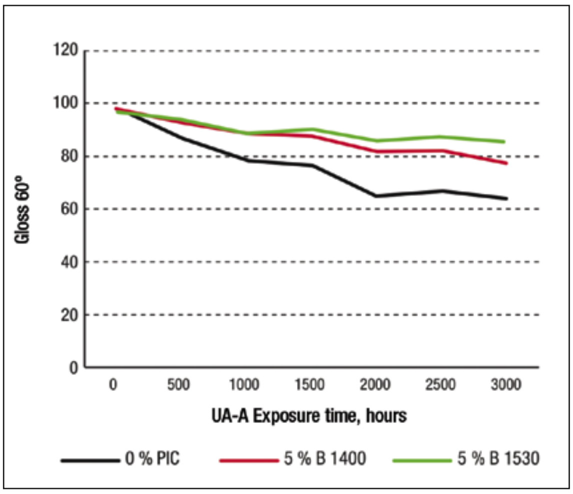


Fig. 5: Relationship between the quantity and type of the Crosslinker, gloss development through UV-A exposure.

the options available for crosslinking technologies for food contact.

A few polyurethane-based liquid coating systems have been approved for direct food contact. Their market share is steadily increasing, as in the case of internal coatings for food cans. Polyurethane coatings are now well established as a particularly efficient alternative to traditional systems.

PU powder coatings are not as yet widely used in this area, but significant reduction of volatile components (VOCs) will give the technology a foothold in this area as well.

Polyurethane chemistry will continue in the future to play a major role in the global success of powder coatings. Most of the polyurethane powders used already satisfy a number of market requirements relating to chemical resistance, matting, robust production processes, visual appearance, UV resistance, and anti-graffiti properties.

Highly promising new developments and energy saving

The market demands energy savings or increased productivity from faster throughput times. Polyurethane chemistry meets these demanding requirements, and new developments ensure that it will continue to do so in the future.

Particularly noteworthy here are developments in the area of low-temperature curing. Curing at temperatures below 170°C is undoubtedly the main development goal for PU powder coatings. This requires fine tuning of the interplay between catalyst, crosslinker, and binding agent: Significant reduction of the curing temperature by novel catalysts will require lower-melting binding agents to ensure that the flow behavior of the coating continues to be satisfactory.

Over the last few years we have taken up this challenge, with the result that curing temperatures of 120-140°C are already possible today. The cleavage of the uretdione structure can be activated by diazabicyclononene, for example, and allows curing times of less than 30 minutes at 140°C, although with the above-mentioned restrictions in the choice of binding agent and somewhat reduced storage stability. However, with somewhat reduced quantities of catalyst, PU powder coatings can be produced that cure at a temperature of 150°C, with only minimal adaptation of the formulation.

As a result of these developments the curing window of PU powder coatings can be significantly increased and a wide range of PU crosslinkers offered that meet customers' specific requirements. In addition to process requirements (curing temperature and time), we also take account here of the properties of the powder coating such as resistance to yellowing and excellent chemical and heat resistance. ■

Allrounder for powders

INTERVIEW with Dr. Guido Streukens, Evonik Operations GmbH

In powder coatings, as in other fields, polyurethane chemistry shows off its well-known strengths: uv and chemical resistance and good mechanical properties.

Is there a reason, in your view, for the more widespread use of PU powder coatings in North America and Japan?

Apart from the intensity of solar radiation in these regions, weathering effects in particular also play an important role. Polyurethane ensures outstanding UV resistance and meets the requirements better than alternative systems. Other factors, in addition to raw-material availability and price, include legal regulations.

What is the greatest advantage of PU over other powder-coating technologies?

Apart from the UV resistance of polyurethane powders, a further advantage lies in the outstanding mechanical properties of the coating. Good chemical resistance is the reason that polyurethane is used in anti-graffiti coatings. Moreover, polyurethane is very easily matted without dry blending and in a one-shot process. This helps save time and money.

How much and how often must the gloss level normally be readjusted, and how well does this work?

A readjustment of gloss level is necessary for about every 30th batch. Powders that are matted using additives are very easily corrected, in contrast to dry-blend technologies. For polyurethane this is done by mixing batches of different gloss levels. A deep matt batch will often be set aside and used specifically for correction. ■

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