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SAY GOOD-BYE TO GRAFFITI

Technology plattform for crosslinkers. By André Raukamp, Dr Guido Streukens, Corey King, Evonik.

Whether they are on your car, your floor, or your furniture, scratches on finished surfaces are annoying. An innovative technology platform for crosslinkers in the EP-MF and EP-EF families offers a toolbox for a variety of customized solutions so that you can formulate scratch-resistant, low-temperature-curing coatings for use on substrates such as wood, plastic, or metals — solutions that can even be used in anti-graffiti coatings.

The new technology platform unites the advantages of silane curing with those of polyurethanes, all within one and the same chemical network. This leads to very hard, durable coatings, while still providing adequate flexibility.

Two isocyanato alkoxysilanes – IPMS (3-isocyanatopropyl)trimethoxysilane and IPES (3-isocyanatopropyl)-triethoxysilane – are at the heart of this new technology. The NCO group binds these compounds to a backbone component, where they combine with the alkoxysilane groups to form moisture-curing adducts (*Figure 1*). These adducts are suitable for both one- and two-part (1K and 2K) coating formulations – and the concept even allows for their use non-isocyanate (NISO) coating systems. When the user applies the product, the only crosslinking mechanism in play is the moisture-curing processes that the alkoxysilanes undergo. The adducts presented here are liquids and, in many cases, can be used with no additional solvent, thus keeping the VOC content of the formulations very low.

The many options available for the PUR backbone maximize the freedom that manufacturers have to customize binders and crosslinkers. In theory, IPMS and IPES react with a wide range of functional groups – the focus here, however, is primarily on the hydroxyl groups of diols, polyols, and (short-chained) OH-terminated polyurethanes – to form a crosslinker/binder having alkoxysilane functional groups and linked by urethane groups. The choice of backbone has a crucial impact on the balance of crosslinker properties and also has considerable influence on the coating characteristics. Whereas the hardness and durability of the siloxane networks are the dominant properties arising from short-chained diols, longer-chained PUR oligomers result in far more flexible systems.

The primary difference between IPMS- and IPES-based adducts lies in their reactivity, and thus in their curing times and temperatures. Methoxysilane-based systems are ten times more reactive than their ethoxysilane counterparts. It follows that, without suitable catalysts, only the methoxy-based, i.e., EP-M adducts are at all capable of curing under conditions that are acceptable for coating technologies. Here we present three different variations of these systems (*Table 1*).

HEAT CURING: A FOCUS ON AUTOMOBILE CLEAR COATS

The products in the EP-M family cure within typical time frames at temperatures between 80 °C and 140 °C. Automobile clear coats represent one example of an application for the heat curing process, and an area where the exceptional scratch resistance of these methoxy-based adducts is setting new standards. Preventing micro-scratches,

RESULTS AT A GLANCE

→ The high density of the polysiloxane network produces a hardness almost like that of glass, resulting in a coating that is highly resistant to mechanical and chemical influences.

→ The flexibility provided by the urethane structures is critical for coating systems subject to high levels of stress.

→ Flexible use of the urethane backbone allows manufacturers to optimize the balance between the two aforementioned properties depending on the purpose at hand.

→ Drying rapidly at room temperature does more than simply increase efficiency and productivity – it also opens the door to a wide variety of potential substrates.

→ This increased compatibility, particularly in the latest generation of silane-PUR hybrids, also opens up entirely new possibilities in the DIY sector. Customers can add pigments or matte effects, for instance, or they can combine these products with other binders or resins.

Table 1: Different adducts for different applications.

	EP-M	EP-MF	EP-EF
Room temperature curing	–	+	+
Heat curing	+	–	–
Separation product	methanol	methanol	ethanol

Table 2: Comparison of the properties of different room-temperature curing systems.

	EP-MF 203	EP-MF 204	EP-MF 205	EP-EF 201	EP-EF 202
Viscosity (mPas)	170	1500	700	350	1600
Solids content (%)	100	100	82	96	96
Full drying time (minutes)	45	60	80	30	45

such as those that arise in car washes, is one particularly important issue here. Given an appropriate choice of backbone component, methoxy-based adducts can also be used in these applications as a 1K system. Adding modules of an existing 2K PU formulation is much more likely to significantly increase scratch resistance, however, while virtually eliminating any need for adapting the overall finishing process.

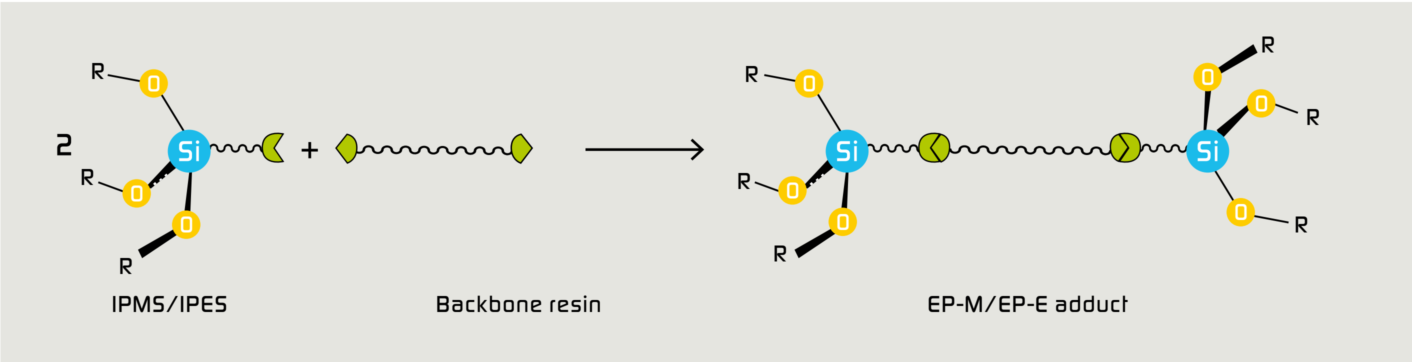
ROOM-TEMPERATURE CURING – A WIDE RANGE OF POTENTIAL APPLICATIONS

While heat curing works well in automotive finishes, room-temperature curing systems are far preferable – if not outright necessary – for many other applications. That does not mean, however, that the requirements of the coating system are any less demanding. Take high-gloss kitchen cabinetry, for instance: because every stain and every bit of dust is immediately visible on these surfaces, it is easy to imagine how often they are wiped down over the course of years. And wood flooring is quite clearly subject to considerable mechanical stress each and every day, making a particularly resilient coating pay off.

In order for coatings made from methoxy-based adducts to meet these demands, special amine-based catalyst systems have been developed that allow methoxysilane-based products to cure at room temperature. Designated as EP-MF grades, these systems are dust dry after less than one hour at room temperature (*Table 2*), opening the door to a much broader array of applications than is available with heat-curing systems. While EP-MF adducts are characterized by exceptionally good adhesion to wood and metal, they can be used on plastic surfaces as well.

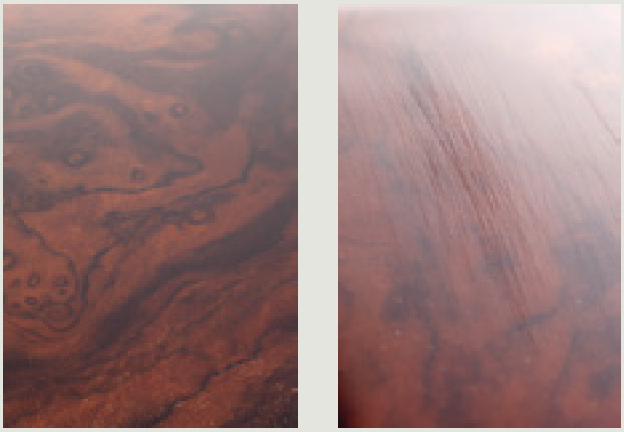
Use of the catalyst makes EP-MF products less miscible with classic 2K PUR systems than heat-curing EP-M grades; the aminic catalyst is not compatible with classic PUR crosslinkers. For this reason, EP-MF grades ➔

Figure 1: IPMS-based silane/urethane hybrid crosslinker having urethane groups and terminated with trifunctional alkoxysilane structures.



are typically used as a 1K system, in which case the high crosslinking density is both a blessing and a curse. While it makes the surface highly scratch and chemical resistant, it also has a detrimental impact on mechanical properties. In response to this problem, adducts with significantly greater flexibility (higher proportion of PUR in the backbone) have been developed (such as EP-MF 205, *Figure 4*). Within the various EP-MF grades, the choice of backbone determines the balance between resistance (mechanical and chemical) and flexibility; with respect to ethoxy-based grades, EP-EF 202, which is also suitable for 1K applications, is more flexible than EP-EF 201, which, because it is highly brittle, best reveals its strengths in 2K formulations. This allows manufacturers to paint flexible components and prevents thermal stress from having a negative impact on the coating.
Figure 2 shows a comparison between 2K PUR (right) and a formulation based on EP-MF 203 (left). Both systems were applied on wood and tested for scratch resistance using a modified crockmeter test. Whereas many scratches, some significant, can be seen on the unmodified 2K PUR, the formulation containing the ethoxy-based adduct was able to resist the abrasive attacks in the modified crockmeter test and retain its original glossy surface.

Figure 2: Varnish comparison (applied on wood panels) using a modified crockmeter scratch test / 2K PUR (right) vs. EP-MF 203 formulation (left).



HIGH CROSSLINKING DENSITY – HIGHLY RESISTANT

The exceptional scratch resistance of silane-PUR hybrids is occasioned by the unusually high degree of crosslinking in the nearly glass-like polysiloxane network. In addition, the high density of the network also makes the surface highly chemical resistant – a property that bears fruit when the wood surfaces described above are cleaned every day. The systems can satisfy much tougher demands than that, however, as is the case when they are used as anti-graffiti coatings.

Figure 3: Varnish comparison (applied on aluminum panels) after using ethanol to remove graffiti paints – 2K PUR (left) vs. EP-MF 205 (center) vs. EP-MF 203 (right).

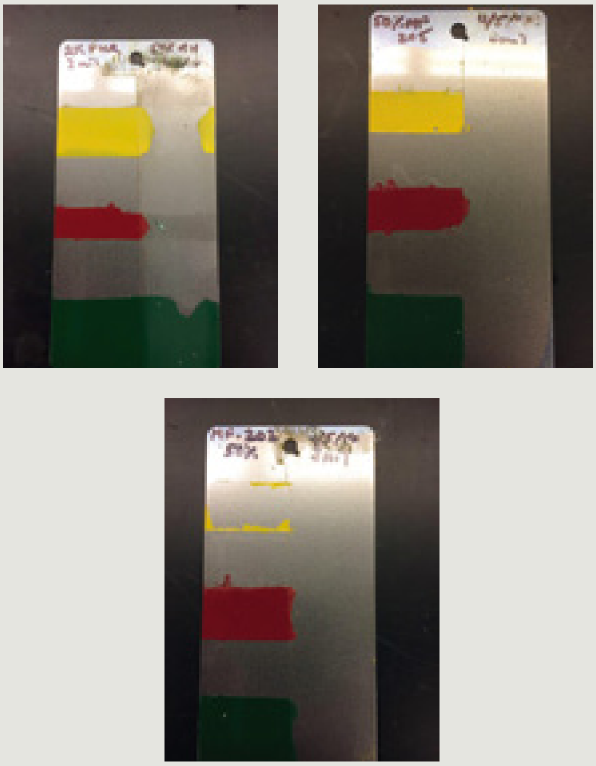
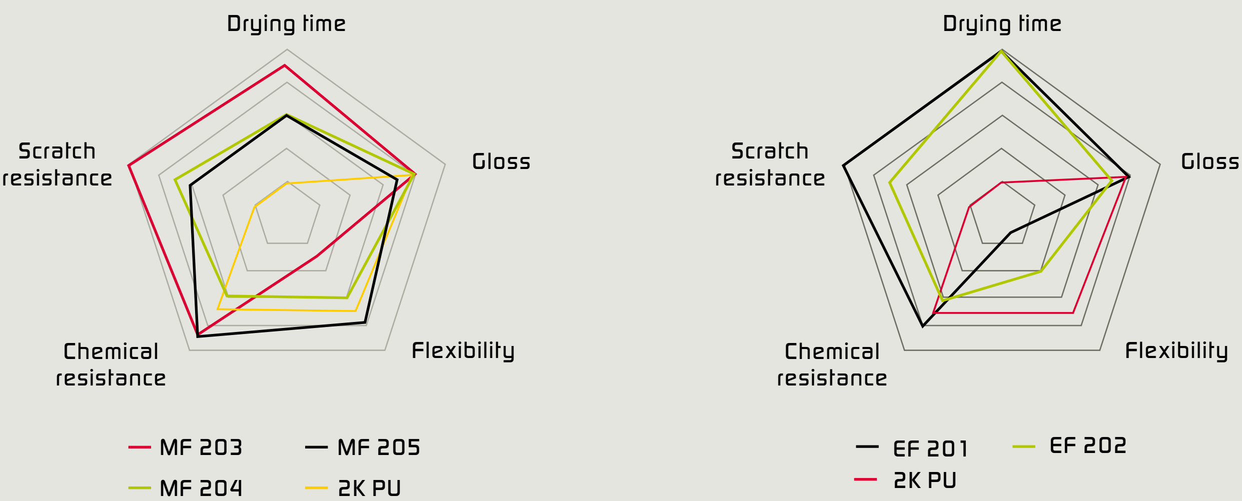


Figure 4: Ongoing development of flexibility in the EP-MF and EP-EF series.



Removing graffiti from trains, for instance, is a chemical and mechanical process that, over time, destroys the finish of the trains to the point of requiring a complete replacement – repainting a train car can cost up to € 30,000 [1]. MF-series crosslinkers form a lasting barrier to chemical cleansers and to the aggressive solvents used for removing graffiti, thus protecting finishes during the graffiti removal process. Extensive tests have also shown that, in addition to lending paints very high, long-lasting resistance to scratches, this powerful protective effect also allows them to hold up extremely well to the elements. As a result, the train not only needs to be repainted less frequently – rapid drying at room temperature also means that it will be out of service for less time when it does need to be painted.

Figure 3 shows a comparison between graffiti paints applied to aluminum panels coated with clear finishes. The finishes were based on three different products: classic 2K PUR (left), MF 205 (a highly flexible adduct, center), and MF 203 (an adduct in which flexibility is low but crosslinking density is high). As can be seen in all three cases, scrubbing for five minutes with a cloth soaked in ethanol removes the graffiti paint. In the case of the PUR finish, however, graffiti removal is only partially successful and the clear coat has been damaged significantly. The highly flexible adduct makes the surface easy to clean; in the case of the adduct with the low flexibility and high crosslinking density, adhesion between the graffiti paint and the finish is reduced to such an extent that some of the paint is removed simply by peeling off the tape masking the left half of the test area.

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“MeOH-free grades greatly simplify occupational safety for professional users.“

2 questions to Dr Guido Streukens

Isn't the use of isocyanate-based components in NISO systems contradictory? *The urethane structures contained in our adducts are based on isocyanate, that's true. What's critical here is that end users do not come into contact with isocyanates when working with the system – the product they hold in their hands has instead been completely converted to polyurethane.*

Could you give us some examples of DIY applications? What current gaps does the new system fill? *The demand for high-quality coating systems in DIY applications is especially high when it comes to wood finishes. But it goes without saying, of course, that professional users also benefit from MeOH-free grades, as these greatly simplify on-the-job safety.*

NEW HYBRID CROSSLINKERS FOR DIY APPLICATIONS

The key advantage that IPES-based systems have over IPMS adducts is that they release ethanol during curing rather than methanol. Methanol emissions limit use to professionals, while handling is considerably easier with ethanol.

Theoretically, this reduces the reactivity of the ethoxysilane group to the point that rapid system curing becomes difficult. Only recently has a suitable catalyst been developed that delivers the necessary reactivity without otherwise compromising the system. IPES-based adducts catalyzed in this way fall within the EP-EF group.

In addition to the broader usability that comes from eliminating methanol separation, the newly developed – and now amine-free – catalyst also greatly expands the range of applications. Unlike EP-MF grades, EP-EF systems are fully compatible with 2K PUR systems. This means that, in addition to their classic use as the sole component of a 1K coating, they can also be added to existing 2K PUR coatings in order to enhance scratch and chemical resistance. Alternately, 2K formulations could also be developed that consist of classic acrylic polyols on the one hand and the EP-MF adduct as the curing agent on the other. Varying the grade and quantity of the polyol is an easy way to make the system more flexible, requiring fewer adducts compared to MF in order to cover a broad portfolio of properties.

This 2K approach would also make it significantly easier to create matte or pigmented coatings than has been the case up to now. The corresponding additives or pigments are not generally anhydrous, and, as such, cannot be incorporated into the adducts without compromising stability. This is not a problem, however, if they are introduced via polyol components.

REFERENCES

[1] DB Sicherheit [Deutsche Bahn Security], March 2019