Scratch/mar resistance is one of the most important physical characteristics of a coating system. Measuring techniques are briefly reviewed with a focus on the automotive coatings industry. Single-scratch techniques are compared with the simpler methods of simulating scratching.

In addition to good levelling, high gloss and the development of any special effects, resistance to mechanical damage – by stone chipping and scratching – is particularly important in order to obtain a high-quality appearance for automotive clearcoats. The brushes and dirt in a car wash, for example, produce scratches measuring a few micrometres in width and up to several hundred nanometres in depth. With this background, several measuring methods have been discussed over the last 15 to 20 years in the automotive and paint industry. The objective has been to obtain a clear characterisation of the scratch/mar resistance of clearcoats.

Procedures that create a single scratch (micro or nano scratch methods) were developed and were improved at the end of the 1990s [1-8]. These methods are different from the more practically oriented procedures that are based on relatively simple methods to try to imitate or even come close to reality (such as the car wash brush method).

IMITATING CAR WASH BRUSH DAMAGE

The clearcoat to be tested (applied on a standard metal sheet) is moved back and forwards ten times under a rotating car wash brush. The polyethylene brush is sprayed with washing water during the simulated cleaning procedure. Because the metal sheets used for the test are clean, a defined amount of quartz powder is added to the washing water as a substitute for street dirt (in the Amtec method). A gloss measurement, e.g. in 20° geometry, is used to evaluate the scratch resistance. The initial gloss and gloss after the cleaning procedure are measured. The percentage of residual gloss relative to the initial gloss is taken as a measure of scratch resistance. High values evidently indicate good scratch resistance.

The instrument is schematically shown in Figure 1 [8]. A commercial car wash brush instrument is manufactured by Amtec-Kistler in Germany. This method was developed in a project working group of the DFO (Deutsche Forschungsgesellschaft für Oberflächenbehandlung) two decades ago and has been specified in the DIN EN ISO 20566 standard. More details can be found for example in [9].

ADAPTING A TEXTILE TEST: THE CROCKMETER

The crockmeter is used by large car manufacturers and represents a different type of stress on the coating. The crockmeter has been the standard device of the American Association of Textile Chemists and Colorists (AATCC). It has mainly been used to test textiles for colour fastness and abrasion. This instrument (made by Atlas Materials Testing among others) is fitted with an electric motor, so that a uniform stroke rate of 60 double
Scratch/mar resistance is one of the most important physical properties that characterise the mechanical quality of a coating system. Relevant measuring techniques are briefly reviewed in respect of applications in the automotive and coatings industry.

Three simple methods of evaluating scratch resistance are in general use: a car wash brushing simulator, the crockmeter used originally in the textiles industry, and a rotating/oscillating device that often uses paper as the scratching medium.

More sophisticated techniques involve the creation of a single nano-scratch under controlled conditions with evaluation of the forces involved and damage created.

Limited correlations between the laboratory car wash method and both crockmeter and nano-scratch test have been established.

DMA has been used to study correlations between scratch damage and the nature and extent of cross-linking.

Results at a Glance

- Scratch/mar resistance is one of the most important physical properties that characterise the mechanical quality of a coating system. Relevant measuring techniques are briefly reviewed in respect of applications in the automotive and coatings industry.
- Three simple methods of evaluating scratch resistance are in general use: a car wash brushing simulator, the crockmeter used originally in the textiles industry, and a rotating/oscillating device that often uses paper as the scratching medium.
- More sophisticated techniques involve the creation of a single nano-scratch under controlled conditions with evaluation of the forces involved and damage created.
- Limited correlations between the laboratory car wash method and both crockmeter and nano-scratch test have been established.
- DMA has been used to study correlations between scratch damage and the nature and extent of cross-linking.

A special testing material is attached to the bottom side of the cylinder, which is 16 mm in diameter; its downward force is 9 N. Ten double strokes are carried out over a length of 100 mm. For this method too, the percentage of residual gloss is used as a measure of scratching. In [8] a good correlation between crockmeter and laboratory car wash methods can be observed in the range of good and bad scratch resistance. Within the range of medium scratch resistance, however, no clear correlation is detectable. The reason for this could be the different degrees of strain in the two scratch test methods. The Amtec test is the one with a rather higher strain load.

**AN ALTERNATIVE SCRATCHING TEST – THE “ROTA-HUB”**

The “Rota-Hub” scratch tester was developed by Bayer AG approximately 15 years ago. In this test, a carriage moves in both x- and y-directions. A rotating disc with the scratching medium (e.g. paper) is attached to the carriage. The rotating disc is lowered onto the sample. In this way the sample is strained by a rotating disc that at the same time moves in x- and y-directions. Feed rate, rotation velocity and contact pressure can be randomly selected and have been optimised.

For the automotive industry, copy paper has proved to be a suitable scratching material because it causes scratches similar to those caused by a car wash. The resulting damage is a meander-shaped scratch pattern that can be measured using gloss and haze parameters [10].

**SINGLE-SCRATCH TECHNIQUES ALLOW DETAILED ASSESSMENTS**

In micro-scratch experiments single scratches of characteristic and realistic structure can be generated. The indentation depth depends on the applied force and the indentation body (indenter). Indentation depth is usually in the range of 1 µm or less.

A diamond indenter (radius at the point 1–2 µm) is pushed onto the sample surface, applying a defined force to generate the scratch while the sample is moved in a linear direction at constant velocity underneath the indenter (see Figure 2).

The applied normal force can be constant or increase progressively during the scratching procedure. Basically it is possible to measure the tangential forces and the indentation depth during the scratching procedure. Deformations or damage can be observed with a microscope or additionally with a video camera. The profile of the scratches generated can be measured using AFM technology.

In combination with the parameters measured during the scratching procedure it is possible to calculate physical parameters which allow conclusions to be drawn about the elastic and plastic deformation behaviour and fracture behaviour.

**MEASURING TRANSFORMATIONS: A PROGRESSIVE LOAD TEST**

In this context a method was developed in the DuPont Marshall Laboratory (Philadelphia, USA) that generates and evaluates a single
scratch on a surface (nano-scratch method). This method has been used for tests along with development work for clearcoats. A commercial instrument by the Swiss company CSM (now part of the Anton Paar company) was tested in the course of a project at the Research Institute for Pigments and Paints (Forschungsinstitut für Pigmente und Lacke e.V. (FPL), now part of IPA/Stuttgart) around the year 2000 and later. This instrument is based on the method developed at the DuPont Marshall Lab.

The objective of several projects – where manufacturers of paints, raw materials and automobiles worked together – was the evaluation of the nano-scratch tester regarding its reproducibility, accuracy and applicability as a realistic way to determine scratch resistance.

THE CRITICAL LOAD POINT AND ITS SIGNIFICANCE

The key point in this method is the determination of the critical load where the first irreversible cracks or fractures are generated, and which therefore indicates the transition from reversible plastic deformation to significant/lasting damage. For that, the normal load is constantly increased and the indentation depth and tangential load are simultaneously recorded. The transition from plastic deformation to the fracture range is indicated, for example, by unsteadiness or fluctuations in the load detected and the indentation depth. As a typical dimension in addition to identifying the critical load, it is common to determine the residual indentation depth after scratching – typically at a normal load of 5 mN – in the range of plastic deformation.

In Figure 3 the transition range of an acrylate/melamine system is demonstrated. The top picture shows an AFM image of the scratch ridge itself where cracks are clearly visible. The bottom picture is taken with a microscope at a magnification factor of approximately 1000; see also [8, 11, 12]. If values from nano-scratch tests are compared to results from car wash tests (see Figure 4 [8]), some correlation to the critical load can be observed. From this it can be concluded that the Amtec test causes significant permanent damage rather than strains within the plastic range [13].

DYNAMIC MECHANICAL ANALYSIS AND FORMULATION VARIABLES

For certain clearcoat systems, partial healing of scratches can be observed over a period of time. In literature this is known as the reflow effect [14]. Thermal relaxation phenomena may provide a physical explanation of this effect.
In connection with scratch/mar resistance the cross-linking density of clearcoats is also a critical factor. Dynamic mechanical analysis (DMA) has been established as a method to determine cross-linking density [14-16]. Several ranges can be characterised when observing the behaviour of the storage modulus $E'$ as a function of temperature. The glass transition range is followed by the rubber-elastic range, which can be more or less distinct depending on the degree of cross-linking.

In this range the value of the storage modulus $E'$ is related to the cross-linking density. The value of $E'$ at the local minimum is often chosen as a quantitative measure of cross-linking density.

Some clearcoats were examined by submitting free films to a tension test using a “DMA 7” instrument by Perkin-Elmer. In this context, measurements of paint systems are described, e.g. in [16]. Figure 5 shows a comparison of the results of DMA analysis and values obtained in car wash simulations [8].

A clear correlation between $E'$ as a measure of cross-linking density and the value for scratching can be observed. The quality of the scratching level (high residual gloss) increases with increasing cross-link density [17]. Figure 6 shows a short comparison of different network types and brief remarks on their properties [18, 19, 20]; with type D being a favourite for automotive clearcoats.

OBSERVING AND REDUCING WEATHERING EFFECTS

The influence of weathering on scratch resistance is demonstrated in Figure 7, showing the gloss retention after Amtec testing of various clearcoats as a function of exposure time under SAEJ1960 (xenon arc) weathering. All samples that were investigated show a significant drop of residual gloss after even a short exposure time.

A clear differentiation can be seen between the clearcoats with UV absorber (CC1, CC2, CC3, CC1c) and without (CC1a, CC1b, CC2a) is noticeable. Afterwards the residual gloss decreases slightly [21, 22]. Other studies can be found, for example in [23].

FURTHER RESEARCH AND CORRELATIONS SUMMARISED

Several methods of determining the mar (scratch) resistance of clearcoats have been presented above. Methods that create a single scratch are different from more practically oriented procedures that are based on relatively simple methods to try to test or even come close to reality (such as the car wash brush method).

The methods were reviewed, briefly considering also other physical properties such as cross-linking density or weathering. Recent investigations show that scratch/mar resistance is always an important factor in characterising the physical properties of coating surfaces, for example in analysing automotive clearcoats containing silane modified blocked isocyanates [24].

Their results showed that a close correlation existed between the scratch resistance data obtained from car-wash and nano-scratch tests for certain clearcoats. Also, the scratch resistance of exterior clearcoats and polycarbonate hardcoats were examined and discussed recently in [25].

Studying the literature, there is often no clear separation between the expressions mar and scratch resistance. Really, ‘mar’ should refer to light surface damage encountered in the real field that are usually shallow and narrow while ‘scratch’ refers to medium or more severe types of damage [26]. However, several authors handle this uncertainty by writing scratch/mar.

REFERENCES


Figure 6: Different cross-linking network types in coatings.

Figure 7: Gloss retention (Amtec) during SAEJ1960 weathering test.
“Important is the knowledge of fundamental physical data in combination with practical results.”

3 questions to Michael Osterhold

Which of the test methods described will prevail in the future? Several methods have been discussed over the last 20 years in the automotive and paint industry. As one result, a more practically oriented procedure based on the car wash brush method has been standardised by DIN and is widely used. However, methods that create a single scratch can yield deeper insights into the physics of coatings.

Which innovative developments in measuring methodology are foreseeable and will lead to improved testing procedures? The development of the nano-scratch method that generates and evaluates a single scratch on a surface was one of these innovative steps allowing a more scientific view into the mechanical behaviour of coating systems. Important is the knowledge of fundamental physical data in combination with practical results (structure/property relationships).

Which of the presented methods is the most suitable for digital transformation and automation in measuring and testing? Most of the obtained testing results can be stored directly into databases. Against the background of evaluating e.g. a reasonable structure/property relationship a data analysis with statistical methods is of key importance. Before starting an investigation a sensible design of experiments (DoE) could be extremely helpful. A preference of a special method concerning digital transformation cannot be given.