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WHO SHINES THE LONGEST?

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95 automotive clearcoat systems were tested with dry and wet scratching – before and after weathering – and for their chemical resistance. The tests of this benchmark study revealed considerable differences between the systems.

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Clearcoats form the outermost of usually four layers in automotive OEM coatings. In 2019, around 310,000 metric tons of clearcoat were consumed worldwide for this purpose. 40 % were two-component (2K) polyurethane (PU) coatings, 30 % one-component (1K) TSA coatings (thermosetting acrylics). The remainder was divided among 1K technologies of various chemistry, namely acid-epoxy, carbamate and PU-modified TSA systems [1].

In 2018, we tested and compared automotive clearcoat systems from eleven automotive manufacturers, eight coating producers and one manufacturer of coating raw materials. The coating samples were coded in the process. A similarly designed benchmark study was already conducted in 2009 and 2010 [2]. It revealed to the participants where there was a need for development and action.

Apart from the individual conclusions, the results of the relaunched study allow us to examine the extent to which the different chemical technologies are reflected in the test results. They also show the extent to which the performance and property profile of the systems on the market differ as a result of the specifications of the individual OEMs.

95 clearcoats were examined, including six formulations based on raw materials from the testing company (*Table 1*). 80 coatings were 2K PU systems, the remaining ones 1K systems of different technologies (*Figure 1*). This shows that mainly companies from Europe participated, where 2K PU clearcoats are more widespread than the global average. It was possible to classify the 2K PU clearcoats into 52 standard systems, 15 systems with nanoparticles, ten silanemodified systems and three nano- and silanemodified systems.

THE TESTS

The automotive clearcoats were tested over a 12 month period in Leverkusen:

1. Test for wet scratching [3]: A laboratory-scale car wash according to Amtec-Kistler simulated the scratching that car washes cause on automotive clearcoats. During the washing process with a polyethylene brush, the test sheets were sprayed with a silica powder suspension (1.5 g silica powder to 1 l of tap water). The test plates were then cleaned with water and white spirit. The gloss values before and after scratching as well as after reflow at 60 °C were measured reflectometrically at a 20° angle. [4]

RESULTS AT A GLANCE

→ Silanemodified 2K PUR automotive clearcoats perform best in the comparative test, especially if they are modified with nanoparticles.

→ There are considerable differences within the standard 2K PUR systems, especially in terms of scratch resistance, with an overall excellent reflow capability.

→ Thermosetting acrylic coatings perform well as a 1K technology.

→ Weathered clearcoat surfaces are generally less resistant to wet scratching than unweathered coatings.

→ Diluted acid, pancreatin and tree resin affect automotive clearcoats more than diluted alkali or water, regardless of their chemical technology.

The test for wet scratching was repeated with test sheets that had been exposed to moisture and irradiated for 1,000 h in the specified cycle of the SAE J 2527 weathering standard [5].

2. Dry Scratch Test [6]: The friction pin (cuboid, 22 mm x 22 mm) of a linear abrasion tester, the Crockmeter, covered with polishing paper (3M 281Q Wetordry, 9MIC), was moved over the coating surface using ten double strokes and a test force of 22 N. Gloss values were measured as for wet scratching.

Table 1: Participating coating systems.

Description	Details (all systems NCO:OH=1.0)
Standard 2K PU system with HDI trimer	PAC : SCA-PAC, 80:20 – “Desmodur” ultra N 3390
2K PU system with highly functional polyisocyanate (F=5)	PAC : SCA-PAC, 80:20 – “Desmodur” N 3580
2K PU system with HDI and IPDI trimer	PAC : SCA-PAC, 80:20 – “Desmodur” ultra N 3390 / “Desmodur” Z 4470 (80:20)
2K PU system with bio-based hardener	PAC : SCA-PAC, 80:20 – “Desmodur” eco N 7300
2K PU system with silanemodified hardener	PAC : SCA-PAC, 80:20 – “Desmodur” 2873
2K PU system with self-healing effect	Self-healing PAC – “Desmodur” N 3580

3. Chemical Resistance Test [7]: Chemicals were applied onto a test panel coated with the respective coating build up according to a specified pattern. The pattern took into account the distance between individually adjustable heating elements in a gradient oven in which temperatures of 36 °C to 68 °C prevail, depending on the location. After 30 min in the oven, the chemicals were removed with water and cleaning solvent. The temperature at which the coating surface began to show changes such as cracks, bubbles and loss of gloss was determined. After 24 h of standard climate storage and after two hours of reflow at 60 °C, the sheets were visually inspected again.
4. Nano-scratch Test: This test in which an indenter generates a scratch mark under a defined load was carried out at the Fraunhofer Institute for Production Technology and Automation (IPA). The test sheet was pulled under the indenter three times at a speed of 3 mm/min. During the first scan, it scanned the surface under minimum force without mechanically impacting it and measured the topography
During the second scan, it penetrated the material with a specified normal force increase (40 mN/min) up to a specified final load

Table 2: Wet scratching of non-weathered automotive clearcoats (2K systems: green background, 1K systems: blue background).

	Average values		Smallest value after scratching in %	Highest value after scratching in %	Smallest value after 2 h 60 °C Reflow in %	Highest value after 2 h 60 °C Reflow in %
	Residual gloss after scratching in %	Residual gloss after 2 h 60 °C Reflow in %				
Standard quality	68	82	51	87	70	96
Silanemodified	82	86	71	92	76	93
Silane & nano	82	87	76	87	83	91
Nanomodified	77	84	64	85	72	91
Carbamate	67	74	57	81	63	83
PU mod. TSA	65	72	62	70	69	77
TSA	78	80	69	86	72	89

(0.1 mN to 45 mN). During the third scan, it again scanned the surface with minimum force and determined the groove depth. An optical evaluation was then made, specifically recording the area of the first crack.

5. Measurement of microhardness and glass transition temperature: The systems hardly differed from each other in this respect. This is hardly surprising, since they have to meet similar OEM specifications. Automotive clearcoats should be sufficiently hard to withstand chemicals on the one hand, and on the other hand have a certain flexibility so that they do not react to even slight mechanical stresses with brittle fracture. The glass transition temperatures were close to 60 °C for all automotive clearcoats – reflow of the coatings when the surface is heated by the sun is therefore possible in principle.

WET SCRATCHED: THE RESULT

During wet scratching of unweathered automotive clearcoats (*Table 2*), there were large differences even within a single category. For example, the lowest residual gloss value after wet scratching for 2K PU standard coatings was 51 %, the highest value 87 %. The following discussion of the mean values (*Figure 2*) necessarily ignores this wide range.

The average values demonstrate that the silanemodified as well as the silane- and at the same time nanomodified 2K PU coatings perform better than the other technologies. This applies in particular to the residual gloss, which was measured directly after scratching: At 82 %, the values are far higher than, for example, the average value of the 2K PU standard systems (68 %). In the case of the residual gloss, which was determined after the coating had been allowed to reflow for two hours at 60 °C, the systems are almost on a par: Here, values of 87 % (nano- and silanemodified systems) and 86 % (silanemodified systems) compare with an average residual gloss of 82 % for the 2K PU standard coatings. Individual representatives of the 2K standard systems achieve values for wet scratching before and after reflow which correspond to those of nano- or silanemodified coatings.

On average, the 1K TSA coatings tested surpass 2K standard PU systems in their residual gloss directly after wet scratching, but do not attain the value of the silanemodified 2K systems. After two hours at 60 °C, their residual gloss hardly increases, with the result that they are then behind the 2K PU standard systems. On average, 1K carbamate coatings have a similar residual gloss to 2K standard PU coatings directly after wet scratching; however, their reflow capability is clearly inferior. The reflow effect is important in practice because micro-scratches can heal themselves when exposed to sunlight. This means that the coating surface regains its original appearance.

After 1,000 hours of weathering, the coating surfaces of all chemical systems are significantly less resistant to wet scratching than unweathered surfaces (*Figure 3*). The aging effect is amplified under OEM specifications that require at least 4,000 hours of testing. Thanks to their more flexible polyurethane structures, the aging effect is less pronounced with 2K systems than with 1K systems. It is particularly strong with the 1K carbamate systems: Here, the average residual gloss value drops from 67 to 29 %. This value contrasts with the 72 % residual gloss after weathering and scratching achieved on average by coatings in the category "nano- and silane-modified 2K PU systems".

Figure 1: Number of coatings tested, ordered by chemical technology.

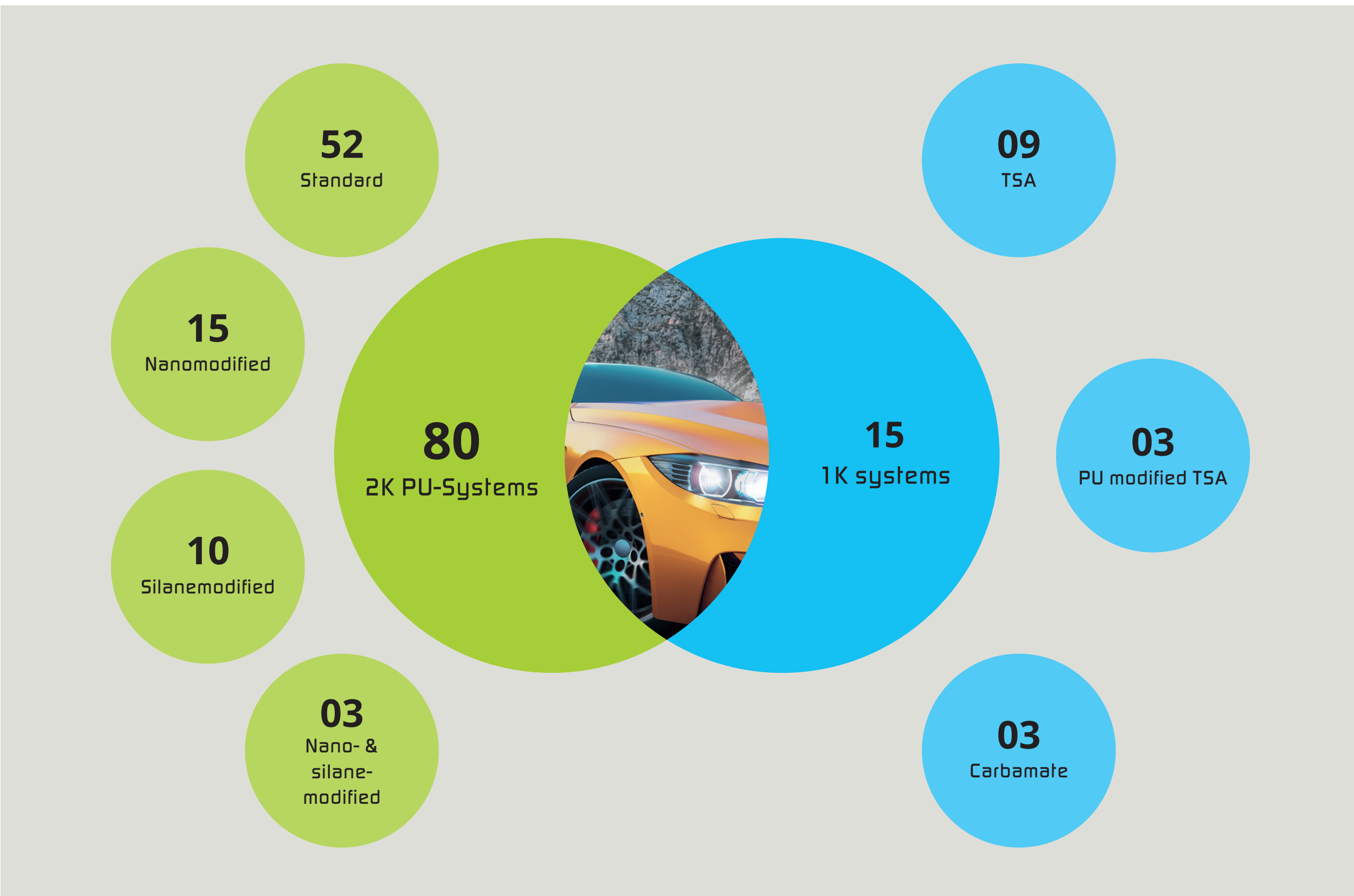


Figure 2: Wet scratching of the unweathered paint surfaces, before (red) and after 2 h heating to 60 °C (black).

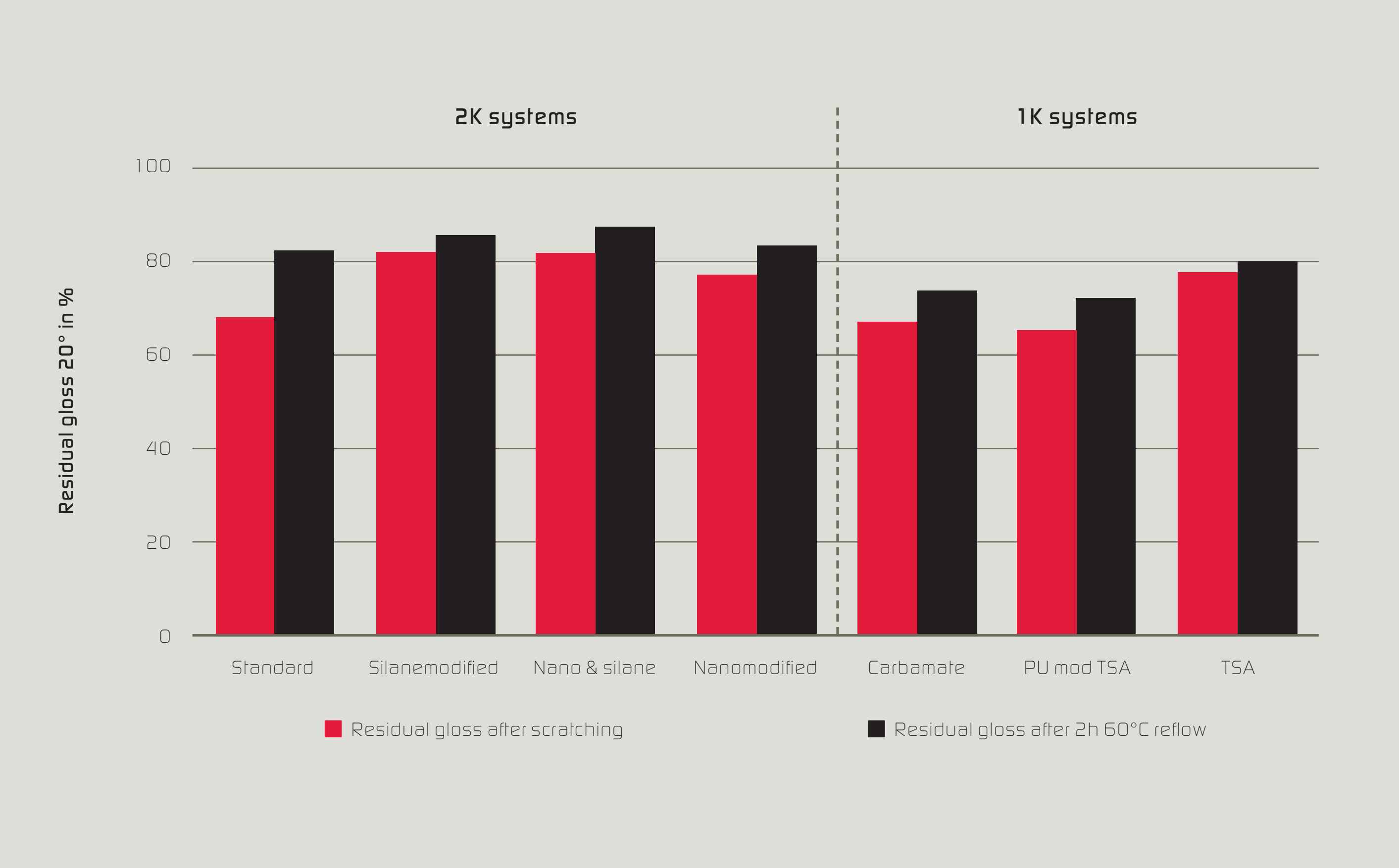
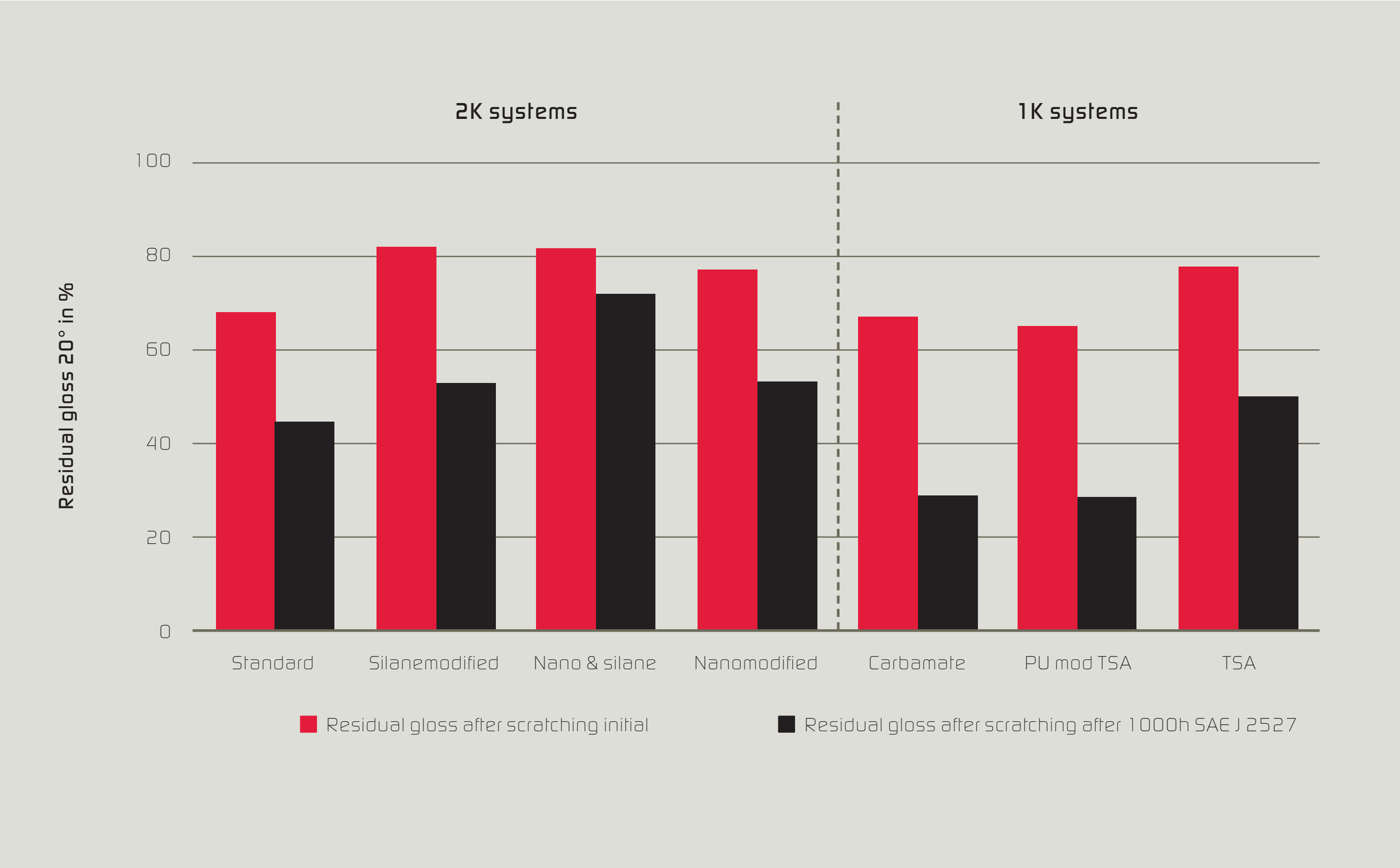


Figure 3: Wet scratching before (red) and after (black) 1,000 h weathering



In contrast to unweathered surfaces, the weathered nano- and silane-modified paint layers are superior to the weathered 2K PUR coatings, which are exclusively silane-modified (53 % residual gloss), in terms of their resistance to wet scratching.

DRY SCRATCHED: THE TRENDS

The tests for dry scratching confirm the trends after wet scratching. The results for the 2K automotive clearcoats illustrate the wide range of residual gloss values for the 52 standard systems (*Figure 4*). On average, the residual gloss value directly after dry scratching is 43 % compared with 76 % for the silane-modified 2K PU coatings and 78 % for the nano-modified 2K PU coatings. The three 2K PU coatings that perform best are those that are both nano- and silanemodified (94 % residual gloss).
These are development systems whose concept obviously works: Nanoparticles increase the dry scratch resistance in particular, while the silane modification influences the binder matrix and thus particularly improves the resistance to wet scratching.
Furthermore, the results of the tests for dry scratching show that the reflow ability of most 2K PU standard coatings is considerable when heated to 60 °C for two hours: On average, the residual gloss then increases by 33 %. A 2K PU development system with a biobased trimer of pentamethylene diisocyanate (PDI) as hardener achieves almost the same values directly after dry scratching and after reflow as a system based on hexamethylene diisocyanate (HDI) of petrochemical origin.
In the nano-scratch test, 1K and 2K automotive clearcoats behave differently (*Figure 5*). In 1K systems, the coating surface cracks at lower forces than in 2K systems.
In other words, the change from plastic deformation to brittle fracture occurs at lower loads. After brittle fracture, the coatings no longer heal through the reflow effect. The Nano-Scratch-Test proves that 2K PU systems do not irreversibly scratch as quickly as 1K systems.
The residual depth at maximum force, on the other hand, is not clearly correlated with whether 1K or 2K coatings are used. With residual depths between 0.2 and 0.6 µm, rather large individual differences exist between the representatives of the respective technologies, which can be explained by the density of the polymer network and the elasticity of the areas between the linking points of the network. A particularly beneficial combination of high normal force at the first crack and a low residual depth at maximum force is demonstrated by 2K PU coatings with a silanemodified network.

CORROSION FROM SULFURIC ACID AND THE LIKE

The results of the chemical resistance tests in the gradient oven show that all automotive clearcoats react sensitively to sulfuric acid solutions and pancreatin. Pancreatin is used in laboratory practice as a surrogate for bird droppings. Diluted sodium hydroxide solution, which originally tested the hydrolysis resistance of polyesters, and water are less problematic for the coating surface (*Figure 6*).
At the same time, coating damage caused by pancreatin shows a pronounced reflow effect: Minor damage heals after two hours of heating the paint surface. Such minor paint damage, which was detected during the sampling after one hour, is due to plastic deformation of the surface, which is caused by the fact that pancreatin crystallizes during drying.
When comparing the chemical technologies with regard to the influence of diluted sulfuric acid, only minor differences are found. When it comes to pancreatin damage, 1K-TSA systems have a particularly good reflow capacity; otherwise, the 2K PU systems, which are both nano- and silanemodified, prove to be somewhat more resistant to pancreatin than the other coatings.
Silane modification of 2K PUR clearcoats improves their resistance to chemicals. Overall, the nano- and at the same time silanemodified development systems performed best in the chemical tests. They proved to be more resistant to tree gum, diluted sodium hydroxide solution and water than other coatings, because they have a higher glass transition temperature and a locally high network density at the siloxane bonds.
The test for chemical resistance was carried out not only with fresh coating surfaces, but also with those that had been aged for six and twelve months, respectively, in standard climates.
The results remained the same: No aging effect occurred. According to SAE J 2527, twelve months of standard climate usually has less effect on chemical and physical aging than 1,000 hours of weathering.

THE FUTURE

In the comparative test, the nano- and silanemodified 2K PU development systems exhibit a superior level of properties making their use in automotive OEM coatings likely in the near future, at least in the premium vehicle sector.
1K TSA systems perform well in the test. However, they are likely to miss out on an opportunity opened up by reactive 2K PU systems: The automotive industry is currently increasingly concerned with coating plastic and metal parts on automobiles with clearcoat at temperatures of around 80 °C (140 °C is usual) in an energy-efficient manner. This is possible with a technique based on a thermolatent PU hardener [8, 9]. The two low-temperature systems in the comparative study do not stand out in terms of either optical appearance or durability, but perform similarly to conventional clearcoats.

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Figure 4: Dry scratching for all 2K PU systems investigated.

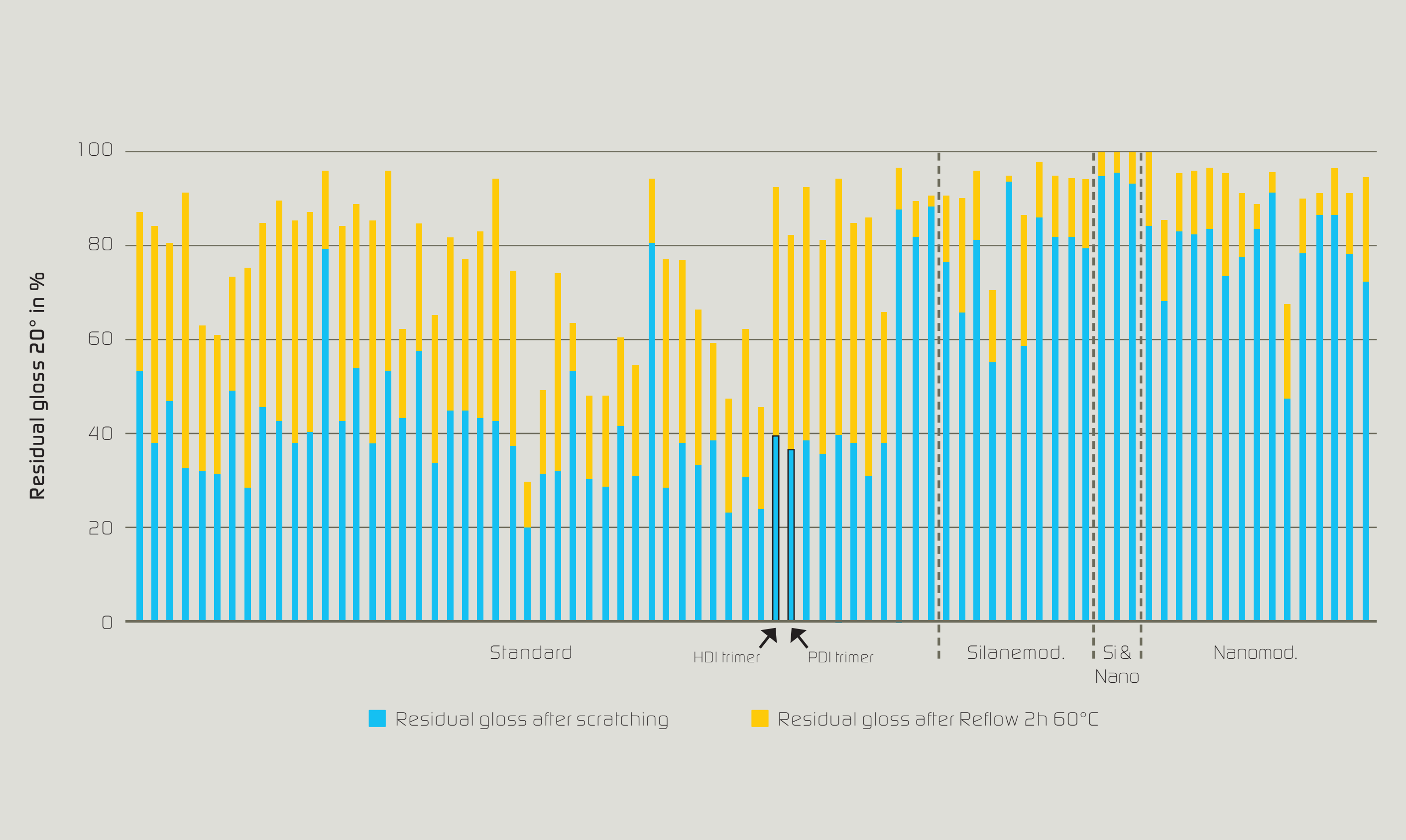

Figure 5: Nano-scratch tests for all tested automotive clearcoats.

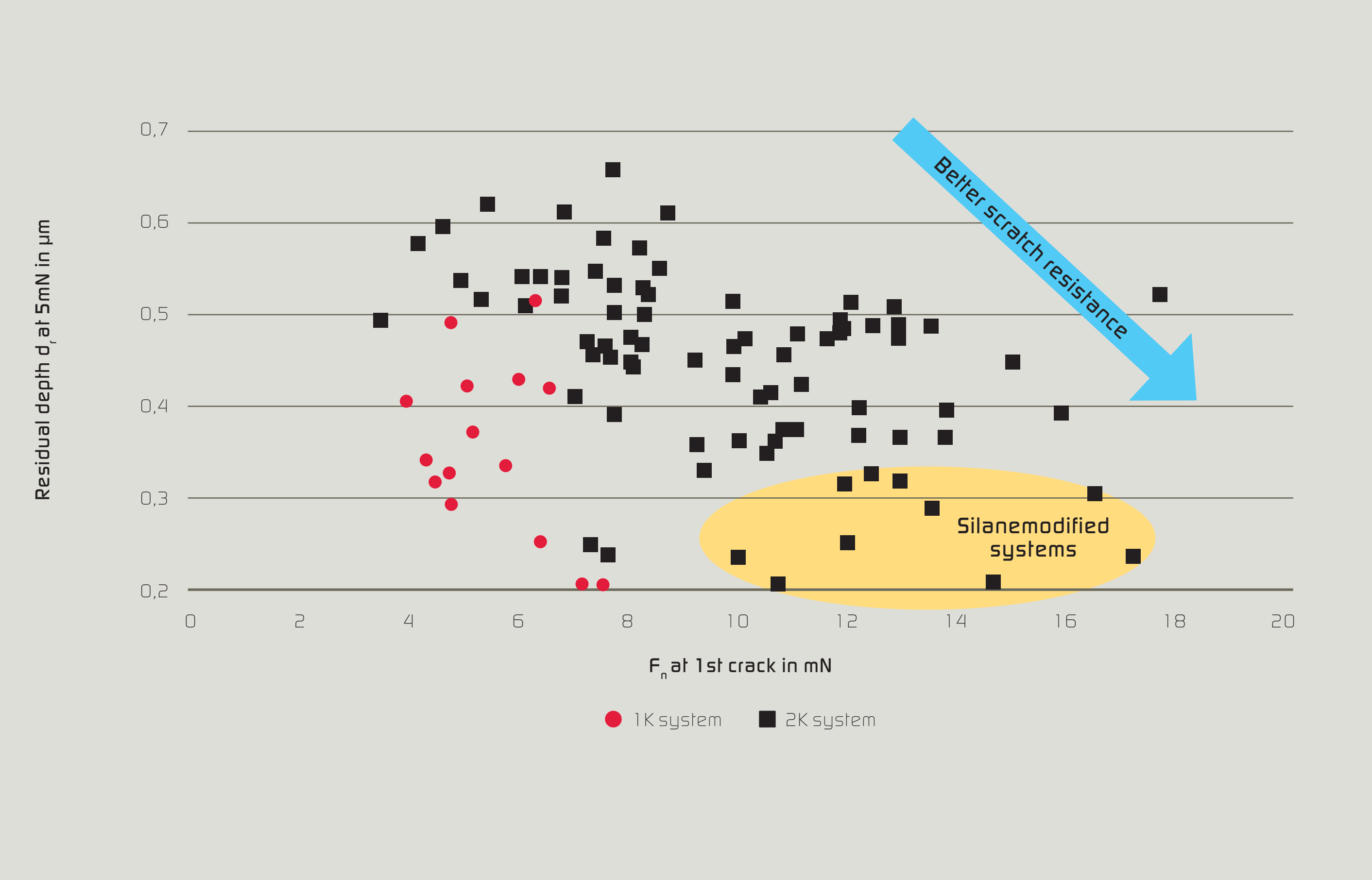

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Figure 6: Tests for chemical resistance, classified according to exposed chemicals and chemical technologies of the coatings.