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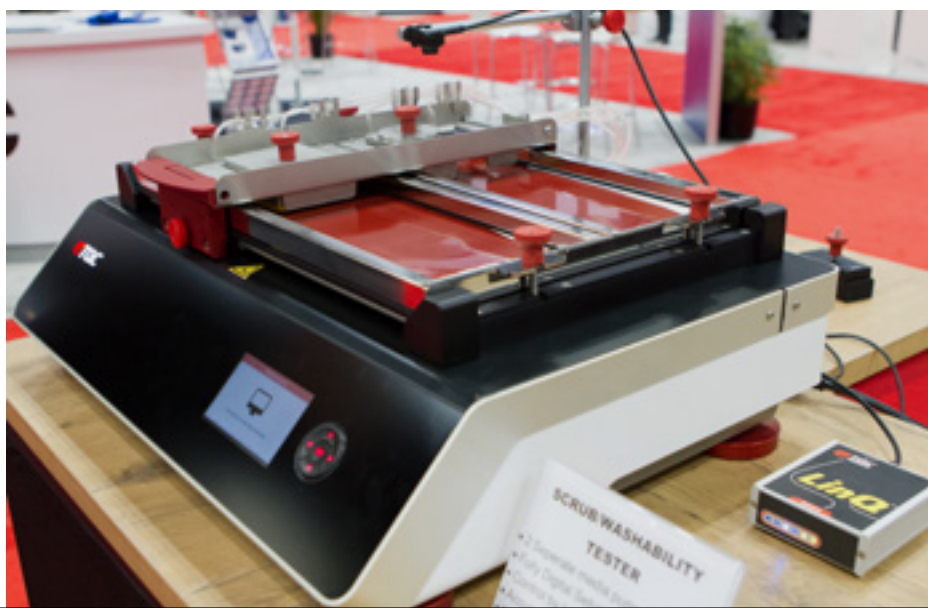
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TESTING TIMES FOR COATINGS

No matter which paints and coatings or their constituents we may have in front of us, they all have to undergo extensive testing, verification and measurement methods. If the test results prove unsatisfactory, further research is conducted and all the stops are pulled out to enhance the formulation.

As a formulator, your challenge is to stay at the forefront of research and to keep up with developments. This can be difficult at times.

European Coatings Journal would like to help out here. We have put together this handy dossier on measuring and testing especially for you, packing it full with all the knowledge and technical papers that have appeared on this topic in the European Coatings Journal over the last four years.

Silke Karl

MARKET REPORT

An overview of test and measurement standards

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Evaluating anticorrosive properties

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AN OVERVIEW OF TEST AND MEASUREMENT STANDARDS

Received wisdom is that “Quality counts and will prevail”. However, if high-performance products, such as paints, are to both reach and maintain specified levels of quality, test and measurement methods are essential. By Damir Gagro [published in ECJ 11/2015].

This then raises the question: which methods and standards are commonly employed in the paints and coatings industry?

Countless test and measurement methods exist on how to determine the properties and performance characteristics of coatings. These methods vary according to the type of paint and the area of application. An overview of select conventional methods that are used for both product monitoring and compliance with quality specifications is presented below, along with pending changes in various test standards.

COMMON TEST METHODS

The test methods here fall into five categories: physical, optical, analytical, corrosion, and weathering. The physical test methods are designed to measure the following:

- Adhesion strength (ISO 2409:2013 “Cross-cut test” or ISO 4624:2002 “Pull-off test for adhesion”)
- Scratch resistance (ISO 1518-1:2011 “Part 1: Constant-loading method” and ISO 1518-2:2011 “Part 2: Variable-loading method”)
- Surface resistance (ISO 2815:2003 “Buchholz indentation test”)
- Resistance to liquids (ISO 2812-1:2007 “Part 1: Immersion in liquids

other than water”)

- Coating thickness (ISO 2178:1982 “Magnetic method” and ISO 2360:2003 “Amplitude-sensitive eddy-current method”)
- Optical tests for measuring colour and gloss are covered by the following standards:

- ISO 11664-4:2008 (Colorimetry)
- ISO 2813:2014 (Determination of gloss value at 20 degrees, 60 degrees and 85 degrees)

These two standards can be used to measure the appearance of the coatings that will result from individual paint batches.

COMBINATIONS OF CYCLIC TESTS

The following standards specify methods for determining various contents of substances in a formulation and can be combined with other methods, for instance, to benchmark the yield of one system against a reference product:

- Determination of pigment content - Part 1: Centrifuge method (ISO 14680-1:2000)
- Determination of pigment content - Part 2: Ashing method (ISO 14680-2:2000)



“South Florida has long been considered a benchmark for outdoor weathering. A year’s sun in Florida can simulate multi-year weathering elsewhere.”

- › Determination of non-volatile-matter content (ISO 3251:2008)
- Various corrosion tests are presented in the following standards:
- › ISO 9227:2012 - Corrosion tests in artificial atmospheres (Salt spray tests)
- › ISO 6270-1:1998 - Determination of resistance to humidity (Part 1: Continuous condensation); Part 2 (ISO 6270-2:2005): - Procedure for exposing test specimens in condensation-water atmospheres
- › ISO 3231:1993 - Determination of resistance to humid atmospheres containing sulphur dioxide

The various salt spray tests (neutral salt spray, acetic acid salt spray and copper-accelerated acetic acid salt spray) are suitable for checking that the comparative quality of a metallic material, with or without corrosion protection, is maintained. Combinations with cyclic tests are also possible, e.g. a salt spray test combined with the condensation-water test and phases of controlled temperatures and humidities. A good example of this is presented in ISO 11997-1:2005. Although the standards mentioned are geared towards the automotive industry, they also find application in machine and plant engineering. The effect of solar radiation, heat, and moisture on the physical, chemical and optical properties of coatings is established by means of artificial accelerated weathering or artificial accelerated irradiation exposures in appropriate equipment. Relevant standards here include:

- › Methods of exposure to laboratory light sources. Part 1 – General guidance (ISO 16474-1: 2013)
- › Xenon-arc lamps (ISO 16474-2:2013)
- › Fluorescent UV lamps (ISO 16474-3:2013)

BETTER SIMULATION OF REALITY IN THE LABORATORY

A frequently asked question, of course, is how good is the match between laboratory test results and reality? Again, look no further than the automotive industry for a good example. The corrosion behaviour of materials and components and the corrosion protection afforded by coating systems have been simulated in accelerated test methods. It has been recognized, though, that conventional test and measure-

ment methods have failed to keep pace with changes in materials. Consequently, not only have concentrations now been adjusted, but low-temperature phases also incorporated into the test cycles. Tests involving exposure to changing climate cycles are consequently growing in popularity within the automotive and commercial vehicle sector, and in mechanical and plant engineering. This is a reflection of the fact that corrosion tests need to simulate reality as closely as possible and that continuous single loading is simply not the best way to accomplish this.

SUPERSEDED STANDARDS SERIES STILL IN SPORADIC USE

Even when existing standards are extended or superseded by new series, it is not the case that the industry abandons the methods therein. If a customer specified a certain standard a few years ago, it is possible that a new test and measurement method will fail to provide results that allow comparisons to be drawn. Consider two examples: ISO 11341:2004 “Artificial weathering and exposure to artificial radiation - Exposure to filtered xenon arc radiation” came into force in 2004. This standard was withdrawn in 2013 and replaced by ISO 16474-2:2013 (“Methods of exposure to laboratory light sources - Part 2: Xenon-arc lamps”). The essential difference in the artificial weathering employed is that the old standard specified two reference temperatures, namely 55 °C and 65 °C. The new standard omits the lower temperature entirely. However, users in, e.g., the rail vehicle sector and machine-making, have been testing at a black standard temperature of 55 °C for years. A difference of 10 °C in tests that are conducted for 1000, 2000 or 4000 hours simply cannot yield comparable results. It can therefore be assumed that ISO 11341 will continue to be used by these and other users. The second example is the determination of flow time from a DIN cup (DIN 53211). This test standard was withdrawn away back in 1996 and was replaced by ISO 2431:2011 (“Determination of flow time by use of flow cups”). The flow cups specified in the two standards differ in the geometry of the inclination angle of the drainage slope, the nozzle length and the fill volume. Even if the nozzle diameters were identical, comparable results could not be achieved. Spray paint shops often still employ the DIN cup and therefore also insist on using the test method which was specified in the standard and was withdrawn almost 20 years ago. ☞



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Two questions, two answers:

1 What are the challenges when it comes to measurements in the field of paints and coatings?

2 How can comparability between different methods addressing the same aspect be guaranteed?

(published in ECJ 11/2015)

Source: Helko Stahl



1 In coating and varnishes, the measurement of the effects of weathering are indeed quite challenging. This is confirmed by all players in the coating industry value chain. Natural and artificial weathering are highly complex matters. The Köppen-Geiger classification of global climate claims no less than 31 different climates. More than 20 natural weathering testing locations propose their services. Furthermore artificial accelerated weathering devices manufacturers offer a large choice of instruments differentiated by the UV spectrum, the irradiance energy level, the humidification system, the testing protocols, the acceleration factor. In turn this generates some different philosophies, rules, recommendations and understandings of their results' transferability and comparability to treatment results by natural weathering conditions.

After weathering exposure, samples assessment in gloss, colour change, cracking, adhesion to name the main ones is classical. What may prove more challenging is the choice of failure criteria and the targeted performance level to be representative of the life-time of the article. The economical dimension is also critical. On the one hand, failure cases may expose the coating producer, OEMs or raw-material suppliers to costly claims. On the other hand well understood testing procedures and well implemented product guarantees will durably protect the manufacturers.

In summary, there is a too large number of variables, different technologies to simulate the real-life situations. Weathering resistance assessment is not a straightforward measurement, but a permanent attempt to best approach the reality.

“A permanent attempt to best approach the reality.”



Bruno Sallé de Chou
CEO & Founder
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2 In many situations general Industry standards like EN ISO 11341 for coating or OEM standards prevail. In such cases the standard guarantees the comparability between the methods. For the users, comparability is no longer an issue, the validity of the standard is seldom disputed. The objective is rather to comply to the standard.

We also meet a significant number of independent companies in the industry that need to better assess their coating formulation and/or their raw materials. In such a case, the formulator needs a tool to compare new formulations with his current material performance. There is no need to reference to an industry or OEM standard, but rather the requirement for taking sound decisions. Here, some individually tailored comparability between natural and accelerated weathering is much more essential than compliance to standards. The weathering specialists will rather support that guarantee through guidance. They will help selecting the right testing protocol, balancing the right dosage of natural and artificial weathering, choosing the correct coating properties measurement and failure criteria. 



Source: Daimler

1 Every sector of industrial manufacturing strives to make processes as reliable and reproducible as possible.

When it comes to measuring colour tones, this becomes somewhat more complex. Seeing colour is a process that in many ways depends on the viewer. We now know that the ability to see colour is influenced by age, gender, medication, fatigue, nutrition and even the mood of the viewer. A measuring device would therefore seem to make sense as it offers considerably higher reproducibility of measurement values in comparison to human visual judgement.

However, there is also a paradox in that the individual differences already mentioned make it difficult to find common ground with the measuring device. No single viewer can represent the average person with whom a measuring device could be calibrated. This is why the emotional subject of "colour" can easily lead to conflict.

For this reason, it is important to talk about tolerance.

Hardly anyone ever contacts us any more with an order stating "I'd like some kind of green". Even private customers usually have a clear idea of the colour tone they want. These days, it is only the coordinated processes we have put in place throughout the entire supply and production chain that enable us to handle orders like this easily.

2 For demanding industrial processes there is a simple yet effective method: create a standard that is accepted by both sides, compare every subsequent delivery with that standard and make sure that the quality stays within the agreed level of tolerance. That is easier said than done as it requires a huge amount of preliminary work on both sides until everything runs smoothly. This is because the "objective" measurement of a paint coating depends on many param-

"It is important to talk about tolerance."



Michael Klemm
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ters, such as how it is applied, layer thickness, humidity, temperature, drying time and substrate – often wood. All of these parameters are inter-dependent for a consistent result. In the end it is all remains subjective. But it is precisely this difficult task that provides an opportunity to stand out from the competition and forge a closer relationship with customers in a world that is becoming increasingly anonymous. Good communication and a trusting relationship are key to arriving at a result with which both sides are happy. **3**

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DETECTING “SELF-HEALING” EFFECTS

Evaluating the anticorrosive properties of nanocontainers, micro- and nanocapsules. By M. Wanner, K. Krawczyk, T. Schauer, Fraunhofer IPA, E. Lachery, S. Peelerbroeck, M. Poelman, Materia Nova, C. Schreiner, V. Stenzel, Fraunhofer IFAM, M. Cybik, C. Mayer, Universität Duisburg-Essen (published in ECJ 04/2016).

Special nanocontainers, micro- and nanocapsules can be incorporated in an anticorrosive primer formulation to provide self-healing properties that take effect as soon as the primer is mechanically damaged. As the matrix continuity and the interfaces are affected, we cannot fully evaluate the performance of such ‘self-healing’ primers by eye. Electrochemical impedance spectroscopy (EIS) combined with thermocyclic electrolytic loading (TEL) contributes significantly to evaluating such systems.

One suggestion to achieve a more efficient and durable corrosion protection with coatings is the concept of self-healing, also known as self-repair, which aims to stop the degradation processes at an early stage. This concept was first published about 20 years ago [1-2]. Generally, it is based on the use of encapsulated monomers, which start the healing action on being released from the capsule by a triggering crack. Several overviews of self-healing technology for polymers are given elsewhere [3-6].

SELF-HEALING ADDITIVES TO PREVENT CORROSION

In terms of protecting metal substrates against corrosion using coatings, the self-healing effect can either be a restoration of the mechanical and barrier properties of the matrix or it can be the corrosion protection alone. Options for self-healing have been described in the literature [7-8] in relation to inhibiting corrosion processes at weakened and damaged sites in coatings. The standard procedure involves using microcapsules, similar to those used for polymer self-healing, but filled with a liquid or soluble solid corrosion inhibitor.

If such microcapsules are integrated into a coating and are destroyed by mechanical impact, the released contents are transported to the metallic substrate together with the corrosive medium.

When a corrosion inhibitor (e.g. benzotriazole, Ce^{3+} salts) comes into direct contact with the metal at the damaged site, corrosion inhibition is initiated and this prevents the coating degrading prematurely. Using nanocontainers or nanoreservoirs in self-heal coatings is a concept that has been described in the literature [9-10], which relies on

RESULTS AT A GLANCE

→ EIS in combination with a thermocyclic electrolytic loading (TEL) can be regarded as a powerful tool for a quantitative short-term evaluation of anticorrosive primers furnished with ion-exchanging nanocontainers and/or inhibitor-containing micro- and nanocapsules.

→ Continuously consistent equivalent circuit models were identified, which allow differentiated interpretations of the EIS data obtained from the intact and damaged primer samples exposed to TEL.

→ These data strongly suggest that two-layered primer systems (bottom: nanocontainers, top: nano-/microcapsules) could be promising candidates for powerful self-healing anti-corrosive systems.

incorporating corrosion inhibitors into porous or layer-structured nanoparticles.

CONDUCTING THE EXPERIMENTS

The liquid corrosion inhibitors "G50" (HighTac) and "Rewocoros AC 28" (Evonik) were encapsulated according to the following general procedure, which uses the so-called 'ouzo-effect': A mixture of inhibitor, monomer and ethanol was added to a well-stirred aqueous solution of a surfactant. The contact between the hydrophobic and the aqueous phase results in a diffusion process in the system. The ethanol diffuses into the aqueous phase leaving behind the anticorrosion agent. Small droplets are formed and stabilised by the surfactant.

The actual nanocapsules are formed by surficial polymerisation from the emulsion. The polymerisation of the capsule membranes takes place at the interface of the resulting hydrophobic droplets in water and is initialised by the autoprotolysis of water.

Nanocontainers based on hydrotalcites and montmorillonites were synthesised and respectively modified with anions and cations by ion exchange. Different combinations of both of these nanocontainers were prepared and crushed together (particle size: 300–400 nm) in order to obtain a double container that allows the release of two types of components and the formation of protective precipitates (zinc molybdate: "Nano91", calcium molybdate: "Nano92").

Using "Nano91", "Nano92", the encapsulated versions of "G50", Ø 150 nm, and "Rewocoros AC 28", Ø 130 nm, (abbreviated to "G50 c" and "Rew AC 28 c") as well as the liquid inhibitors themselves (abbreviated to "G50" and "Rew AC 28"), the following primer formulations were generated: According to *Table 1*, 'mixed' inhibitor formulations were also manufactured that contained "G50 c" and "Nano91" or "Nano92" in the ratios 1:1, 1:0.6 and 1:0.3.

Table 1: Formulations of test primers; numbers represent mass percentages.

Components	Standard	G50	G50c	Rew AC 28	Rew AC 28c	Nano91	Nano92
"Bayhydrol A 2227/1"	30.62	30.96	30.21	30.58	30.21	30.96	30.78
"Surfynol 104 BC"	1.02	1.03	1.01	1.02	1.01	1.03	1.03
"Borchi Gen SN 95"	1.99	2.01	1.96	1.99	1.96	2.01	2.00
"Crenox R-KB-4"	5.26	5.31	5.19	5.25	5.19	5.31	5.29
"Heucophos ZPA"	16.23	16.41	16.01	16.21	16.01	16.41	16.33
resp. Inhibitor	0	0.10	1.01	0.10	1.01	0.10	0.10
"Bayhydrol A 2227/1"	14.34	14.50	14.15	14.32	14.15	14.50	14.59
Water demin.	6.07	5.21	5.99	6.07	5.99	5.21	5.24
STIT 2354*	15.39	15.39	15.39	15.39	15.39	15.39	15.49
Water demin.	9.07	9.07	9.07	9.07	9.07	9.07	9.13

*Curing agent formulated by and obtained from Covestro, which consists of 77.20% Desmodur N 3900, 19.30% Butoxyl and 3.50% Dynasilen Glymo

Figure 1: Charge carrier paths (red arrows) and equivalent circuit model for the primers without (left image) and with (right image) an artificially inflicted defect under electrolyte impact; the capacitive elements are in parallel to the resistive ones (not depicted).

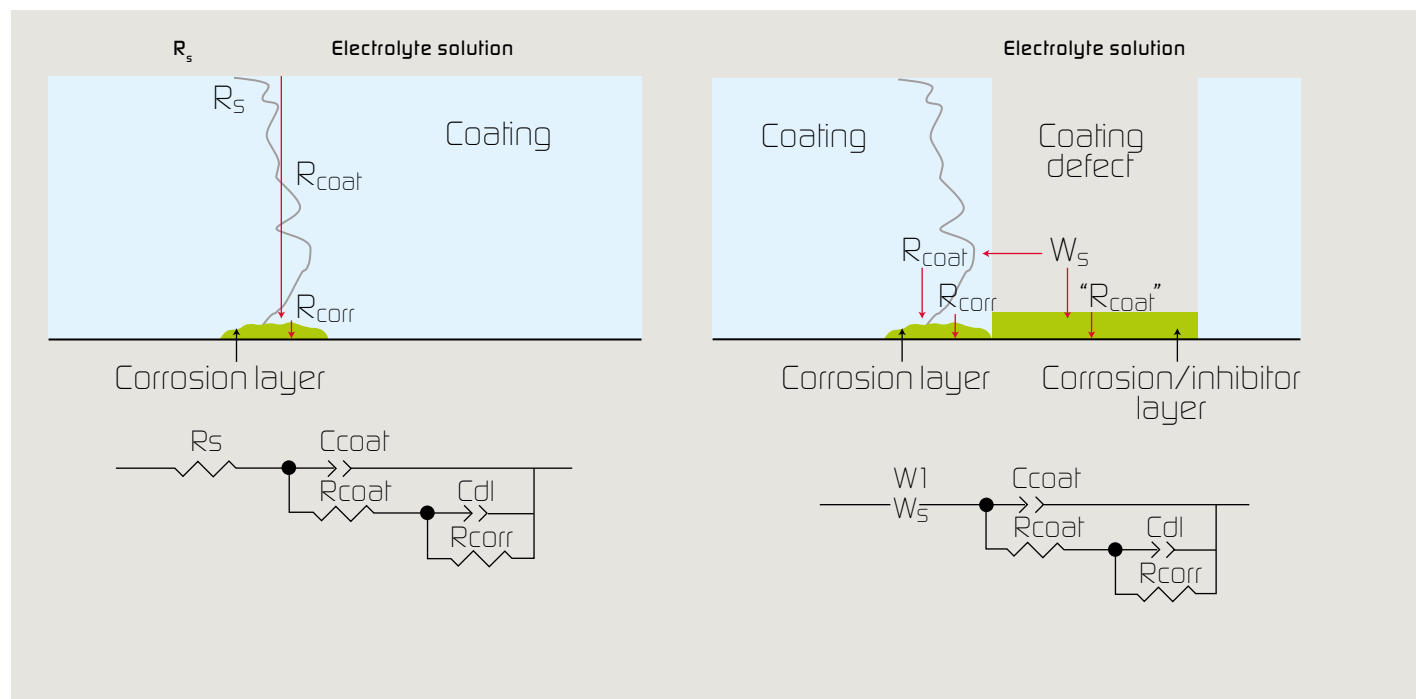
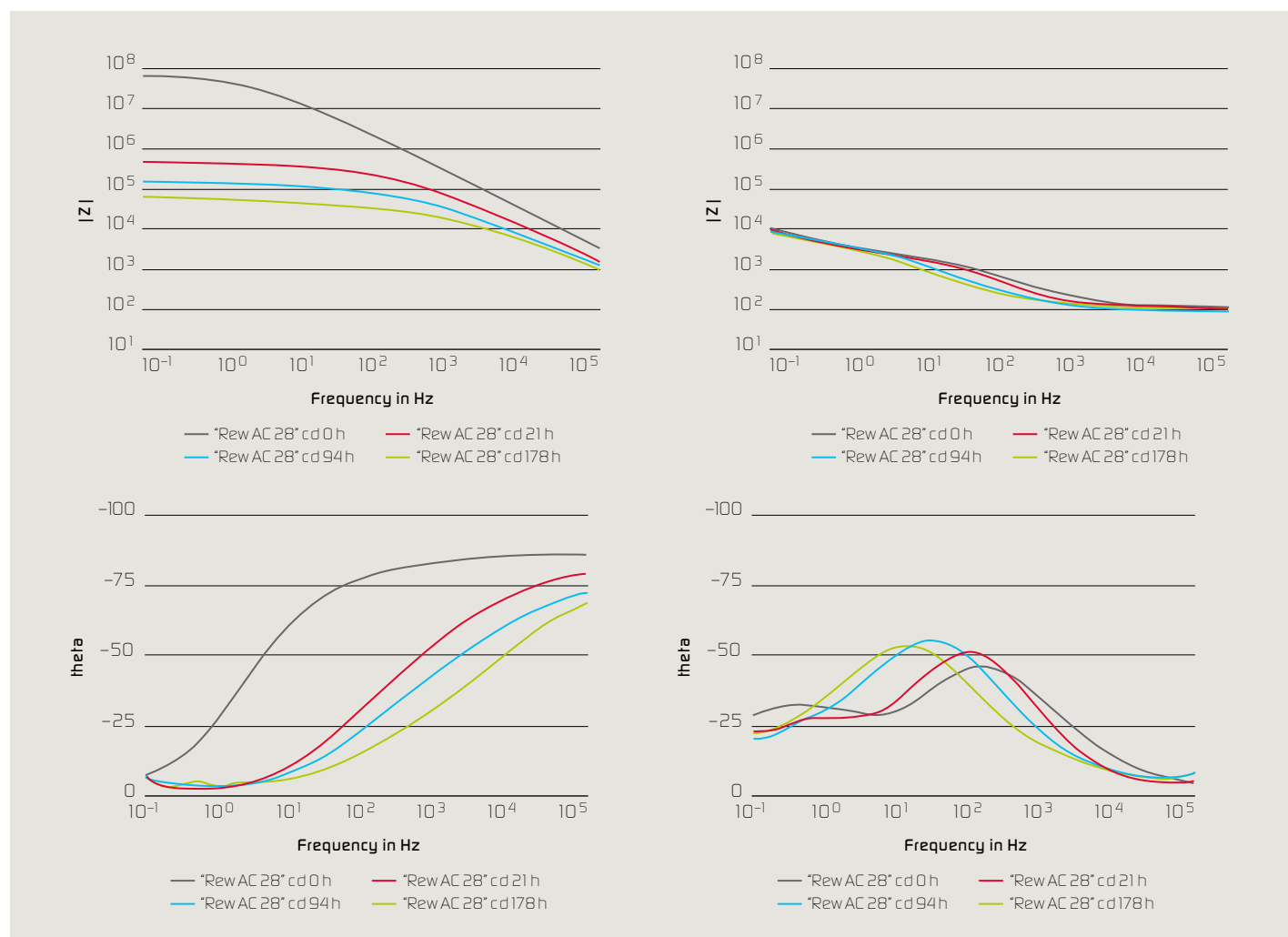


Figure 2: EIS data of an intact (left) and injured (right) area of the TEL affected "Rew AC" 28 c primer.



Using a doctor blade, the primer formulations were applied to degreased steel panels ("Gardobond C") resulting in dry film thicknesses of $25 \pm 2 \mu\text{m}$. Two PVC tubes ($\varnothing 25 \text{ mm}$, $h = 20 \text{ mm}$) were glued to the surface of the film. In one of which, a 6 mm long and 0.5 mm wide slit was inflicted centrally, which met the substrate. After conditioning for 7 days, the PVC tubes were filled with 7 ml Harrison solution and sealed with a glass plate, $d = 0.1 \text{ mm}$. These samples were exposed to thermocyclic electrolytic loading (TEL, sinusoidal cycling between 20°C and 70°C in periods of 1 h) [11] and characterised by EIS (Atlas 0441 High Impedance Analyzer) using a Pt wire as the counter electrode (two electrode geometry; modulation amplitude: 15 mV, frequency range: 100 kHz – 0.1 Hz) after defined intervals of TEL. Simulation of EIS spectra was performed using ZView 3.1.

CORROSION AS A SECOND COATING

EIS spectra obtained from the sample areas with and without an artificially inflicted defect, were simulated according to the equivalent circuit models depicted in Figure 1. The left model implies pores, which reach the substrate. These pores enable the electrolyte solution to reach the substrate and induce corrosion. The model on the right additionally includes a defect, which acts as an additional, significantly larger path for the charge carriers between the substrate and the counter electrode. This means, in this case, that the percentage of charge carriers migrating through coating pores is very small. In cases, in which the mesh size of the matrix is in the range of the charge carrier sizes, charge transfer is determined by a molecular diffusion mechanism. This non-linear behavior (anomalous diffusion) could be simulated by a Finit Layer Warburg element (FLW; here: W_s) [12].

Due to the finding that all EIS spectra obtained from the injured areas of the primer samples during the TEL are consistent with the right-hand equivalent circuit model in Figure 1, it may be supposed that the corrosion layer growing in the defect (partially involving liquid inhibitors that come from broken capsules) acts as a second 'coating'. Here, " R_{coat} " could be regarded as a measure for the formation of corrosion in the defect, whereas R_{coat} (as relevant in the model without defect) appears to be of minor importance. In both models, however, R_{corr} and C_{dl} (not depicted in the diagrams) represent the extent of

undercutting corrosion and delamination, respectively. By way of example, Figure 2 shows the EIS data obtained before TEL (0 h) and after 21 h, 94 h and 178 h of TEL of the "Rew AC 28 c" primer.

SYSTEMATIC INTERPRETATION OF EIS DATA

As expected, the barrier is significantly decreased in the case of the damaged sample areas, and electrochemical processes occur even before the thermocycling is processed. All these spectra could be simulated consistently by the respective equivalent circuit model displayed in Figure 1 by low standard deviation (typically $\chi^2 < 0.001$, $\sum W_i \chi_i^2 < 0.025$). This enables the data to be interpreted systematically.

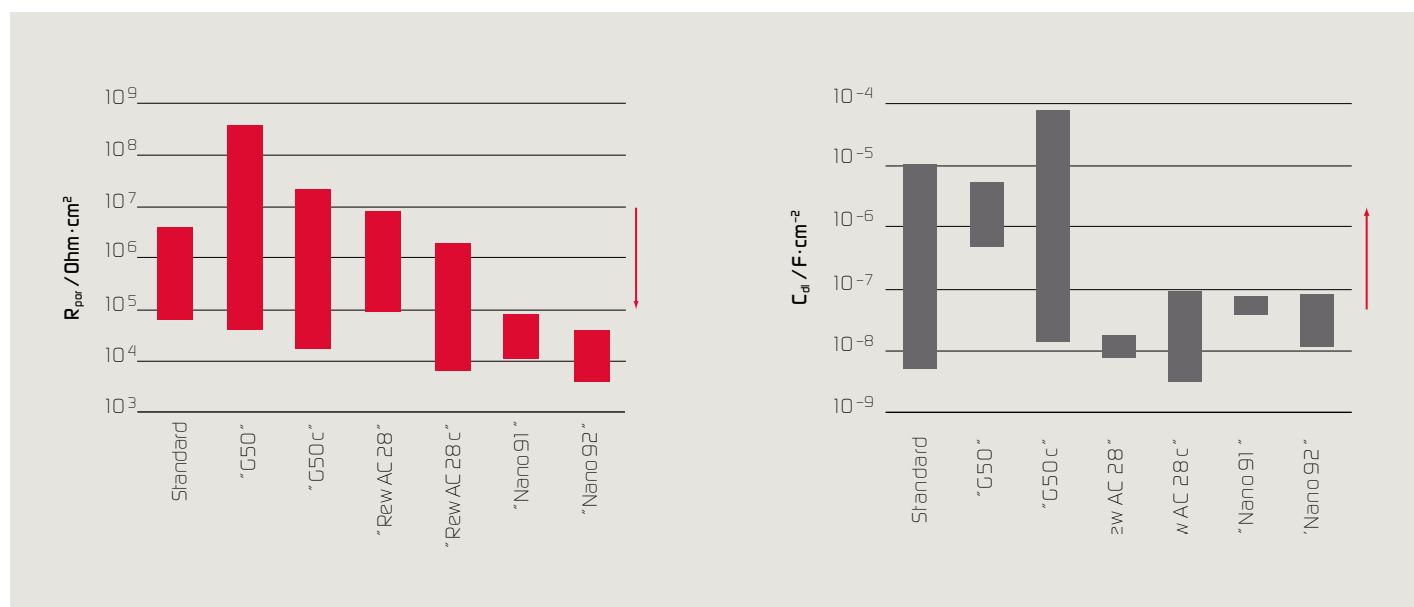
PARTICULATE ADDITIVES AFFECT BARRIER

Figure 3 displays the shifting of the parameters R_{por} and C_{dl} obtained from EIS performed in intact areas between 0 h and 178 h of TEL. The primers that contain "G50" and "G50 c" in particular, initially exhibit larger barrier properties compared with the standard formulation. After 178 h, however, the barrier properties of the standard formulation exceed the barrier properties of all other primer formulations except for "Rew AC 28". The finding that, in particular, the formulations that contain capsules (c) or nanocontainers display lower barrier properties than the standard can easily be attributed to a disturbance of the matrix continuity caused by introducing the specified particulate additives.

SPECIFICALLY VARYING EFFECT ON DELAMINATION RESISTANCE

It seems that introducing specific additives also affected adhesion in the substrate/coating interface. The increase of C_{dl} is by far the largest for the primer "G50 c". Such large C_{dl} values as observed for "G50 c" after TEL (around 10^{-4} Fcm^{-2}) can only be explained by the presence of blisters [13]. In fact, the impact of TEL should induce a build-up of internal stress, which could easily cause fragile capsules to collapse and result in the spread of the liquid "G50" inhibitor. Thus, such 'empty' "G50" capsules should behave like blisters and cause such extraordinary large C_{dl} values. In contrast, such an effect is not observed for "Rew AC 28 c", which may be explained by the smaller dimension of these capsules and their better persistence under impact of TEL. All

Figure 3: Shifts of R_{por} and C_{dl} obtained from EIS performed in intact areas between 0 h and 178 h of TEL; the red arrows figure the variation in time.



“The method can be implemented for “conventional” anticorrosive primers as well.”

3 questions to Matthias Wanner

Could the method also be used for an evaluation of anticorrosive primers? Yes, the method can be implemented for “conventional” anticorrosive primers as well. The equivalent circuit models used do not depend on the presence of inhibitor capsules or nanocontainers.

The results suggest that two-layered primer systems are promising candidates for self-healing corrosion protection, does the project group plan any further research? Presently, we check the compatibility of such systems with the durability profile demanded by the market. This implies standardised impact resistance and polarisation tests. In case these tests indicate a comparable performance to recent conventional market systems, we can imagine transferring the concept to market.

How prevalent are self-healing materials in heavy corrosion protection? They are not yet that what you would call “established”. However, we expect a growing interest especially for applications, where coating repairs are complex and where coating failing could result in fatal consequences.



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other systems, however, show improved delamination resistance in comparison with the standard. The nanocontainers in particular provide considerable adhesion persistence, which is indicated by low increases of C_{dl} induced by TEL.

SELF-HEALING, ANTICORROSIVE PRIMER SYSTEMS

Further results obtained from primer areas with a defect suggest that the presence of fragile capsules containing corrosion inhibitor could contribute to decelerating the corrosion processes in the event of an inflicted defect. From this, one might expect that primer systems, which contain nanocontainers in the bottom and inhibitor containing capsules in the top volume, could be promising candidates for powerful ‘self-healing’ anticorrosive systems. In fact, very recent results obtained from such systems impressively confirm this assumption. ④

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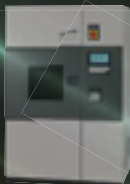
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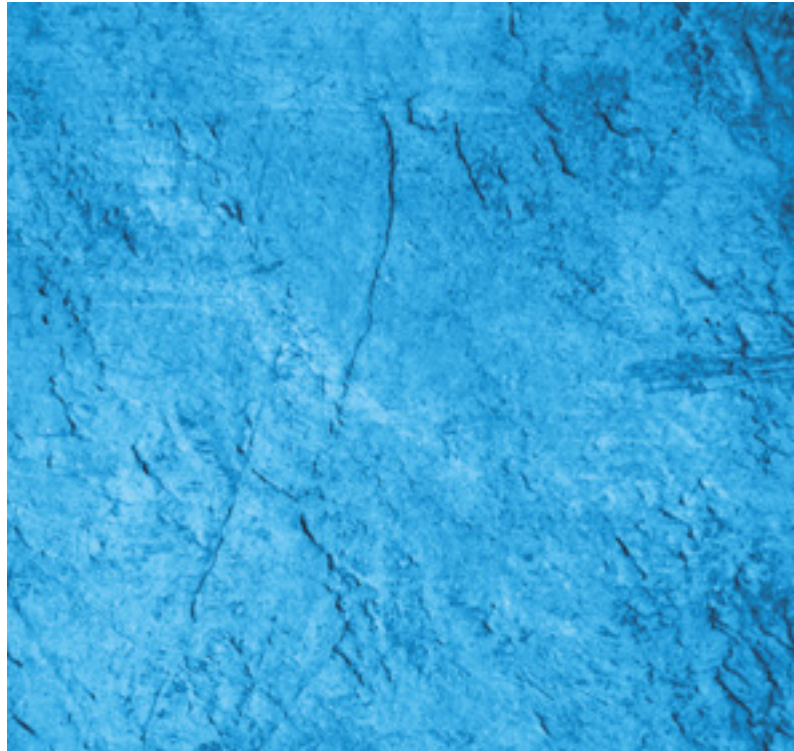
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PATTERNS OF ROUGHNESS

How surface structure evolves from substrate to topcoat.
By Michael Osterhold, freelance consultant (published in ECJ 7-8/2016).

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The visual impression of a painted surface is influenced by its surface structure (levelling, waviness, orange peel etc.). Two different measuring methods have become established in the automotive and paint industry. Some comparisons between these methods and the effects of successive paint layers on surface structure are reported.

In addition to colour, angle-dependent effects and gloss, the visual impression of a painted surface is especially influenced by its surface structure (levelling, waviness, orange peel, appearance). To characterise the structure of a surface, two different measuring main methods - profilometry and 'wave-scan' - have become established in the automotive and paint industry.

Mechanical profilometry combined with Fourier techniques (FFT, Fast Fourier Transforms) yields detailed information on the surface topography, and substrate influences or other effects on the final coating appearance can be described [1-18]. To simulate the visual impression obtained from optical inspection of surface structures, the German company BYK-Gardner developed its 'wave-scan' instruments.

In addition to measurements on glossy surfaces, i.e. topcoats /clearcoats, the "wave-scan dual" allows the appearance of surfaces with medium gloss levels, such as primer-surfacers and sometimes EC (electrocoat) to be determined. Basic relationships and relevant application examples from the areas of metal and plastic substrates and their coatings, investigated with profilometry and 'wave-scan' techniques over a period of time, will be summarised in this paper.

SCOPE OF MECHANICAL SURFACE CHARACTERISATION

Surface profiles presented here were measured by mechanical profilometry using the "Hommeltester T 8000" (Hommel-Etamic, Germany). For all measurements, a dual-skid tracing system or what is called a datum system (without skids) with a diamond tip radius of 5 µm were used. The vertical resolution of this mechanical profilometry system is approximately 0.01 µm. The surface profiles were recorded over a scan length of 48 or 15 mm. A cut-off wavelength of 8 mm for the 48 mm long scans was used to separate roughness and waviness profiles.

The evaluation of the mechanical profile measurement according to typical roughness parameters - e.g. average roughness Ra - gives integrated information about the surface structure. In comparison to roughness parameters, Fourier techniques (FFT) yield a more detailed characterisation of the surface structure.

For wavelengths from 1 to 10 mm (integral 1, long wave) and from 0.1 to 1 mm (integral 2, short wave), the intensities of the autopower spectra are added up and used for further evaluation of the surface structures (see e.g. [14]).

In *Figure 1*, typical surface topographies from substrate to topcoat are shown in a pseudo-3-dimensional representation. The sample is moved by a precise positioning table for a small distance between two line scans. In general, a decrease of the amplitudes and a change in wavelengths can be observed as each coating layer is applied.

OPTICAL SURFACE CHARACTERISATION

The optical determination of coating structures was carried out with the "wave-scan dual" or with an earlier instrument, the "wave-scan DOI". Here, the measuring principle is based on the modulation of the light of a small laser diode reflected by the surface structures of the sample. The laser light shines on the surface at an angle of 60°, and the reflected light is detected at the gloss angle (60° on the other side of the perpendicular).

During the measurement, the instrument is moved across the sample surface over a scan length of approximately 10 cm. The signal is divided into five wavelength ranges within the range of 0.1 to 30 mm and processed by mathematical filtering. For each of the five ranges a characteristic value (Wa 0.1-0.3 mm, Wb 0.3-1.0 mm, Wc 1.0-3.0 mm, Wd 3.0-10 mm, We 10-30 mm) as well as the typical instrumental values longwave (LW, approx. 1-10 mm) and shortwave (SW, approx. 0.3-1 mm) are calculated.

Low values imply a smooth surface structure. Additionally an LED light source is installed and illuminates the surface at 20° after passing an aperture. The scattered light is detected and a so-called dullness value (du, < 0.1 mm) is measured. A change to an IR-SLED for the low gloss area allows samples with medium gloss surfaces to be measured.

RESULTS AT A GLANCE

- In addition to colour, angle-dependent effects and gloss, the visual impression of a painted surface is influenced by its surface structure (levelling, waviness, orange peel etc.).
- Two different measuring methods for this structure - profilometry and 'wave-scan' - have become established in the automotive and paint industries.
- Some comparisons between these methods and the effects of successive paint layers on structure are reported.
- In general, each paint layer produces a smoother surface, but the substrate still has an influence on the final appearance. Therefore, plastic substrates must be chosen carefully when appearance of metal and plastic parts is to be matched.
- Mechanical profilometry with Fourier techniques allows detailed investigations into surface topography from substrate to topcoat. The optical method has some limitations by dullness and a distinct surface structure.

PAINT APPLICATION AND CURING EFFECTS ON METAL

An example of earlier studies on steel substrates [10] will now be considered. Three different phosphated steel surfaces with different roughness levels were evaluated. The samples were chosen in order to cover the range of roughness from smooth to rough substrates (R_a 0.8 to 2.3 μm) supplied for automotive body sheets, where - typically - sheets with an average roughness between $R_a = 0.8 \mu\text{m}$ (smooth) and $R_a = 1.6 \mu\text{m}$ (medium, upper limit) were used.

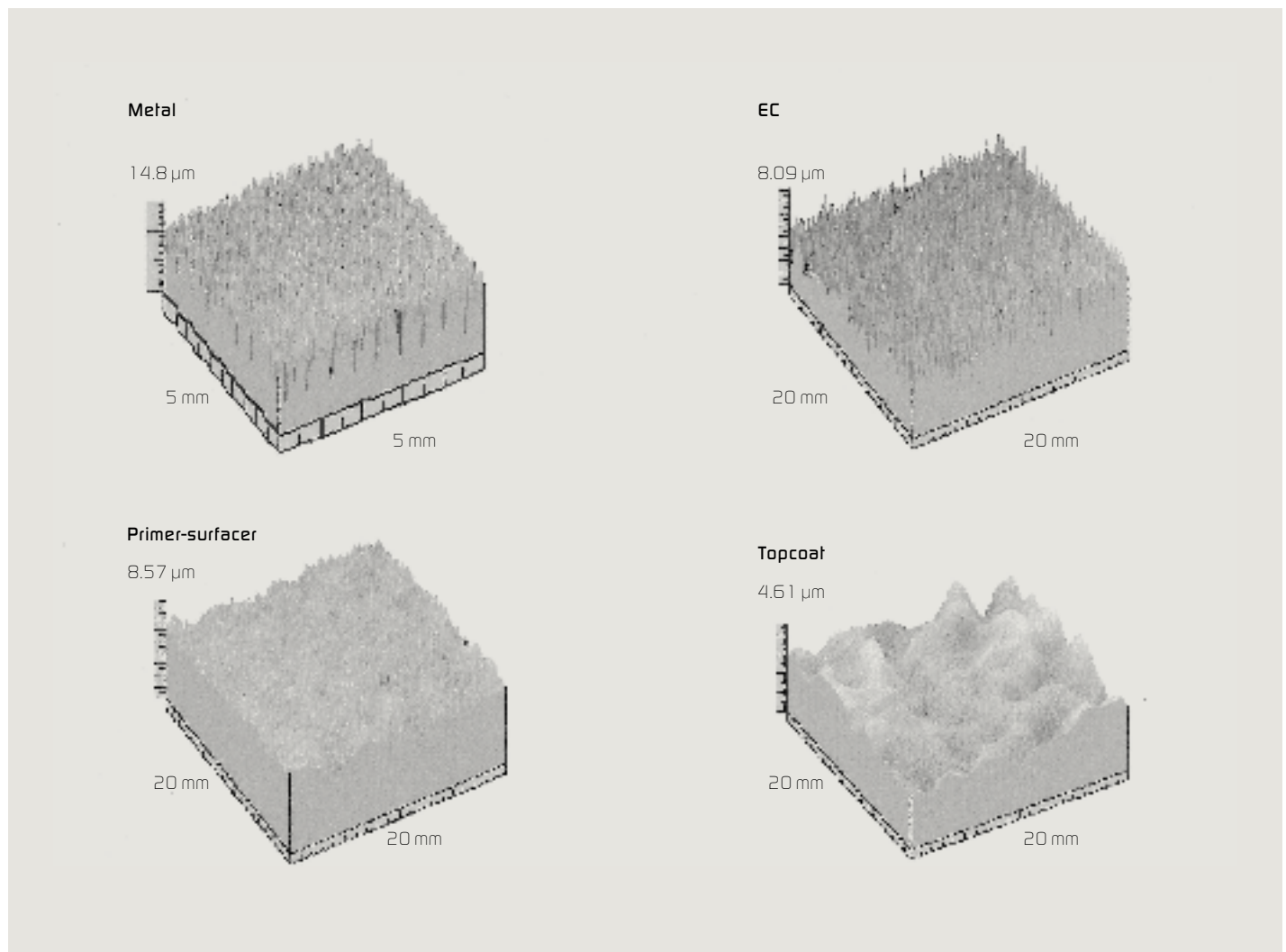
All samples were coated with cathodic electrodeposition paint, primer-surfacer and automotive topcoat with typical layer thicknesses. One set of painted substrates was stoved in a horizontal position, a second set vertically.

As shown in *Figure 2*, the integrated values increase as a function of substrate surface roughness and stoving position. For the vertical position, a strong enhancement of the long waves can be observed, while the short wave values barely increase compared to the samples stoved horizontally. The short wave values depend mainly on substrate conditions (i.e. roughness), and not strongly on stoving position.

MATCHING THE FINISH OF METAL SUBSTRATES ON PLASTICS

Investigations on plastics coatings are of special interest in order to achieve a similar structure development on a painted car indepen-

Figure 1: Topographies of metal substrate and applied coating layers (note differences in scales between the diagrams).



dependently of the different substrate materials (steel or plastics) used. Against this background, parameters influencing the surface of plastics parts have recently become more important.

Polymeric substrates with different amount of glass fibres were painted with a typical coating system for plastics. The complete coatings were measured by wave-scan and mechanical profilometry [12]. Optical and mechanical measurements (R_a) both show the same trend, an increasing measured value of structure for an increasing amount of glass fibre. In addition to the effect of the amount of fibre present, a dependence on the type of the fibre used could also be observed in a different study [13].

This effect is also demonstrated in *Figure 3*, showing a comparison of two substrates with high and low surface structure. The amplitude of the structures is reduced, but the basic structure of the substrate is partially transferred through each individual coating layer and finally influences the appearance of the topcoat.

These results are very important because of the effect, that the substrate structure clearly influences the final coating structure. Based on surface structure measurements, a preliminary selection of plastic substrates can be made to obtain an optimal structure (smoothness) of the coating system applied [15].

MEDIUM GLOSS SURFACES: VARIATION OF SUBSTRATE

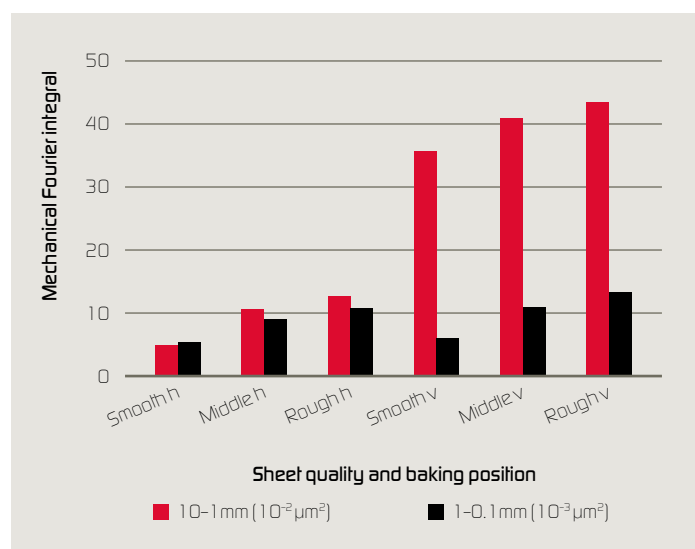
Several test sets have been measured to investigate the effects of coating variation (EC and primer-surfacer) and substrate topographies on the different coating layers. These studies are described in detail in [18]. The investigations and main results of varying the steel substrate will be summarised here.

Most of the 28 substrates studied were in the range which is regularly used in the automotive industry for outer car body parts (R_a 0.9-1.5 μm , peak count RPC > 60 peaks/cm. In *Figure 4* the profilograms of substrates and the corresponding EC surfaces are demonstrated by four selected samples.

The R_a values of substrates 1-3 were in a roughness range from 0.9-1.5 μm , with peak counts of 60-75 points/cm. Substrate 4 shows a good R_a value of 0.8 μm , but a very low number of 12 peaks/cm.

The painting of this substrate is more difficult because of the low peak number and it would not be used for the outer shell of a car body.

Figure 2: Mechanical Fourier integrals obtained by measurements on topcoats (h = horizontal, v = vertical position in stoving oven).



The EC application as well as the whole subsequent coating process was carried out with the same material and under identical application conditions.

The measurement of the EC (*Figure 5*) could be carried out without any difficulty with the “wave-scan dual” and shows a comparable ranking of EC and topcoat structure for the four sample substrates (*Figure 6*). Considering the whole sample set, the linear correlation coefficient of profilometric structure measurement between substrate and EC structure is $r \approx 0.9$ for the long wave range (integral 1) and $r \approx 0.7$ for the short wave range (integral 2). There is a correlation coefficient of 0.8 between EC and clearcoat structure for horizontal application [18].

THE BROADER PICTURE SUMMARISED

Further studies considering the influence of sheet-type, substrate roughness, deformation and paint system on the appearance of the painted surface have been summarised in [15]. Additional investigations into the variation of paint systems with lower gloss (EC, primer surfacer) can be found in [18]. The influences of the forming/deep-drawing process, leading to an increased waviness of metal substrates, were reported in [19].

Investigations of the mechanisms for the formation of surface structures on paint layers take into account, for example, the flow behaviour of the liquid paint driven by viscosity, surface tension and other parameters. Modelling and simulations of the interrelations of intrinsic physical and process parameters are used to understand the causes of paint film appearance [20-22].

Mechanical profilometry can be applied to all substrates and coating layers. The use of the “wave-scan dual” is limited by dullness and a distinct surface structure. The optical investigation of EC is possible, if the surface structure of the substrate used in combination with the self-structure of the coating material is not too unusual. In general work primer-surfacers can usually be investigated without this kind of reservation.

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Figure 3: Comparison of two substrates and coating layers (mechanical profilometry, roughness profiles, scan length 48 mm, Y-scale $\pm 2 \mu\text{m}$).

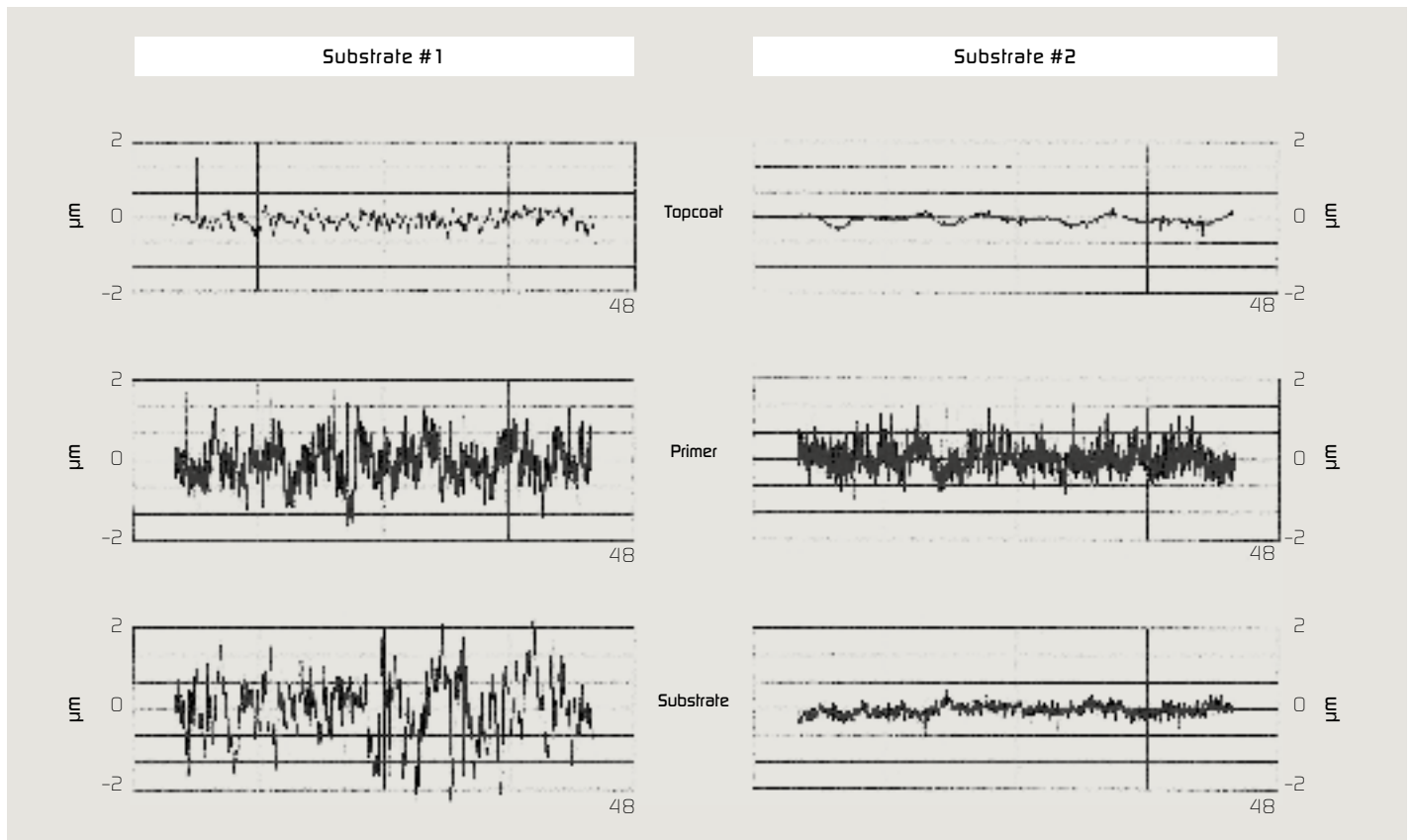
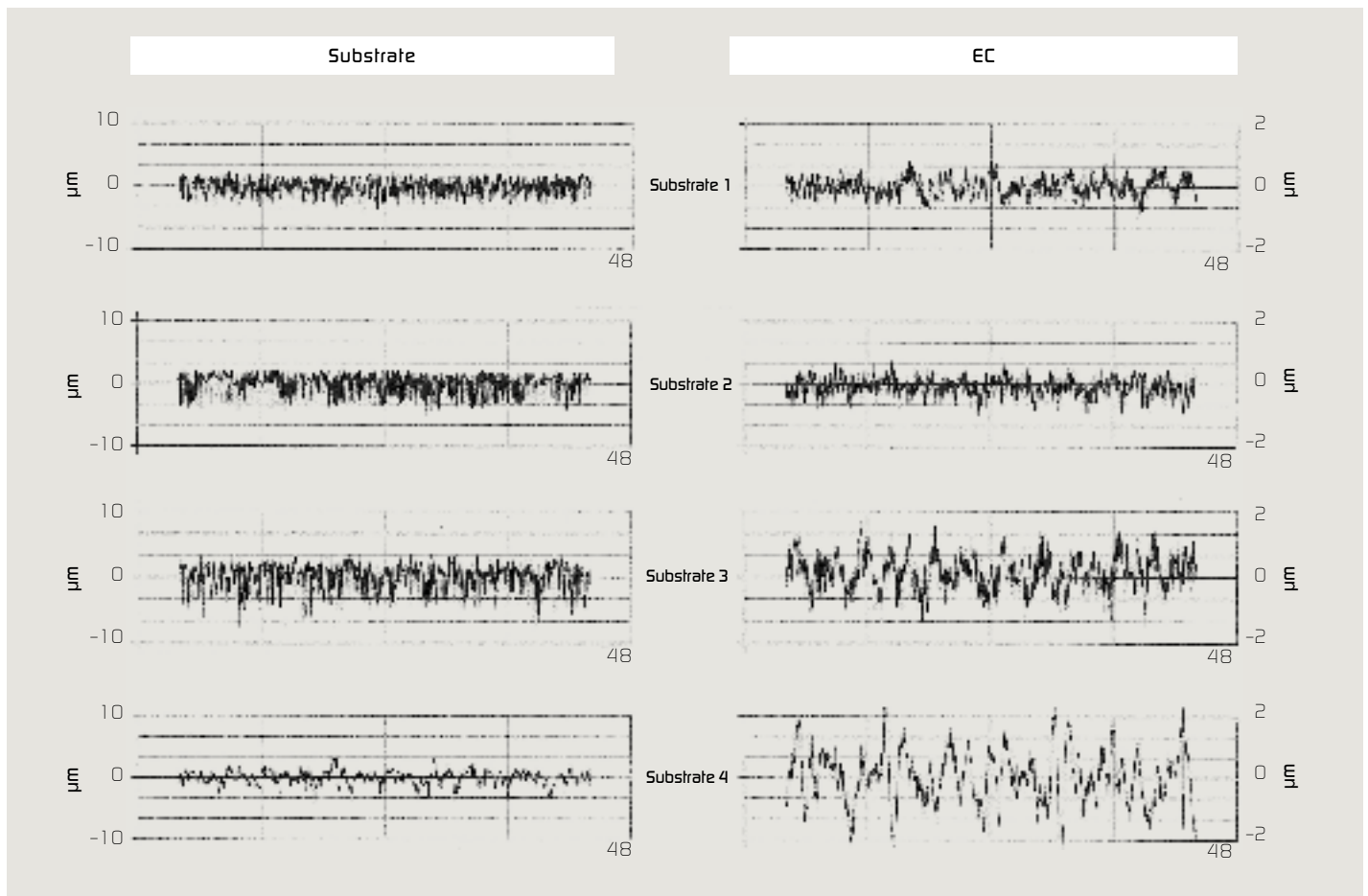


Figure 4: Roughness profile of panels and applied EC surfaces (substrate variation). Scan length 48 mm, Y-scale $\pm 10 \mu\text{m}$ (substrate) but $\pm 2 \mu\text{m}$ (EC).



“A constantly high level of appearance cannot be guaranteed without continuous measurements.”

3 questions to Michael Osterhold

Why is surface characterisation of substrates and coatings so important? Due to the sometimes poor reproducibility of visual inspections in the past, the ‘wave-scan’ was developed to yield quantitative values for evaluating the surface structure of coatings. In the course of time car and paint manufactures’ quality assurance processes increasingly rely on this time-saving investigation method. The detailed topography of a surface can be described by profilometry.

What would be the consequence if surfaces would not be characterised? A constantly high level of coating appearance cannot be guaranteed without continuous measurements during the coating process. Effects due to unintended process variations or unexpected changes in product quality would be possibly not detected. Other influences (e.g. substrate topography) on the final coating appearance would be unknown and so more difficult or even impossible to control.

Which method would you recommend and why? Profilometry allows to detect the surface structure from substrate to topcoat and was used in the past mainly for fundamental investigations (e.g. substrate influences on topcoat appearance) in laboratories. The wave-scan instruments on the other side provide an easy and fast evaluation of coating structures in the daily work also under production conditions.



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Figure 5: Structure spectra, SW and LW of EC (substrate variation).

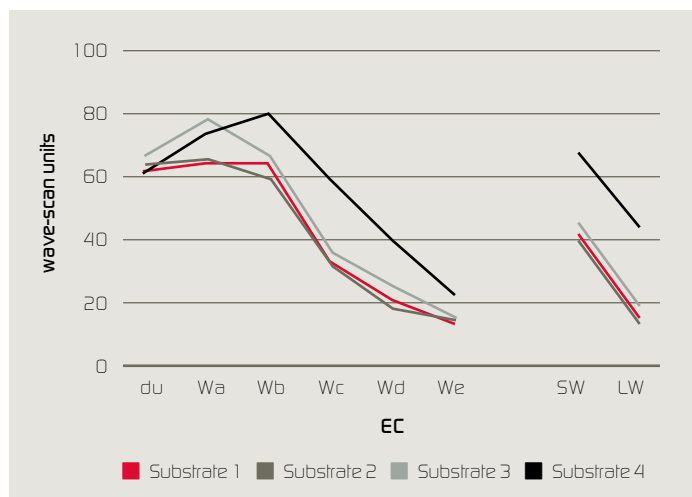
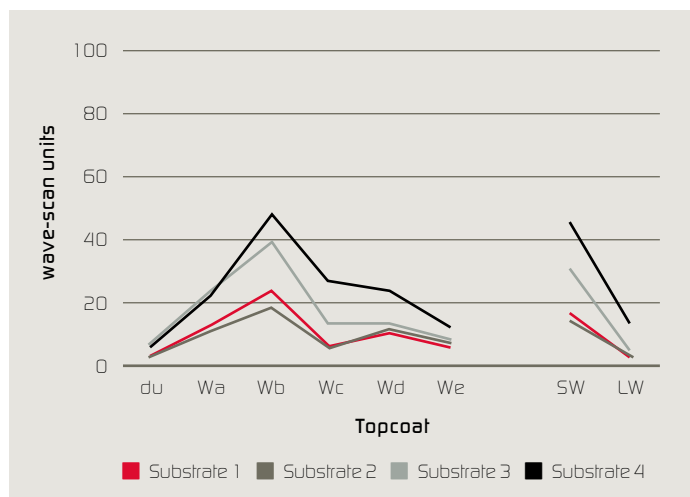


Figure 6: Structure spectra, SW and LW of topcoats (substrate variation), horizontal application.





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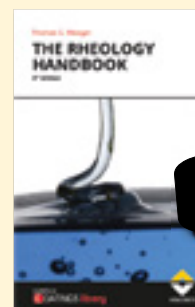
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IMPROVING RHEOLOGY MEASUREMENT

Yield point and thixotropy characterisation of coatings studied in detail. By Michael Osterhold, Scientific Consultant (published in ECJ 11/2016).

The 'Rheology' Working Group of the German "Standards Committee on Coatings and Coating Materials" (NAB) within the DIN organisation has closely studied the measuring characterisation of yield points and thixotropy. Reliable test procedures were established, while some methods were found to be unsatisfactory for general use.

Many application and technical properties of coatings are influenced by their flow behaviour. High product quality can only be guaranteed through an exact knowledge of the rheological behaviour of the coating and the raw materials used.

Because of the increasing use of waterborne systems, flow anomalies such as thixotropy, yield points or viscoelastic behaviour can be observed more often. This behaviour is not normally observed in conventional solvent-borne coatings. If, however, SCAs (Sagging Control Agents) are added to directly control rheological properties, phenomena such as thixotropy, yield points or viscoelasticity can also appear [1- 3].

Yield point and thixotropy influence important material properties such as storage stability, pumping behaviour or levelling and flow. Against this background the 'Rheology' Working Group of the Standards Committee for Coatings and Coating Materials (NAB) within the

DIN (German Institute of Standardisation) has intensively studied the measuring characterisation of yield points and thixotropy in recent years. Two technical reports on these items have been prepared [3, 4]. The use of rotational rheometers to evaluate yield point and thixotropy is considered below.

SIGNIFICANCE OF YIELD POINT AND THIXOTROPY

The yield point is defined as the lowest shear stress above which the behaviour of a material, in rheological respects, is like that of a liquid; below the yield point its behaviour is like that of an elastic or viscoelastic body. Thixotropy describes a flow behaviour where the viscosity decreases under a constant mechanical load to reach a constant limiting value, and after the load is reduced, the initial viscosity is completely regained over a (variable) period of time. In practice, only a limited time frame is considered, and within this time the initial state is not always reached again.

Important material properties can be characterised in terms of yield point and thixotropy, for example:

- > Effectiveness of rheological additives
- > Storage stability (e.g. against sedimentation, separation, flocculation)

RESULTS AT A GLANCE

→ Yield point and thixotropy influence significant material properties. The 'Rheology' Working Group of the Standards Committee coatings and coating materials (NAB) within the DIN organisation has closely studied the characterisation of yield points and thixotropy.

→ Two technical reports on these items have been prepared. The procedures used and some results are summarised.

→ Yield points were determined by the tangent method. Reliable results were obtained, but detailed test procedures may have to be defined for different types of material.

→ Somerheological test methods were found not to give reliable results. In addition, the evaluation of thixotropy by flow-curves is considered to be less versatile and reliable than a method combining low and severe shear loads followed by a recovery phase.

- > Behaviour when starting to pump
- > Wet film thickness
- > Levelling and flowing behaviour (e.g. without brush marks or sag formation)
- > Orientation of effect pigments.

METHODS FOR DETERMINING THE YIELD POINT

The individual methods for determining the yield point are summarised and critically discussed in DIN technical report 143 [5]. The results presented for evaluating yield points in this report are based on inter-laboratory tests, which were carried out by the participants of the 'Rheology' Working Group.

In the first preliminary tests, different water-borne basecoats with low yield points and dispersions with distinctly higher yield points were examined. It was found that some methods showed unexpectedly good qualitative relationships. On the other hand, some participants reported problems with the preparation of the samples.

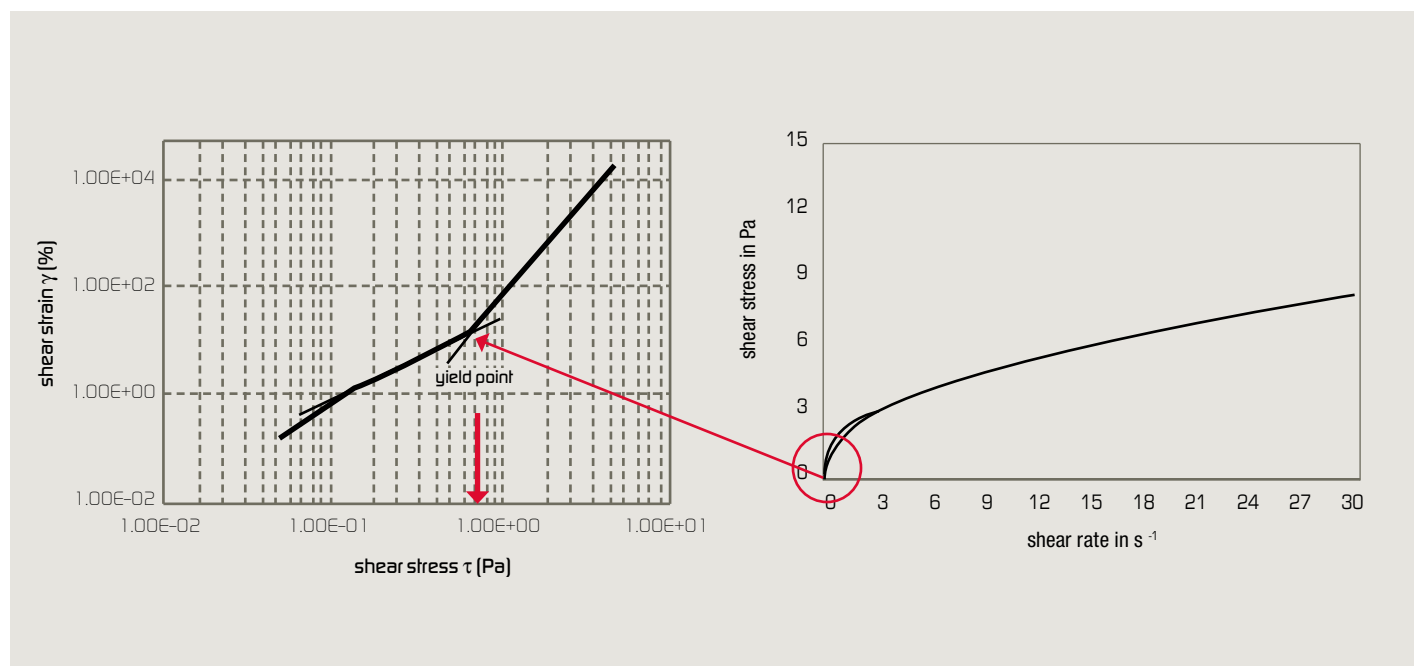
In addition, in the course of the preliminary tests certain methods of measurement were found to be unsuitable for the samples examined and were therefore not studied any further. In this connection, the method of maximum viscosity and the method using a vane measuring system have to be mentioned.

In addition, the method for determining the yield point using a linear stress ramp was not helpful as there are not enough measuring points in the lower measuring range. Also, evaluation procedures based on traditional regression methods (e.g. according to Bingham or Herschel-Bulkley) were not considered in further tests. The results depend too strongly on the theoretical model used and the measuring specifications (i.e., the choice of ramps) according to [3, 5].

YIELD POINT DEFINED BY TANGENT METHOD

Based on the experience from the preliminary tests, the participants agreed on the 'stress ramp' as a method to be used in continued 

Figure 1: Determination of the yield point.



- inter-laboratory tests. The results are presented in Technical Report 143 [5].

In this procedure, both below and above the assumed yield point a viscosity range of one decade should be available for the evaluation. That is to say that the (logarithmic) shear stress ramp should begin at least a factor of ten below the assumed yield point and should reach at least one factor of ten beyond the yield point value.

Exact test conditions were agreed by the Working Group and clearly specified for all participants in the comparative testing programme (see [5]). Five different samples were examined in total: two water-borne basecoats with low yield points of a magnitude of 1 Pa or smaller, two dispersions and one sample with well-known yield point provided by the Physikalisch-Technischen Bundesanstalt (PTB, The National Metrology Institute of Germany).

If a yield point exists, a straight line can be observed in the range of low shear stress. The shear stress τ and shear deformation/strain γ are then proportional at low values. The material investigated consequently shows reversible linear-elastic deformation behaviour (in accordance with Hooke's elasticity law).

At higher stresses, the structure at rest breaks down, the deformation then becomes disproportionately high, and the material shows irreversible viscoelastic or viscous flow behaviour [6-8]. The yield point has been exceeded if the measuring points are no longer on a straight line (tangent).

If it is possible to set up a second tangent through the measuring points at high deformations – also within the flow range – then the crossover point of these two tangents is evaluated as a yield point (Figure 1) [3]. This evaluation method is described in more detail in [5]. In summary, good results were obtained as a result of the specified time schedule of the tests and the previously specified measuring conditions. For a clear characterisation of yield points for various products, detailed test specifications for different substance classes have to be developed.

THIXOTROPY CHARACTERISATION AND FLOW CURVES

After finishing the investigations and the preparation of the technical report on yield point determination, the first tests on thixotropy were initiated by the DIN Working Group on Rheology in 2005. At the beginning, the target was to prove the fundamental suitability of methods. In a second comparative testing programme (inter-laboratory tests) in 2009/2010 special emphasis was given to the determination of precision data for different measuring procedures.

For that purpose, a waterborne basecoat and a clearcoat were investigated with four different measuring methods. A Newtonian liquid supplied by the PTB was used as a reference. The final technical report on thixotropy was published in September 2012 [4].

A widely used method for determining the thixotropy is based on the registration of flow curves with defined parameters for the measuring procedure. It is necessary to fix the time in which a certain maximum shear rate has to be reached (ramp time for up-curve, number of measuring points etc.), the holding time at maximum shear rate and time for the down-curve. Also, it has to be decided whether a linear or logarithmic ramp has to be used (continuously or step-like).

In addition to precise temperature control, a waiting time or pre-shearing just before the actual measurement could be significant. This procedure by means of flow curves is called the hysteresis method or thixotropic loop. Here, the area between up- and down-curve is evaluated as a measure of the degree of thixotropy.

In Figure 2 the flow curve (red) of a blue water-borne basecoat is shown as a typical example of a thixotropic coating system. The arrows indicate the direction of increasing (up-curve $\rightarrow$) and decreasing (down-curve $\leftarrow$) shear rate, respectively. A marked hysteresis can be clearly detected as an indicator of thixotropy.

Figure 2: Flow curves (red) and viscosity curves (green) of a blue metallic water-borne basecoat.

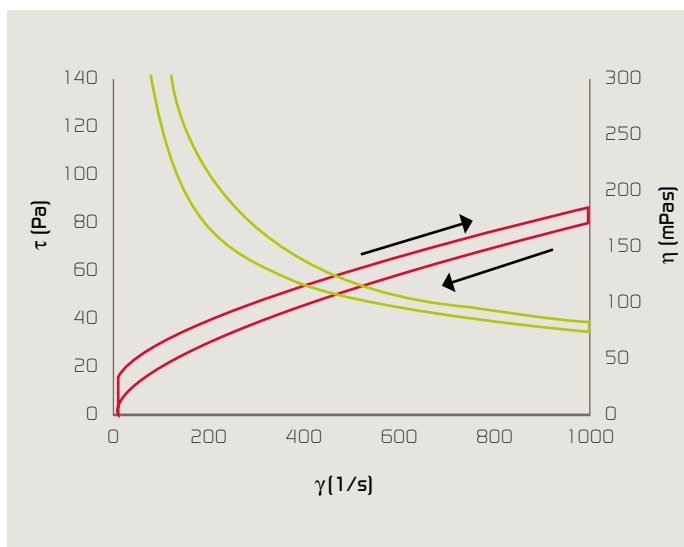
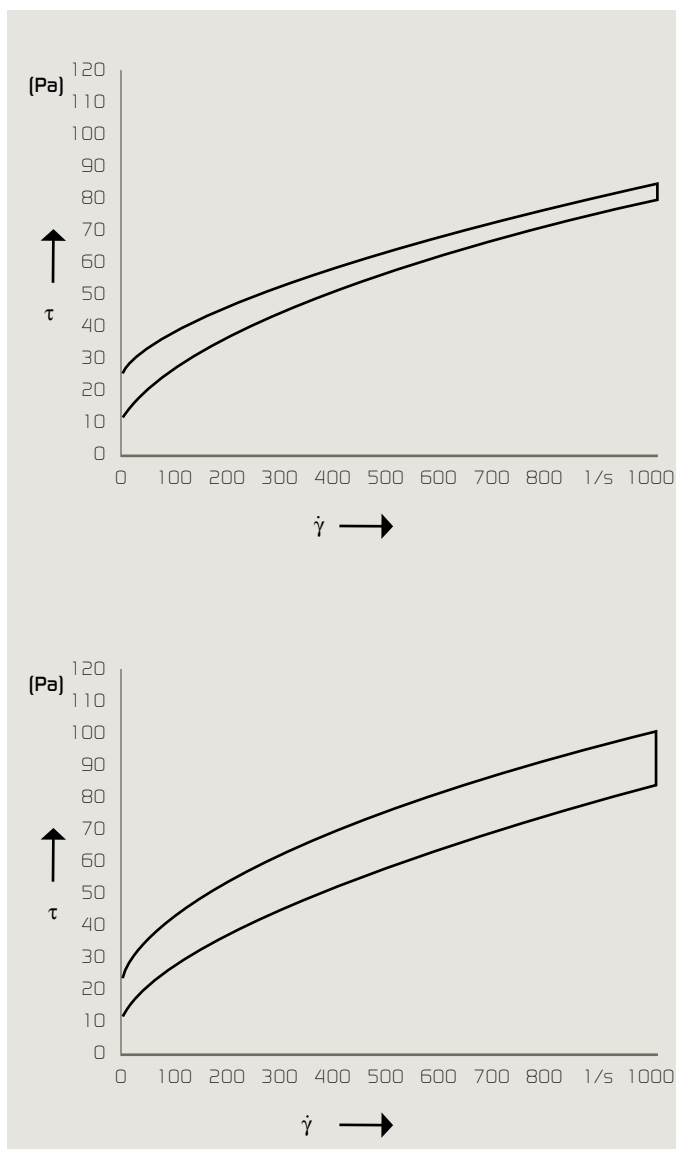


Figure 3: Flow curves of a waterborne basecoat show differences between linear ramps (left) and logarithmic ramps (right).



In addition, two marked yield points can be observed in the low shear rate range. Also shown is the respective (apparent) viscosity run (green curves). The viscosity η decreases for higher shear rates γ to a value of approx. 80 mPas at 1000 s^{-1} , and after reducing the load, i.e. to low shear rates, increases again.

Figure 3 shows a comparison of measurements of a water-borne basecoat with linear and logarithmic ramps [4]. Marked differences can be observed for the hysteresis areas.

SHEAR STEP WITH RECOVERY OFFERS BETTER ANALYSIS

Due to the considerable development of air bearing and controlled-stress rotational rheometers in recent years, combinations of shear and/or oscillation procedures can now be readily applied. Such experiments are usually divided into three segments (see also Figure 4 [4], also called 'shear step with recovery'). In this figure, the pre-set profile and the measuring results are schematically shown for the rotational case. In a first step the sample under investigation is subjected to a low shear rate (rotation), oscillation or shear stress, followed by a severe loading under rotation with high shear rate, and finally the recovery phase at a low load under rotation (shear rate), oscillation or shear stress (recovery/structure re-build).

In the second technical report of the DIN working panel, several aspects of the determination of thixotropy are discussed in detail [4]. Rheological methods and the results of comparative testing of up to nine different laboratories are presented.

The results show that the method for determining thixotropy using flow curves (hysteresis area) is only suitable in some cases. Methods combining low and severe shear loads followed by a structure recovery phase at a low load allow a more accurate presentation of the

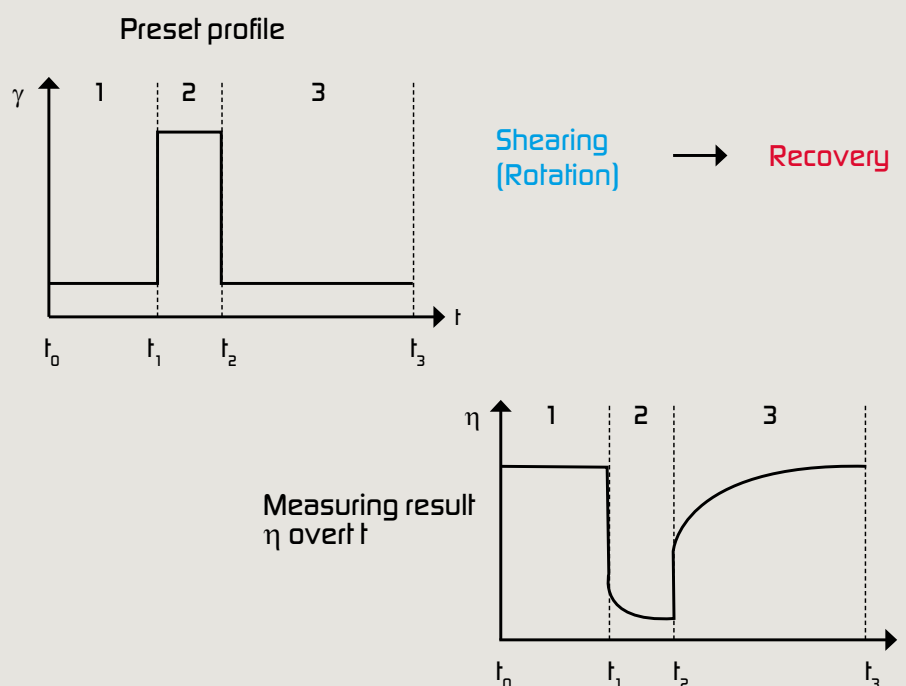
characteristics of the thixotropy.

Considering values in the phase of structure recovery (third segment) related to values in the second segment (high shear), suitable characteristic values such as TI (thixotropy index) or SRI (structure recovery index) can be determined. Precise evaluation methods and proposals for carrying out the measurements as well as pre-sets for the measuring parameters are described in detail in [4].

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Figure 4: Schematic pre-set profile and measuring result for rotation: time-dependent viscosity function of a thixotropic substance, (1) at low, (2) at high shear load with reduction of structure, and (3) again at low shear load with recovery of structure.



“Recording flow curves for determining thixotropy is less than ideal”

3 questions to Michael Osterhold

What conclusions can be drawn from a differentiated consideration of the flow points as regards formulating the flow behaviour of coating systems? *The flow point and thixotropy of a system can be used to characterise important material properties, such as the effectiveness of rheological additives, storage stability, or the levelling or sagging behaviour. In addition, when these parameters are linked to application properties, such as special-effect development in water-borne coatings, interesting connections can be revealed.*

Do the current standard rheometers used in the applications lab for paint development and quality assurance purposes lend themselves to such a differentiated consideration of the flow point, or would new investment be needed? *Simple, speed-controlled rotational rheometers are often used in paint development and especially in quality assurance. They are capable of recording flow curves of the materials used, with the result that a preliminary overview of flow behaviour, i.e. newtonian, shear-thinning, thixotropic, etc., can be obtained. In the case of shear stress-controlled rotational rheometers, shear stress is specified instead of shear rate. With the aid of these instruments, it is possible to generate extremely low shear and thus to determine low flow points. Many paint makers would already have these instruments in their analytical or physical departments.*

If the method for determining thixotropy from hysteresis curves is of limited suitability, does this mean that all hitherto-determined characteristic values relating to the coating systems of paint makers and developers need to be re-defined and re-specified? *The results of the round-robin experiments have shown that recording flow curves for the purpose of determining thixotropy is less than ideal for making quantitative statements (based on the hysteresis area). However, flow curves are quite useful for gaining a first impression of the general flow behaviour of a sample. In the context of “thixotropy”, however, methods based on a combination of low and high shear load, with a subsequent phase of structural regeneration, are more promising. Product-specific values need to be developed for this.*



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MARKING TIME

Methods for characterising scratch/mar resistance reviewed. By Michael Osterhold (published in ECJ 01/2018).

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

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.

strokes/min is reached. The sample is fixed on a flat pedestal. The sample is exposed to linear rubbing caused by a cylinder; other geometries are also described in DIN 55654.

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 differ-

ent 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

Figure 1: Car wash brush method (Amtec).

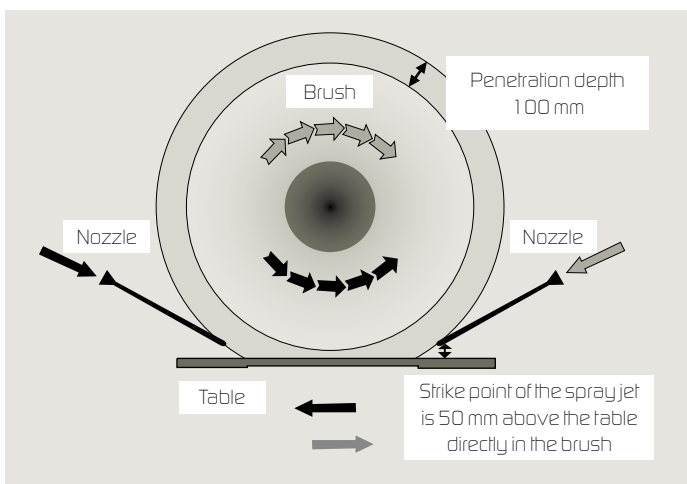
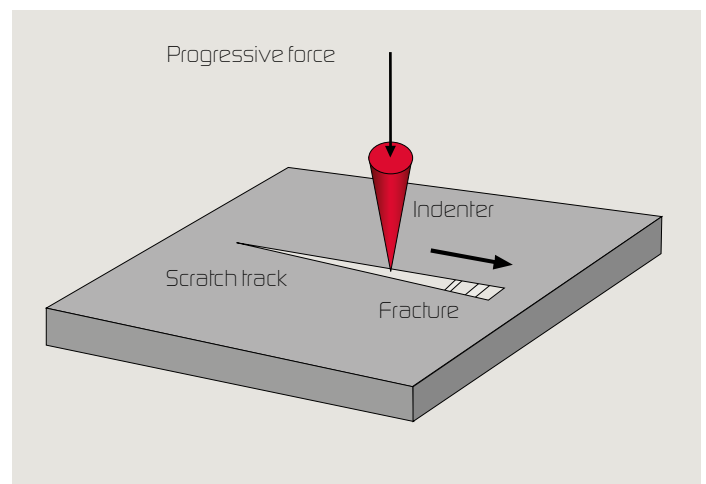
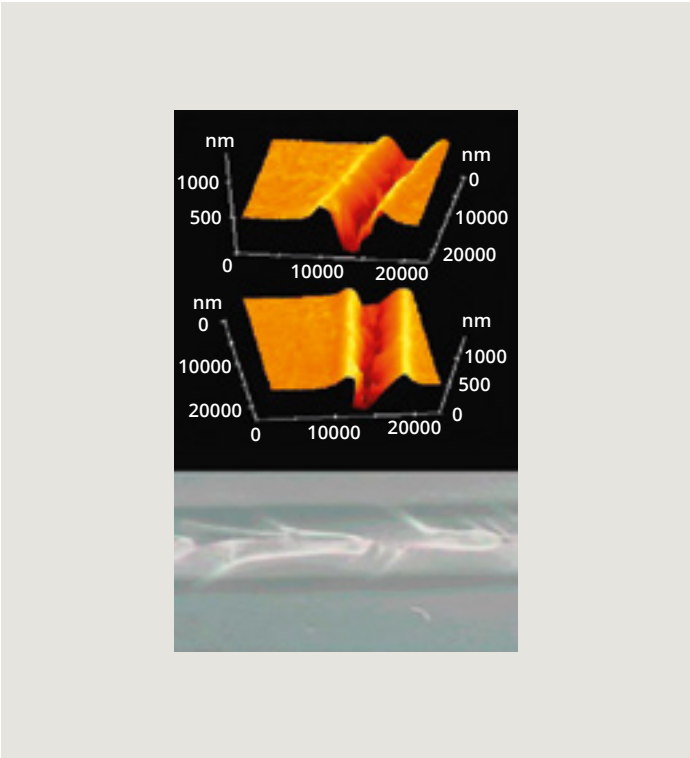


Figure 2: The principle of single-scratch tests.



➤ 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.

Figure 3: AFM image (top) and light microscopic image (bottom) of cracks in an acrylate/melamine system.



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.

Figure 5: Correlation of scratch resistance (Amtec values) and cross-linking density (storage modulus E').

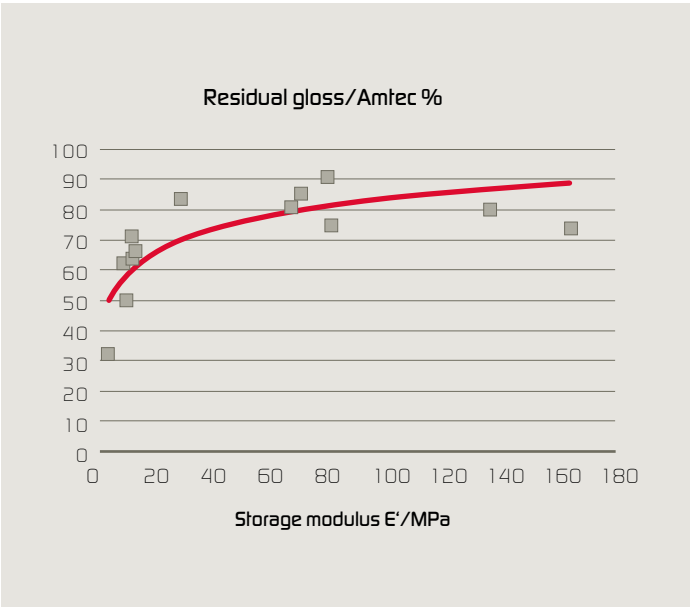
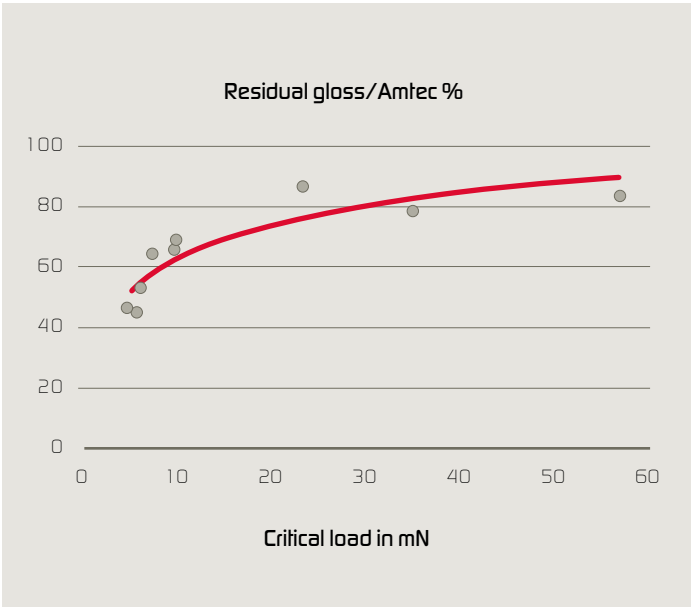


Figure 4: Comparison of values from Amtec measurements with values for critical load from nano-scratch tests.



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. ◀

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

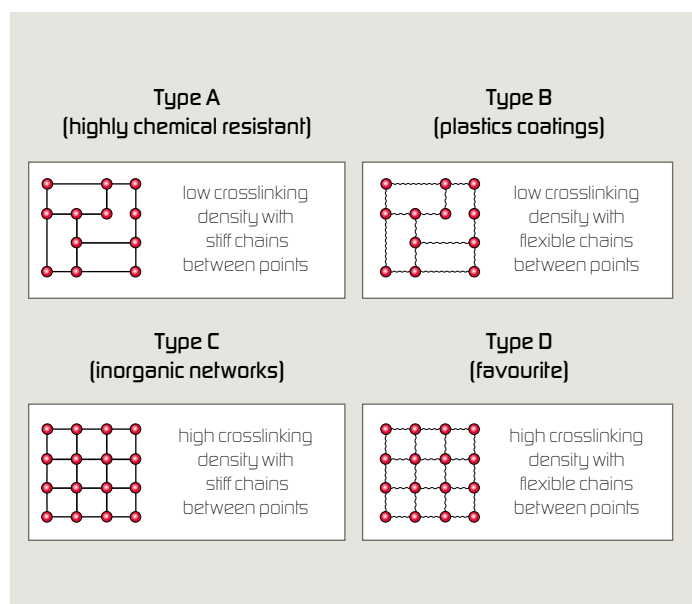
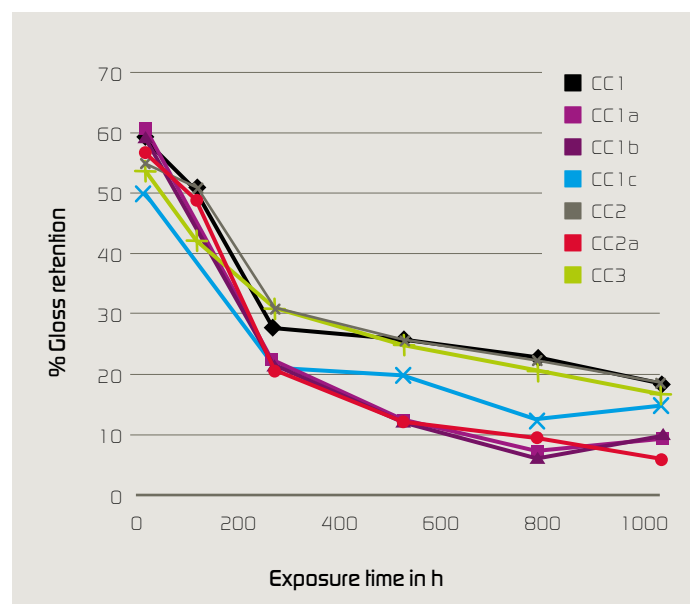


Figure 7: Gloss retention (Amtec) during SAEJ1960 weathering test.



“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.

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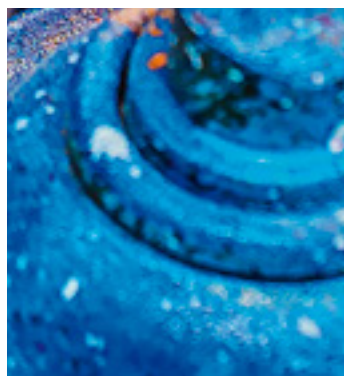
EARLY BEGINNINGS

One of the earliest documented usages of spray paint with compressed air dates back to the 1880s when a hand pumped machine was used to apply whitewash to the walls of the store of the Southern Pacific Railway.



FIRST PATENT

The first patent for an aerosol spray can was granted in 1926 to Erik Rotheim, a Norwegian chemical engineer. With coatings producers Richard and Alf Bjercke, he established a small scale production of spray paint cans.





SHADES OF DIFFERENCE

Visual and instrumental methods of colour assessment analysed. By Werner Rudolf Cramer, Consultant (published in ECJ 04/2018).

Methods of assessing colour and colour differences visually and instrumentally are discussed and compared. Preferred methods of carrying out visual colour assessment are described and explanations are offered for why visual and instrumental assessments may sometimes seem to give conflicting results.

As with other coatings properties, colour is nowadays assessed both visually and with instruments. This assessment serves to determine both the colour in itself and also the comparison between a standard and an adjustment. The traditional method of visual appraisal has been complemented by using instruments, which should be more objective, simpler and safer than the visual one.

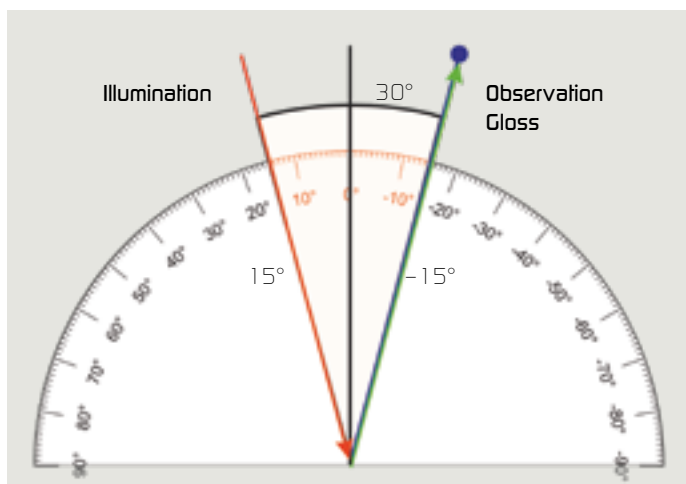
Colour pigments in the coatings, which partially absorb incoming light and partially scatter it in all directions, can be judged relatively easily both visually and instrumentally. Measuring instruments are available with a directional illumination at 45° or with spherical geometry.

The increased use of metallic coatings with aluminium pigments promoted the development of new methods in visual and instrumental assessment: the visual assessments were and are made at the window or in a light booth to obtain comparable and reproducible results. The development of instrumental assessment has resulted in portable devices with multiple measurement geometries. Here again illumination was introduced at 45°; with measurement at 15°, 45° and 110° from the corresponding gloss angle. These angles should correspond to visual aspects but have been chosen arbitrarily, like the additional measurement angles defined at 25° and 75°.

Today, portable measuring instruments still work with these geometries complemented by the -15° geometry. Originally, these ge-

ometries were intended for measuring metallic coatings. In the late eighties, the emerging use of interference pigments in coatings was measured with the same devices and geometries, without taking into account the physical and optical properties of these pigments.

Figure 1: In this example of visual observation, the starting position at the window is +15° for illumination and -15° for observation, i.e. the difference angle between illumination and observation is 30°.



RESULTS AT A GLANCE

→ Methods of assessing colour and colour differences visually and instrumentally are discussed. It is noted that the choice of measurement geometries offered by portable instruments is to a degree arbitrary, and was designed to take account of the characteristics of metallic pigments rather than the more complex behaviour of interference effect pigments.

→ Preferred methods of carrying out visual colour assessment are described. It is noted that the human eye observes a much larger area of colour than an instrument, including a significant range of illumination and viewing angles. This may lead to the perception that instrumental and observed colour values conflict, especially in the case of interference pigments.

→ It is important to measure the appearance of effect coatings across a range of aspecular angles to identify their behaviour, which can include a marked change from reflection to transmission colour.

measurable geometries to be made. Only a few copies of this device were built; one is still fully functional.

AN ORGANISED APPROACH TO VISUAL MATCHING

When making a visual assessment at the window, the sample panel(s) are first positioned so that the observer is looking at the gloss. In this initial position, the gloss angle (= angle of reflection) is the same as the angle of the illumination, and the normal sits between them perpendicular to the

Figure 2: Tilting the panel up, the angle of illumination increases and the aspecular (difference angle between observation and gloss) also increases.

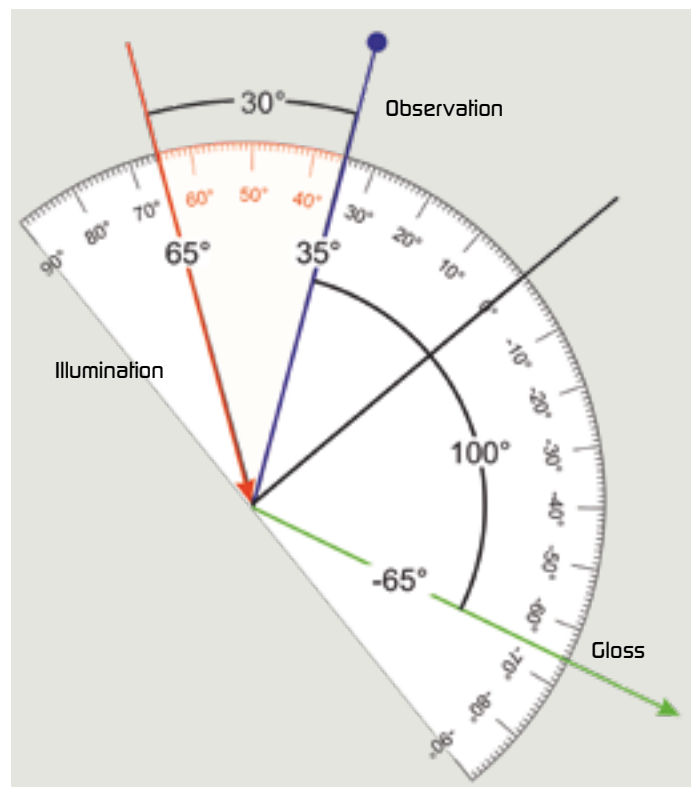
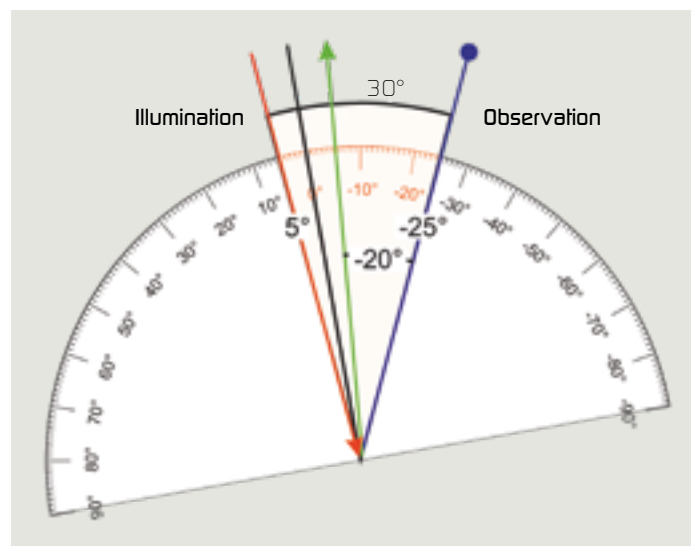


Figure 3: The observation angle increases when tilting the panel down. In the first steps the aspecular angle is negative, i.e. the observation angle is opposite to the gloss angle.



MEASUREMENT ANGLES AND CORRELATION PROBLEMS

The colour and effect of aluminium and interference pigments are highly dependent on measurement geometry, i.e. the combination of illumination and observation, both in visual and instrumental assessment. Ideally, both methods should yield the same result. Finally, assessment by instruments is derived from the visual: the physical reflection value, that is, the measurements by instruments are translated into physiological colour values that reflect the visual impression.

Nevertheless, the criticism is often heard from coating laboratories that observation at the window or in the light cabin does not correlate with the measurement results, particularly in the case of effect coatings. The contradiction is not due to inaccuracy in the measuring methods or errors or with conversions of the colour values, but to the different measuring geometries used in visual and instrumental assessment.

The selection of measuring geometries plays a decisive role for both assessment methods. In addition, the optical properties of interference pigments call for an appropriate choice of measurement geometries.

In summary, three areas that are presented individually and interpreted together need to be considered: the first area comprises visual assessment at the window and in a light cabin. The current portable measuring instruments provide only a small selection of measurement geometries. They supply the second area of investigation; the third area deals with the optical properties of interference pigments. It may be mentioned in passing that the "GK311/M" spectrometer by Zeiss was developed at the end of the 1980s by Dr Hermann Gerlinger's team and used to measure the different areas and the associated measurement geometries. The basic concept comprises an adjustable illumination head and an adjustable measuring head. Both heads are arranged on a steel half rail, and software allows their position to be changed in 5° increments.

It is possible to adjust the illumination down to 65° and up to -45°. The detector is adjustable between 45° and -65°. This allows almost 250

- Figure 4: Tilting the panel further down, the aspecular angle increases. The difference angle between illumination and observation remains the same.

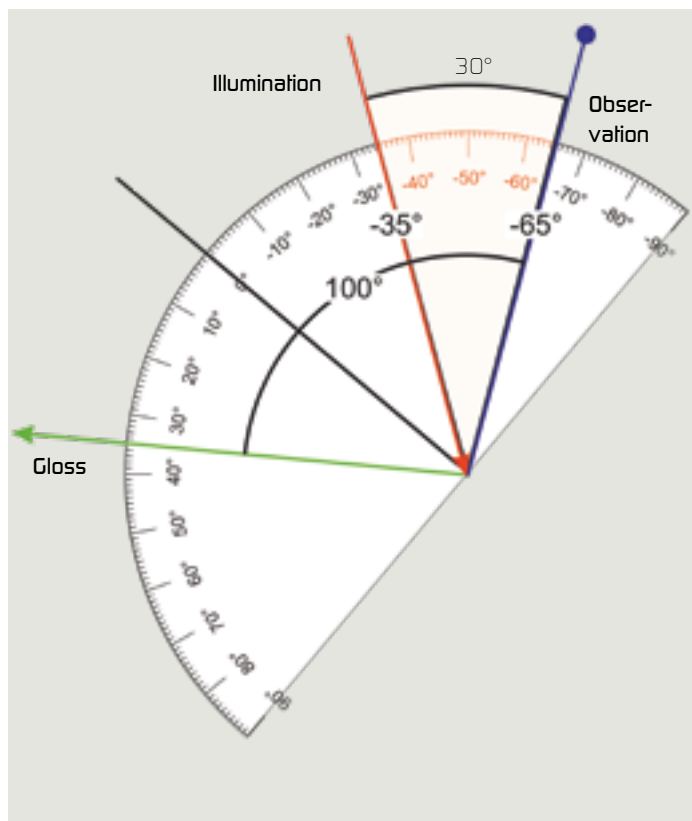


Figure 5: Tilting a panel up and down at a window produces the same colour travel.

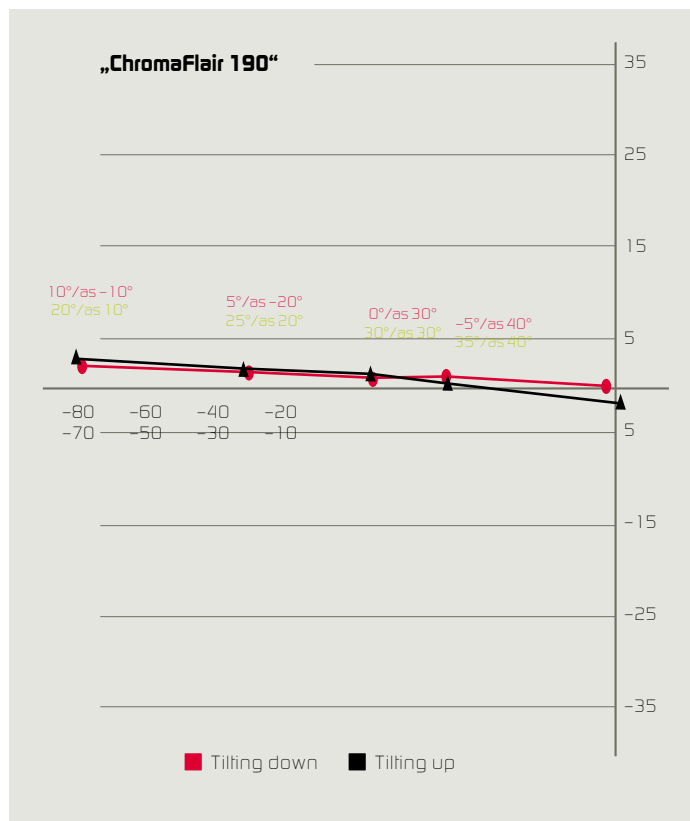
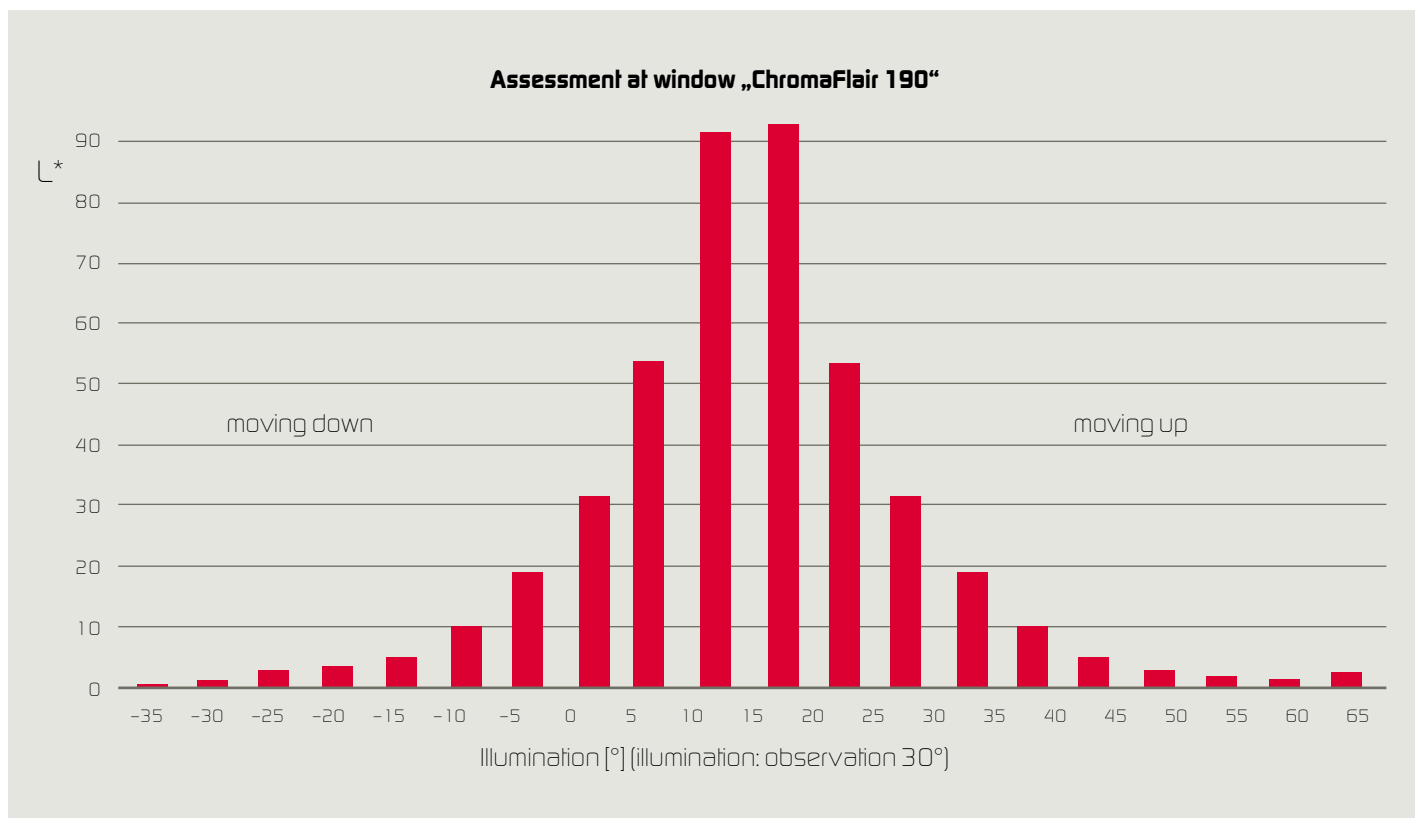


Figure 6: When tilting a panel by the window, the highest lightness is observed near the gloss and will decrease when the panel is tilted away from this. The same or similar values occur due to the principle of the reversibility of light; deviations reveal the orientation of the effect pigments.



sample panel(s). As an example, suppose that the angle of the illumination is $+15^\circ$ to the normal. Accordingly, the gloss angle is -15° . Here the angle convention is used, according to which the angles on the illumination side are designated positive and those on the observer side negative values, although according to optical principles the angle of incidence equals the angle of reflection.

The observer now tilts the sheet or sheets upwards to themselves or down away from them. In all cases, the angle between them and the light source always remains the same, in this example always 30° . In the case of portable measuring instruments, on the other hand, the difference angle (aspecular) between illumination and observer changes with each measurement geometry (Figure 1).

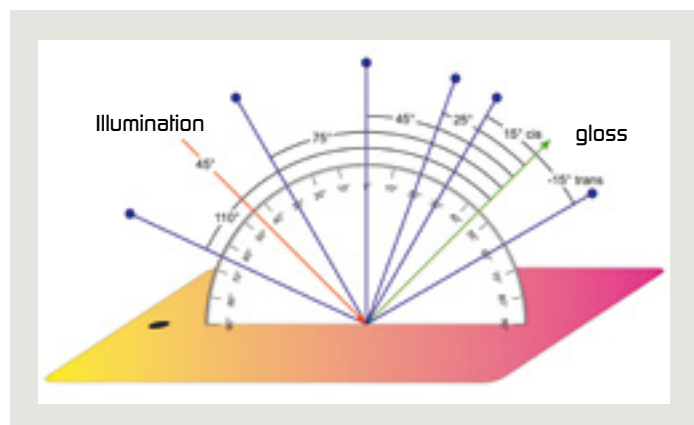
If the observer tilts the sample sheet toward themselves, the angle of illumination increases. At the same time, the difference angle (aspecular) between the observer and the gloss angle increases. For example, if the illumination angle changes from $+15^\circ$ to $+45^\circ$, the gloss angle changes from -15° to -45° . The angle of the observer is then $+15^\circ$, which corresponds to a difference to the illumination of 30° . This results in a difference angle (aspecular) between observer and gloss of 60° (Figure 2).

If the panel is moved away from the observer and tilted down, then initially the illumination angle moves towards the normal, for example, from $+15^\circ$ to $+5^\circ$. The corresponding gloss angle is then -5° and the observation angle -25° (Figure 3). This corresponds to a difference angle (aspecular) between observer and gloss of -20° . If the observer tilts the sheet down further, the angle of illumination moves to the normal and then changes sides, for example to -10° . The gloss angle then lies on the other side at $+10^\circ$. The observation angle changes to -40° and the difference angle (aspecular) between observer and gloss is now 50° (Figure 4).

THE PRINCIPLE OF REVERSIBILITY – AND SOME EXCEPTIONS

An important issue must be taken into consideration when tilting up and down: due to the principle of light reversal, the colour values are almost identical. For example, measurements at $+10^\circ$ illumination and -20° observation theoretically correspond to measurements at $+20^\circ$ illumination and -10° observation. If measurement values are taken when tilting downwards, it will be seen that the results are almost the same as when tilting upwards. Differences are so slight to the eye that one perceives practically the same colours or the same colour gradients. Ultimately, it does not matter whether the sample panel is tilted up or down; the same colour impressions are obtained (Figure 5). The differences are, however, greater with drawdowns. This results in a preferred orientation, which becomes noticeable in measurements. The difference is small in sprayouts, though it may depend on the quality of the spray application.

Figure 7: A portable instrument illuminates at 45° (red line). Measurement is made at -15° , $+15^\circ$, 25° , 45° , 75° and 110° off gloss (blue lines).



Other methods of observation yield the same results: if the sample sheet is held upside down and then tested with its back to the window, then the same conditions result when tilting forwards and backwards. Even in a walk-in light cabin these conditions will be found; other light cabins are designed according to the customer's specifications. Here, the sample panel is often illuminated from above vertically or under 45° and then tilted forwards and backwards. The sequence of geometries is comparable (Figure 6).

One aspect of the visual checks should not be forgotten: the area of a sample sheet seen by the human eye is significantly larger in relation to the measuring spot of an instrument. At a normal distance from the viewer and with a normal size, the viewing angle between the top and bottom edges is approximately 20° .

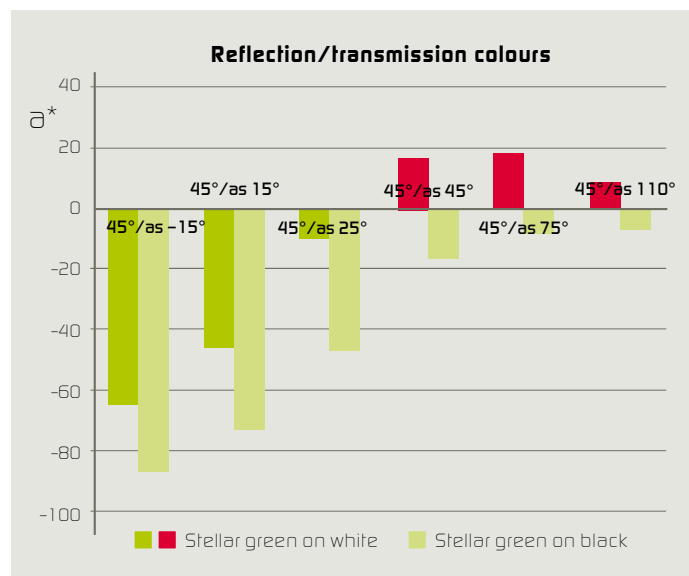
The visual examination starts close up to the gloss; when tilting forwards and backwards, the observer continues to move away from the gloss, as their position to the window and lighting remains constant. The portable measuring instruments maintain the position of the illumination, and the angle to the observation changes with each geometry. In the case of interference pigments, which have a more or less pronounced colour travel, a different process is observed than the one that results from instrumental measurement.

INSTRUMENTAL ASSESSMENT: GEOMETRICAL CONSIDERATIONS

Colour effects and gradients, especially of interference pigments, are highly dependent on the geometries by which they are illuminated and observed. The fact that the portable devices use geometries that are different from those used in visual matching does not say anything about their quality.

The choice of fewer geometries also limits the amount of data that comes with each additional measurement. Even the introduction of an additional geometry at -15° from gloss angle (aspecular), as defined in the ASTM standard test method, has required a great deal of work from many users. What occurs in a measuring device and what the angle designations mean remains incomprehensible to many users even today (Figure 7).

Figure 8: If coloured transparent interference pigments are applied to a white background, the colour change from the reflection to the transmission colour is shown when measuring the gloss line. The transition range is between 20° and 30° from the gloss angle.



- A coating with colour pigments shows little or no colour travel; an aluminium-pigmented coating in particular has a glossiness because of changes in lightness when the measurement geometries change. Its gloss is at its brightest close up and decreases as the observer moves further away. This behaviour can be described using portable devices. The detector moves away in greater and greater steps from the gloss angle at a constant illumination angle. In this way, special phenomena can be recorded that are visually described with other geometries. An example of this is blends with carbon black pigments: as fine-particle pigments they are bluish, as coarse ones, they are brownish. When mixed with the same aluminium pigment, the mixture of bluish carbon black is much darker than the mixture with the brownish when looked at close up to the gloss. The lightness ratio changes depending on the distance from the gloss: the mixture with the bluish carbon black becomes lighter than the mixture with the brownish. This behaviour can also be detected in mixtures with interference pigments. The change in lightness can be described both visually and using instruments.

ANGLE-DEPENDENT BEHAVIOUR OF EFFECT PIGMENTS

An advantage of instrumental assessment over the visual can be seen in the colour properties of coloured, transparent interference pigments: if a coating of this type is applied to a white background, the change from the reflection to the transmission colour is recognisable. These pigments have a typical reflection colour on their surface; light rays that penetrate the pigments generate a complementary transmission colour on the back due to the missing phase shift. The constant illumination angle of the measuring instruments as well as their change from the difference angle (aspecular) to the gloss ensure the correct description of this optical property: between the difference angles (aspecular) of 20° and 30° there is an intermediate area in which change takes place, depending on the type of pigment (Figure 8). Portable devices display part of the colour properties of a coatings and its pigments with their selection of geometries. Visual matching shows a different part of the colour properties and can therefore give different results. Therefore, it is important to combine both outcomes to make an optimal assessment.

APPEARANCE OF METALLIC AND EFFECT PIGMENTS COMPARED

The third aspect of colour assessment deals with optical properties. These are initially independent of the described methods of visual and

instrumental colour inspection. The description of properties raises the question of whether and how they can be adapted to those methods. Aluminium pigments change their lightness when illuminated at different angles with the same difference angle (aspecular). They also change their lightness when observed at fixed illumination angles with different aspecular angles. Looking at the corresponding reflection curves, a change in the level of reflection is noted, but no displacement (Figure 9).

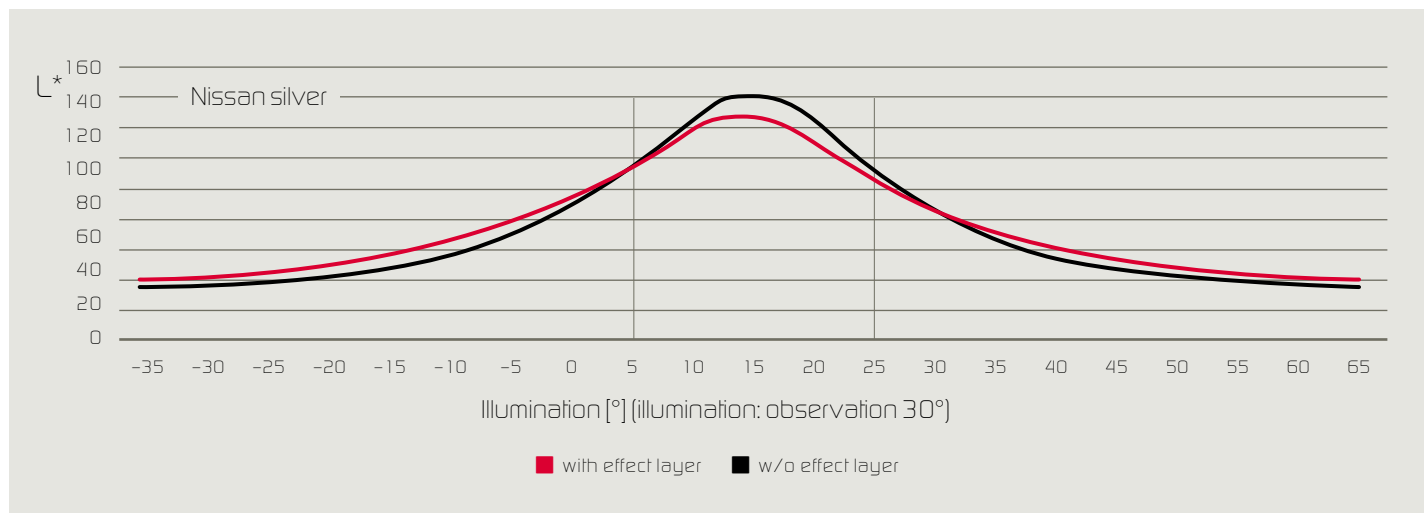
According to the principles of interference, interference pigments react to the change in angle of the illumination. With the same aspecular angle, the reflection curves shift to shorter wavelengths when the pigment or the corresponding coating is illuminated more evenly, i.e. red interference pigments shift to yellowish, yellow interference pigments to greenish and green to bluish. Measurements with changed illumination angles clearly show this behaviour in both the reflection curves and the a^*b^* colour values (Figure 10).

The behaviour is typical for each interference pigment and can also be used for identification. The characteristic anchor shape formed by the interference line with the measurement geometries 15°/15° - 45°/15° - 65°/15° and the aspecular line with 45°/15° - 45°/25° - 45°/45°, is specific for an interference pigment. In the connection of 45°/25° - 45°/15° - 65°/15°, the arm always points 45°/15° - 65°/15° counter-clockwise. These geometries cannot be matched using portable devices; however, due to the principles of light reversal, the 45°/-15° geometry can be used instead of the 65°/15° geometry. It is illuminated at 45° and observed at -60° (corresponding to -15° aspecular) with this geometry. If the light path is reversed, it is illuminated at 60° and observed at -45° (corresponding to 15° aspecular); 45°/-15° corresponds to 60°/15°. The optical properties of an interference pigment can be partially captured using this "trick".

VISUAL AND INSTRUMENTAL ASPECTS SUMMARISED

All three descriptions have their merits: visual assessment is more like the human behaviour of moving the sample sheet back and forth. In most cases, two sample sheets are compared to detect colour differences. Colour differences can also be detected with the portable measuring instruments as long as they occur with the available measurement geometries. Different measurement geometries are, however, required to characterise and differentiate interference pigments. To make visual assessments, it is recommended that the measuring panel should be moved in a parallel fashion from top to bottom while

Figure 9: Application also influences behaviour with regard to lightness. The same coating was applied with and without an additional effect layer. Close to the gloss, the effect layer produces a brighter shade.



“The human eye is and remains the decisive tool for assessing colours and colour differences.”

3 questions to Werner Rudolf Cramer

Why is a visual assessment of colour and colour differences still important? The human eye is and remains the decisive tool for assessing colours and colour differences. Insofar it stands for the final judgement in any workflow that deals with colours. The instrumental assessment of a colour helps and supports the visual assessment. Both methods should be used together to get an optimal assessment.

Are portable measuring instruments as reliable as stationary tools? Portable instruments are no compromise concerning their instrumental characteristics and properties. They can be used as portable instruments as well as stationary instruments in a lab. There might be differences in the choice of geometries which are more or less useful to capture the colour travel of effect pigments.

What are the most significant obstacles when assessing effect pigments (compared with other pigment classes)? The colour travel of interference pigments is a big challenge. On the one hand you have to describe this colour travel, on the other hand you can use it to identify an interference pigment. It has a unique colour travel that makes it different from other interference pigments. This colour travel is also typical compared to other kinds of pigment.

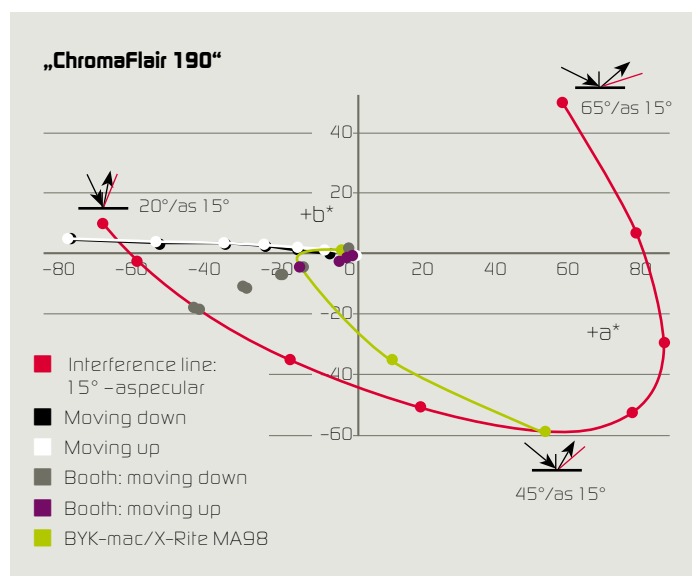


Werner R. Cramer
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simultaneously changing the illumination angle. Holding the sample sheet up and looking over it, it should also be illuminated evenly. If the sheet is lowered, it is illuminated and observed at steeper and steeper angles. To achieve similar results with portable measuring

instruments, the 45°/15° is included in the assessment. Coloured interference pigments ‘bend’ the arm from 45°/15° - 45°/15° counter clockwise, while aluminium pigments ‘run straight’ in relation to the arm 45°/25° - 45°/15°.

Figure 10: Tilting a sample panel at the window or in a light cabin shows the same colour gradient for both tilting down and tilting up. The colour gradient that current portable devices describe corresponds to the gradient when the gloss angle is changed. In all cases, different colour gradients arise from those of the interference.



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INTELLIGENT TESTING

Self-tuning tests to examine coating failure pave the way for an automated future. By Erica Bilodeau, Erik Sapper, Kelby Hull, Chad Immoos, Raymond Fernando· California Polytechnic State University (published in ECJ 11/2016).

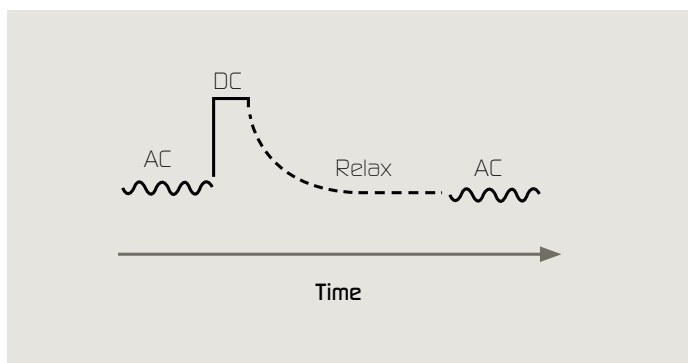
Developing experimental methods that continuously adapt and respond to results offers a way of accelerating coating and material design. Applying autonomous robotics, machine learning, and decision analytics to coatings chemistry makes it possible to automate the testing of new materials. A new way of approaching coating failure enables multiple coating systems and operational environments to be compared.

The design of new coatings and materials is often delayed by inefficient and sub-optimised experimental design. High-throughput and combinatorial methods seek to improve these processes, and have been successfully implemented in many areas of study. Yet these methods are still constrained by initial design space selection, which serves to fix the material design space and test conditions prior to test launch. The fields of machine learning and autonomous decision making have yet to be applied to coatings chemistry. Combined, they have the potential to improve the efficacy and automation of coatings testing.

Current high throughput techniques examine material design spaces, which serve well in determining material compositions for specific applications. Though efficient experimental design can accelerate and

improve these tests, they remain resource intensive. They require the testing of many chemical materials, as well as extensive human labour during the planning, execution, and analysis phases of the experiment. Accelerated environmental tests, such as cyclic salt fog testing (ASTM B117 [1]), despite being industry standards, are not very rep-

Figure 1: Potential profile of an AC-DC-AC test cycle.



RESULTS AT A GLANCE

- New coatings and materials are taking too long to come to market because of inefficient experimental design and testing procedures. The coatings industry has yet to incorporate autonomous robotics, machine learning or decision-making analytics.
- By combining electrochemical testing with autonomous decision-making principles, new test methods are proposed that adapt and respond to experimental results. Crucially, adjustment also happens during testing to accelerate the process, identifying where further testing should take place.
- Similar coating failure modes enable a comparison of different coating systems.
- There is the potential to refine automated decision-making algorithms, which could accelerate coating development even further

representative of real service conditions, and so are poor predictors of future material performance.

AC-DC-AC TESTING TO OBTAIN DECISION-MAKING ALGORITHM

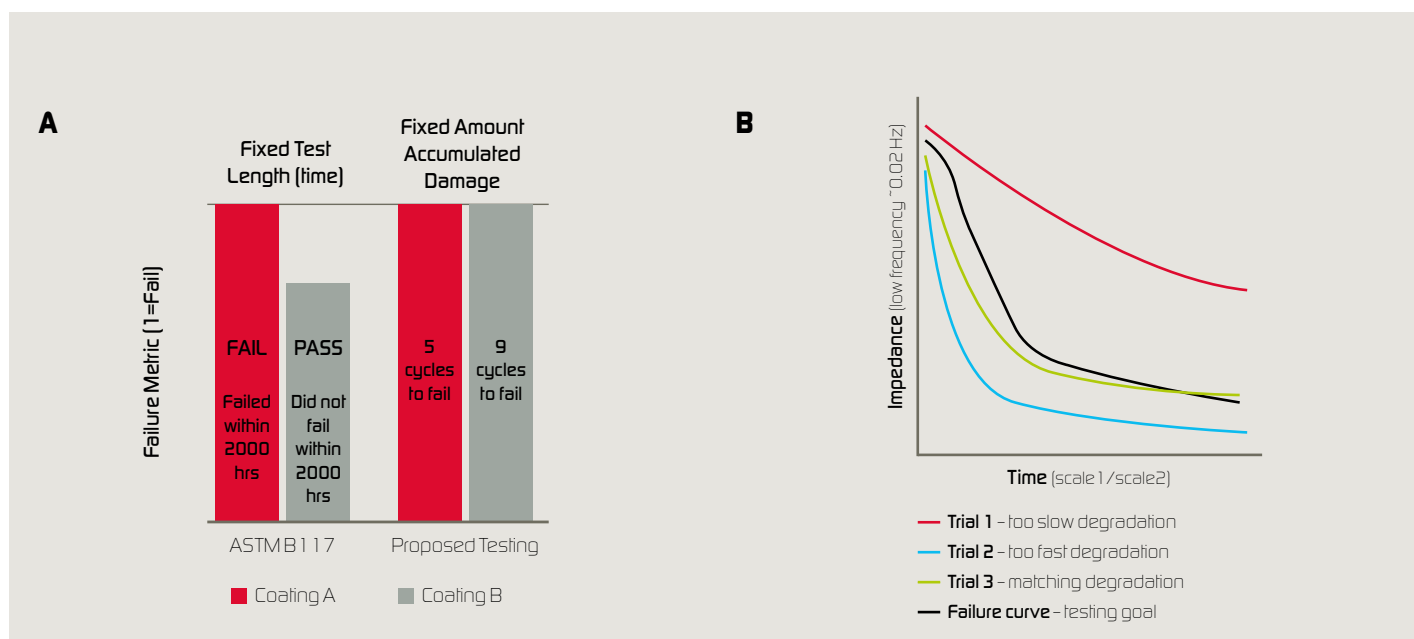
Other tests seek to both measure and accelerate the corrosion of a coated substrate with electrochemical methods, such as AC-DC-AC electrochemical testing [2]. The AC-DC-AC method is an accelerated electrochemical method for monitoring the degradation of a coating on a metal substrate. Electrochemical impedance spectroscopy (EIS) measurements are taken before and after an applied DC potential polarisation, as seen in *Figure 1*. These cycles are repeated until the coating fails, which may be indicated by a number of different metrics such as a reduction in high-frequency impedance, an increase in coating capacitance, and an unacceptable drift in open circuit potential. The AC, or impedance spectroscopy steps, serve to interrogate the system's properties before and after the DC step, which is an applied potential over a period of time that forces the oxidation of the system, thereby accelerating its failure.

In this study, AC-DC-AC methods are used in the preliminary development and testing of an experimental decision-making algorithm with adaptable procedures that may be fitted to many different materials systems. The decision-making algorithm will be applied during AC-DC-AC testing to monitor and adjust AC-DC-AC test parameters so as to arrive at target failure modes and patterns for a variety of coating systems.

INEVITABLE COATING FAILURE OFFERS BETTER COMPARISON

Coating corrosion protection testing such as ASTM B117 was designed around a specific material at a time when hexavalent chromium was the industry standard corrosion inhibitor. Though it is a standard, it

Figure 2, A: Current and proposed testing comparison. B: Graphical representation of data-responsive experiment and the effect of employing adjustable test parameter optimisation based on decision-making algorithms. Shows ideal test progression for low frequency impedance as the failure metric.



is now little more than a quality assurance test for coatings testing. The development of new performance testing is essential to accelerate the development and implementation of new coatings systems. *Figure 2A* illustrates the differences between current and proposed testing. For example, ASTM B117 testing has a fixed test length (e.g. 2000 continuous hours of exposure) with an arbitrary failure metric (usually visual scoring), and pass/fail test outcomes. Some panels will fail the test and some will not fail, those not failing effectively being censored in the failure analysis and any subsequent service life prediction analysis.

The proposed testing procedure, however, has only a fixed amount of imposed accumulated damage. All materials subjected to the test will fail, although they will do so at different times. Importantly, data-responsive changes to live test parameters will ensure that the failure mechanism pathway for all coatings is equivalent. This creates a failure test that examines how a coating fails and how fast, as opposed to whether it will fail or not, which makes it possible to compare the behaviour of different coatings systems.

Forcing all coating systems to fail along one damage accumulation or failure mode pathway allows for parity in the comparison of multiple different coating systems. The general output design of the experimental algorithm is seen in *Figure 2B*, where each rapidly successive trial is adjusted during the experiment to better fit the testing goal, using feedback from the trial as the test progresses. The failure metric of the test can be chosen to best monitor the failure of the material, and the failure curve used to optimise the test is also interchangeable, allowing for in-service exposure data to be used to validate testing (when available).

RESULTS ARE CONTINUOUSLY APPLIED TO IMPROVE TESTING

In this study, low frequency impedance (at $\sim 0.02\text{Hz}$), measured with electrochemical impedance spectroscopy was chosen as a metric for monitoring coating degradation. *Figure 2B* shows the ideal progression of the test, with each subsequent trial helping to refine the test design space and quickly determine the optimum set of adjustable test parameters to be used in the subsequent portion of the test. With this method, customised test parameters are developed that monitor the degradation of a specific material system. The general testing algorithm under development can be seen in *Figure 3*. This test design allows for changes in test parameters within and between trials, as well as versatile and alterable decision parameters, or failure metrics, as deemed appropriate by material type and failure mode of interest.

Preliminary electrochemical tests were performed to demonstrate the abilities of this method. Aluminium 2024-T3 panels coated with an aircraft epoxy topcoat formulation were tested using a typical three-electrode electrochemical system. *Figure 4* shows the low frequency impedance data over time, with different voltages applied during the DC polarisation step of an AC-DC-AC test. The data is shown with a standardised impedance failure curve, which is modelled on data obtained from an electrochemical study of a military primer (MIL-P-23377) [3]. This standardised impedance failure curve is used as the test behaviour goal for subsequent testing. That is, new coatings subjected to the test will be coerced to fail along a similar impedance failure curve. An acceleration on the order from weeks in standard testing to hours or minutes is possible in the newly developed test. This is due to the nature of the AC-DC-AC testing, which forces degradation with each DC step.

As seen in *Figure 4*, each trial has different parameters: each coating was subjected to polarisation holds (DC steps) of different voltages. The duration of each polarisation hold was the same. With decreasing applied voltages, the test results approach the target failure curve. The graph in *Figure 4* illustrates the applied use of the decision

Figure 3: General decision algorithm for testing.

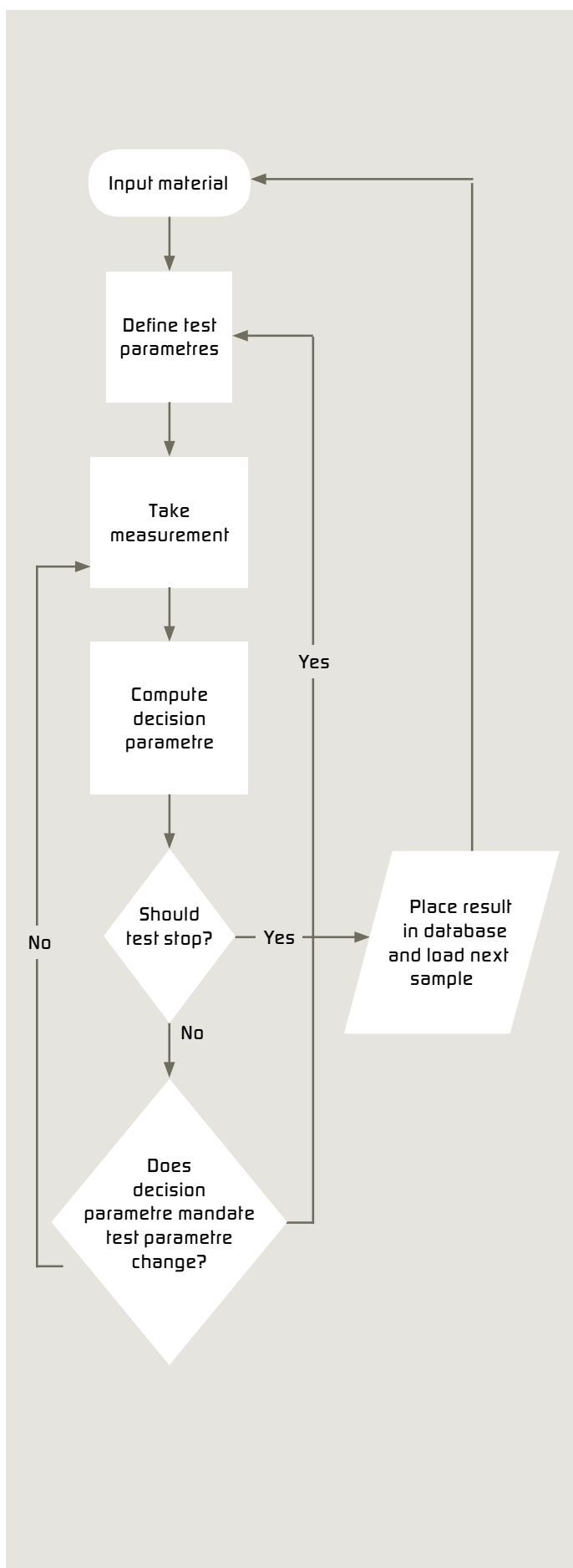
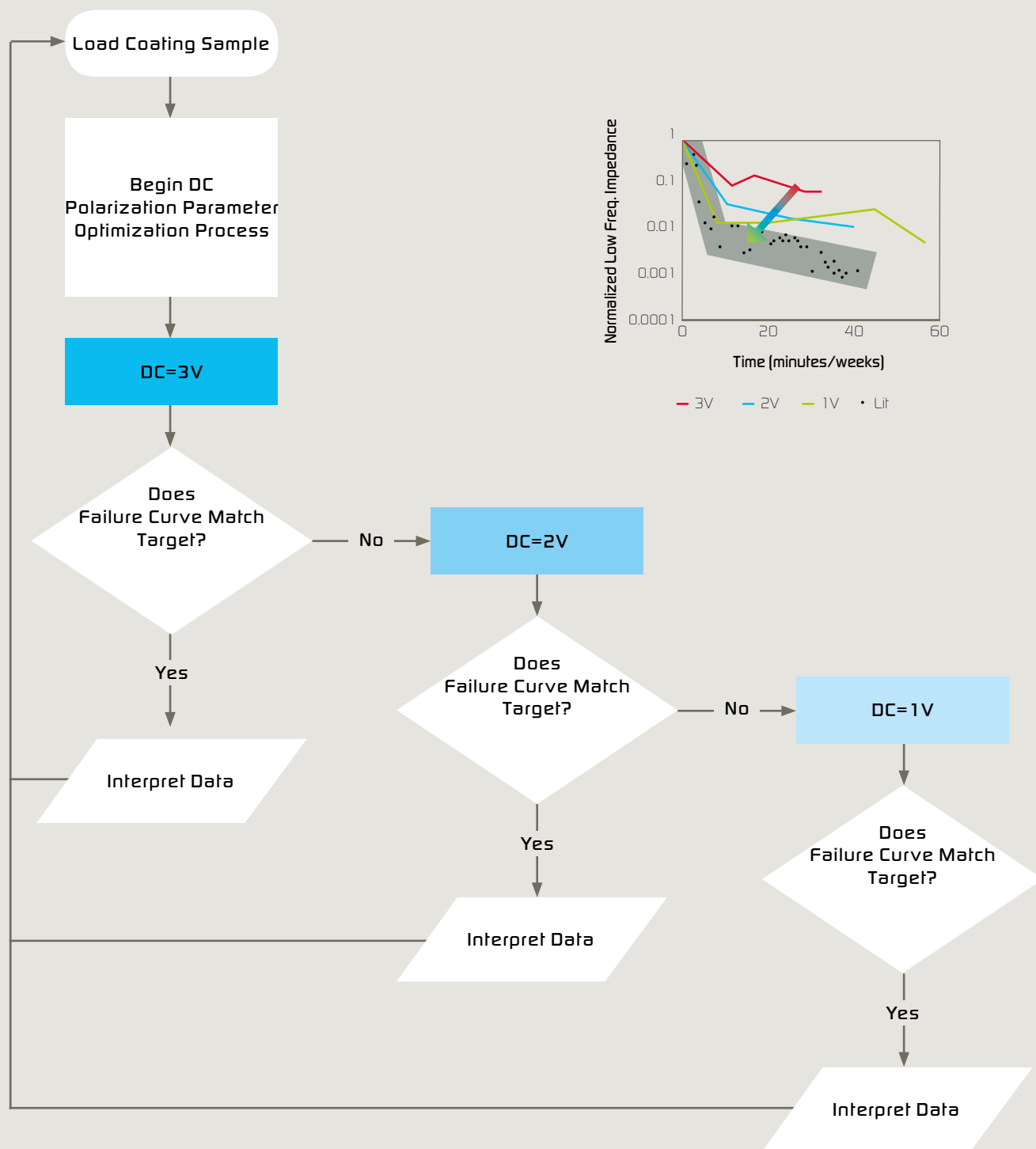


Figure 4: Specific decision algorithm for initial testing of epoxy topcoat on Al2024-T3 panels. Graph: preliminary testing data compared with standardised impedance failure curve [4]. The standard impedance failure curve (with time scale in weeks) representing the literature value is from Bierwagen et al. [3].

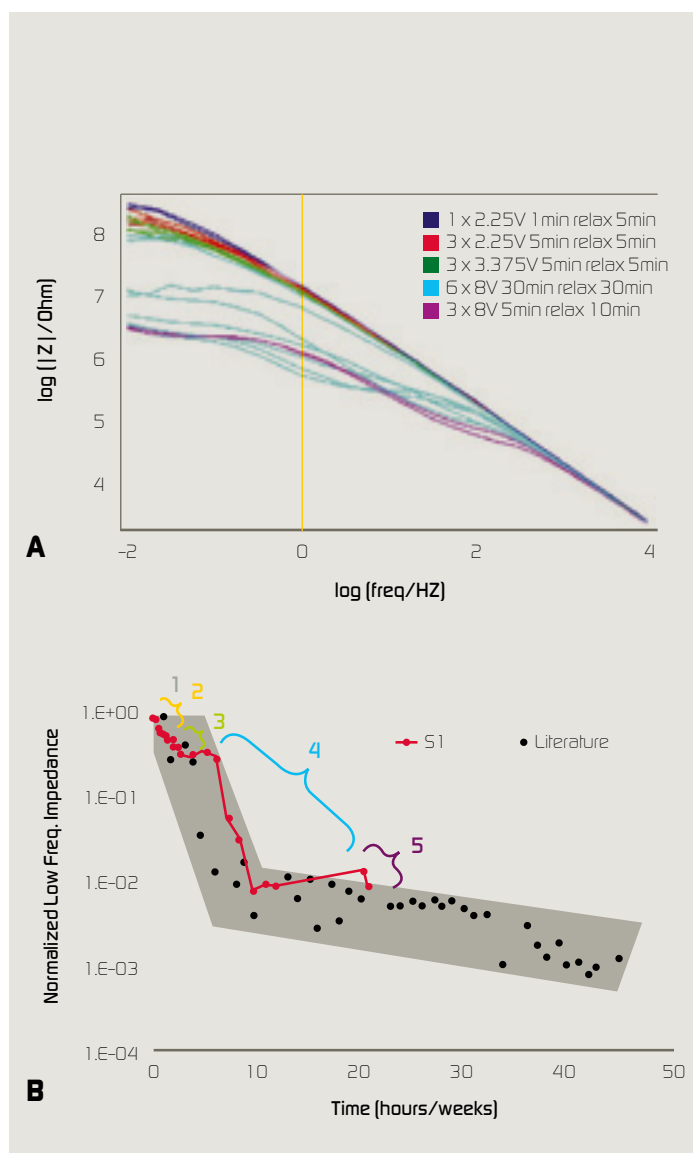


- algorithm, with each voltage decrease chosen in order to push the test data closer to the standardised impedance failure curve. With repetition of this procedure, a specialised test is developed for this coating system.

ONE FAILURE CURVE TO FIT ALL COATING SYSTEMS

Successive testing was performed on Al 2024-T3 panels coated with a non-chromated primer. *Figure 5A* shows a Bode plot obtained in initial tests. Bode plots show the total impedance versus the scan frequency, and are often used to estimate the total coating capacitance (at high frequencies) and the general coating resistance (at low frequencies). Though this appears to be a typical study in impedance spectroscopy, the differences in DC polarisation holds between each AC impedance measurement change the slope of the impedance failure curve over time, which is seen in *Figure 5B*. In this way, the parameters of the

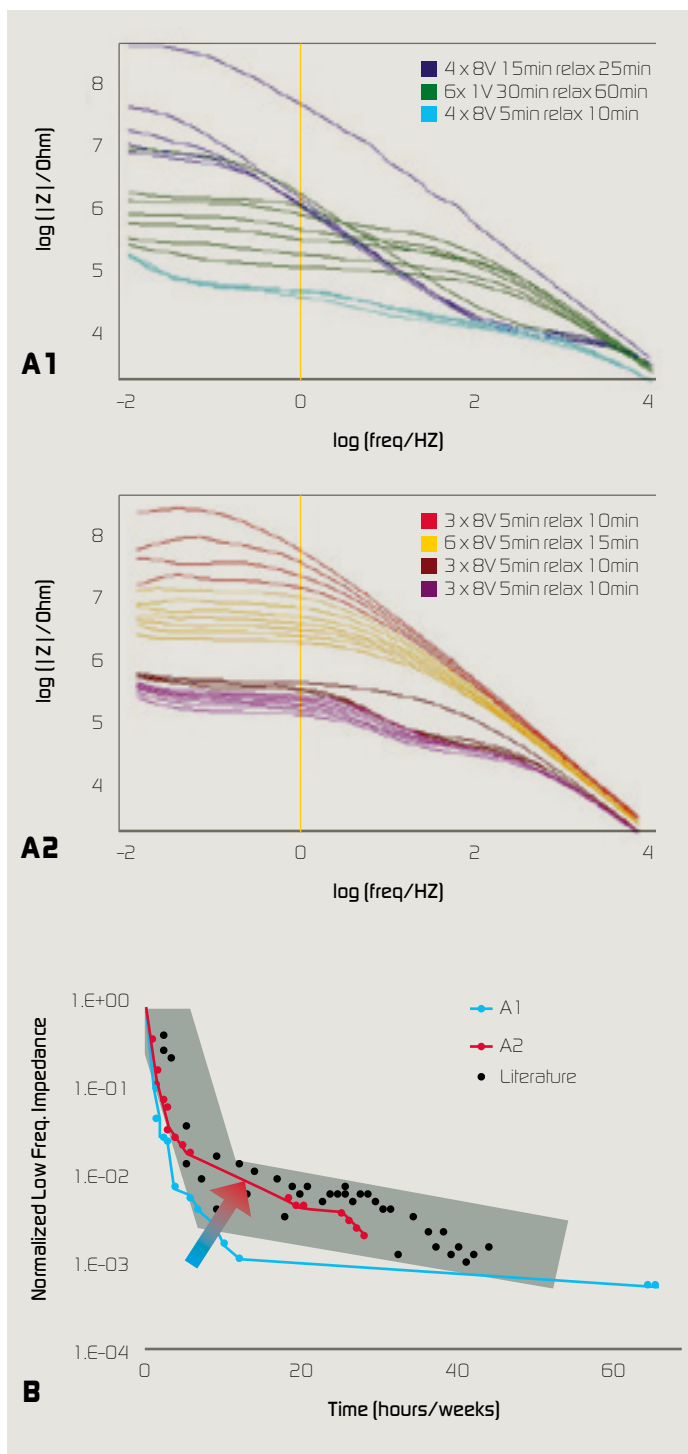
Figure 5, A: Bode plot showing coating degradation, as measured by decrease in low frequency impedance, as a function of test parameters. **B:** Impedance failure plot for test panel S1, showing impedance data taken after different DC polarisation holds. The numbers labelling the curve refer to the key in 5A. The standard impedance failure curve (with time scale in weeks) representing the literature value in B is from Bierwagen et al [3].



test are altered to fit the failure behaviour of the system to a standard impedance failure curve, during a single test cycle.

To demonstrate the ability to compare different coating systems with one standard failure curve, a different non-chromated primer on Al 2024-T3 was tested for comparison. *Figure 6A* demonstrates the changes made during the first test, the second test, and between the first and second tests. In *Figure 6A* panel A1, the long applied voltage duration caused the coating to degrade too quickly, and so the sub-

Figure 6, A: Bode plots for aluminium panels A1 and A2, both coated with the same non-chrome primer. Differences in test parameters between trials elucidate more detailed failure curves. **B:** Normalised impedance failure plot for coatings A1 and A2. Standard impedance failure curve from Bierwagen [3].



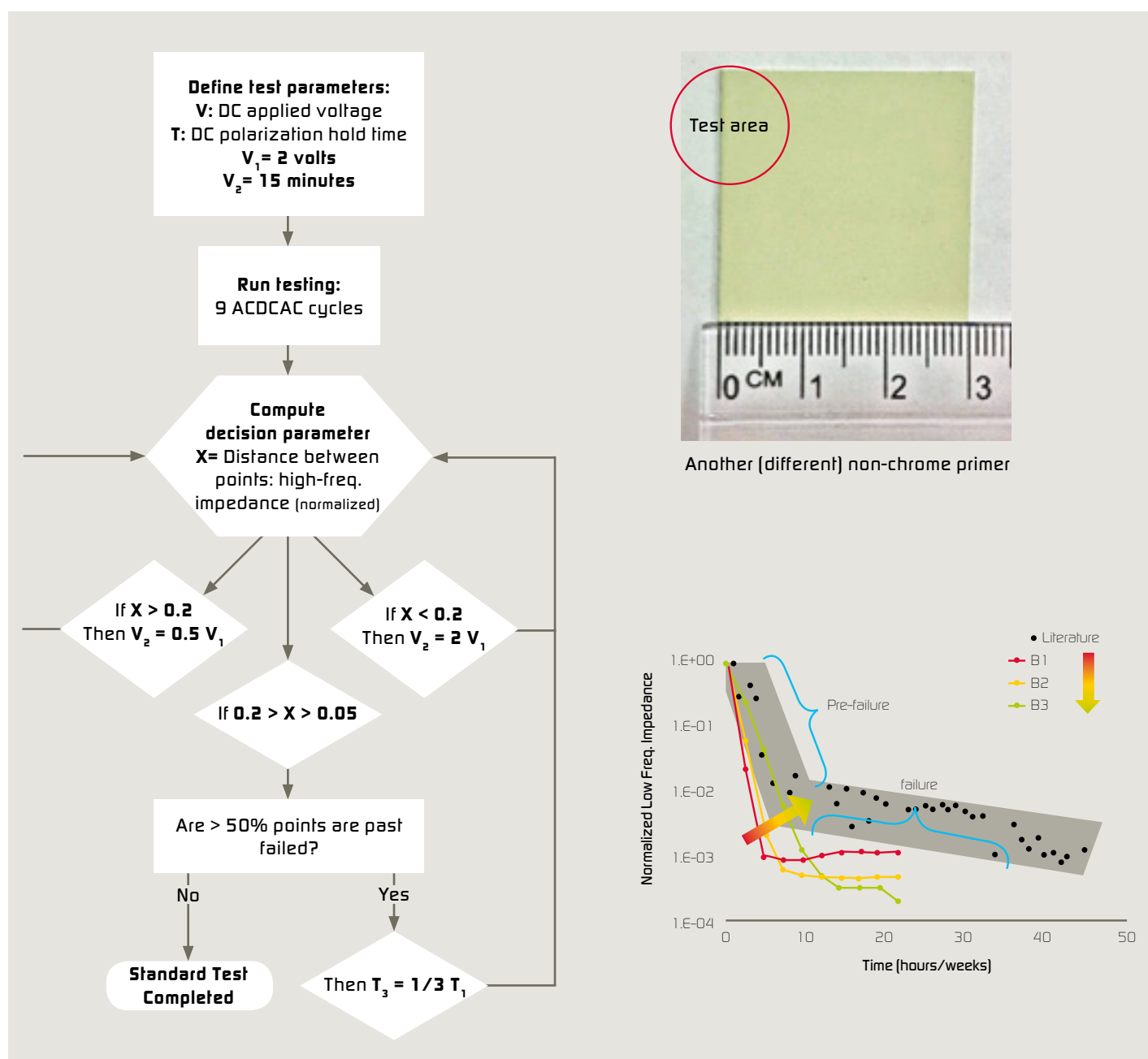
sequent polarisation durations were shortened using the decision-making algorithm. This change in testing is reflected between the two samples, both in the Bode plots as well as in the normalised impedance failure plot seen in *Figure 6B*. Small changes in experimental parameters allow better tracking and examination of coating failure.

As seen in *Figure 6*, the change in experimental parameters between testing samples (A1 and A2) allows for a better fit to the standard impedance failure curve. This correction can be further improved with successive test runs to create a standard test for a specific materials system. The decision-making test algorithm allows for over correction and under correction during testing, quickly defining the test space within which further testing should be directed. This ability lets the test adapt to a design space for different types of coatings and tailors the coating failure modes to be similar, allowing for a comparison between different coating systems.

FINE TUNING TEST PARAMETERS HELPS TO DEVELOP SPECIALISED TEST

There are two parameters that can be tuned in the AC-DC-AC test method: the DC polarisation voltage magnitude, and the polarisation duration. By following the decision algorithm in *Figure 7* and changing one variable at a time, the test can be automatically fine-tuned for any system. This evidence of fine-tuning comes in the form of more data points clustered in the pre-failure linear region before the failure metric begins to level off and stops changing as rapidly. This phenomenon can be seen in *Figure 8*, where each successive test (each consisting of nine runs) has data points that are closer together, ensuring a more accurate representation of the pre-failure state of the coating. It should be noted that each successive test is performed on a fresh coating surface, though the coating is the same (cut from the same panel).

Figure 7: Final decision algorithm used to fine-tune testing of materials system B, and physical setup of test panels. Low-frequency impedance data from material system B, from plots in *Figure 8*. Standard literature impedance failure curve from Bierwagen [3].



The changes from fine-tuning the test parameters observed in Figure 8 are presented in the test plot in Figure 7. With each parameter being tuned, the failure curve approaches that of the target failure region compiled from literature data, and a specialised test is developed for this particular materials system.

POTENTIAL TO AUTOMATE ALGORITHM TO PRODUCE TEST PARAMETERS FOR SPECIFIC COATING SYSTEMS

These proposed test methods are being developed to adapt and respond to experimental results, automatically and as the testing progresses, which allows for on-the-fly adjustment during and between each trial. This experimental algorithm is faster than traditional high-throughput testing, as it can make adjustments while testing progresses instead of simply following preset design space parameters. The test can be formulated around any standard failure curve, so it is possible to directly use in-service failure and degradation data results to model and replicate the failure of the coating in the adaptive test environment. Different failure metrics may also be used, such as polarisation resistance, coating capacitance, and open circuit potential, as determined by the test designer, the objectives of the test, and functionality of the coatings being tested. Future work in this field may take many directions. We would like to further examine the effects of each individual test parameter to better understand how different applied voltages and polarisation durations affect the coating's degradation behaviour. This sensitivity analysis would enable automated decision-making algorithms to be further refined and used in autonomous test beds, which are currently in development. Successful encoding of autonomous decision-making capability into a robotic platform for coating testing evaluation and assessment will eventually enable the testing algorithm to be fully automated, which could then generate specialised accelerated test parameters for specific coating systems.

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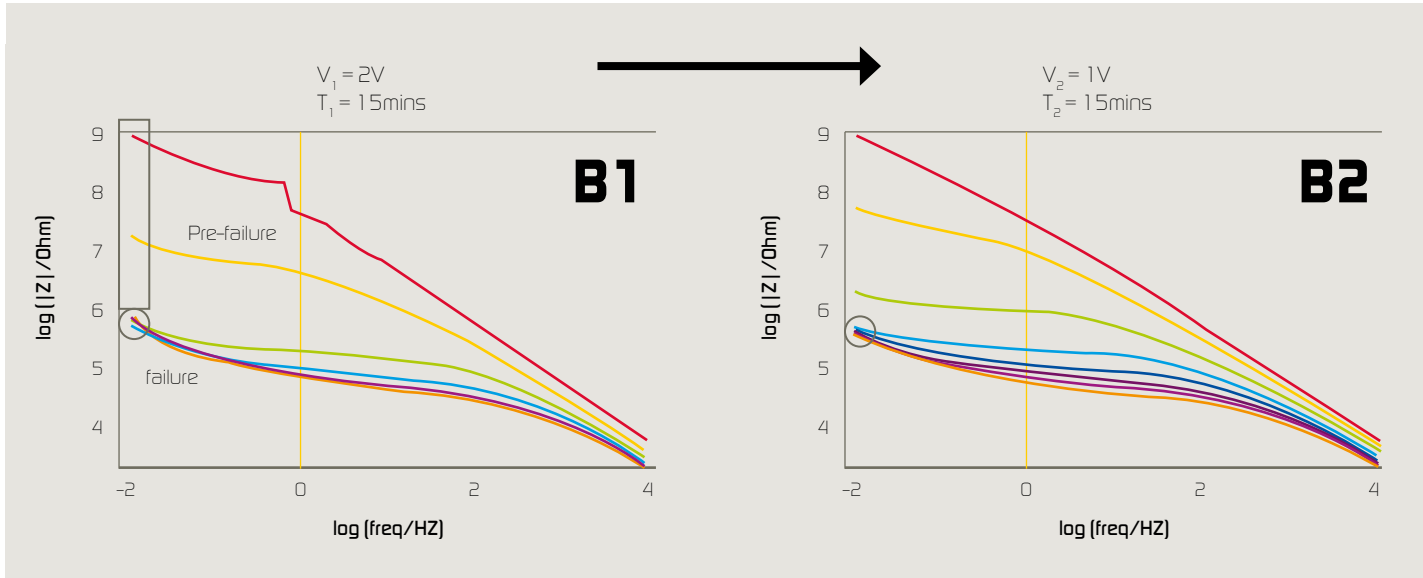
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Figure 8: Study in fine-tuning test parameters on non-chrome primer coated aluminium. Changes in one variable at a time: either voltage magnitude or polarisation hold time.



“Months to years may be saved.”



3 questions to Erica Bilodeau

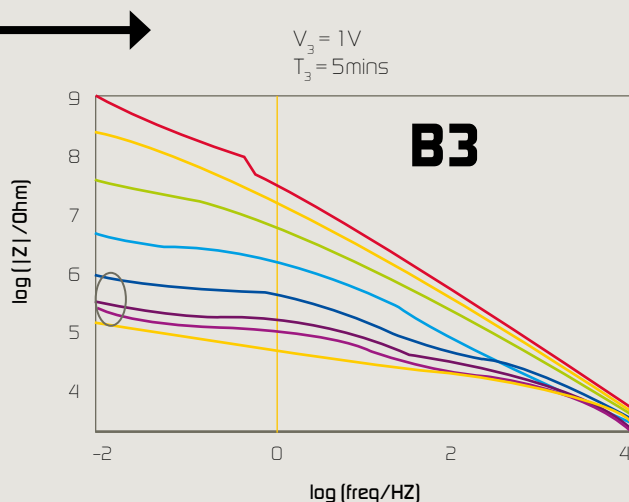
How easily can the test parameters be changed within testing? The ease of changing test parameters depends on the system used for testing. A potentiostat control program that allows for queued experiments is key in the development and implementation of this test. The decision algorithm simply takes into account the test parameters and the normalised data, and suggests changes that are specific to the test.

How much time is saved in comparison to high throughput testing? Compared to standard salt spray testing, months to years may be saved with this method. Before replacing current tests, however, this test would need to undergo certain qualifications depending on the industry where it is used.

Can I adjust the test parameters to individual requirements without problems? Adjusting the test parameters depends primarily on the potentiostat being used. As such, the decision algorithm is simple and robust enough to accommodate changes in the test parameters without difficulty. Any data set may be used as the failure curve testing goal, as long as all performance data is normalised during analysis.

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SHAKING OFF THE COLD

Ice-release finishes retain performance after repeated test cycles. By Cameron Brinn, Kennard Brunson, Dana Klein, Kenneth J. Wynne and Wei Zhang, Polymer Exploration Group LLC (published in ECJ 01/2017).

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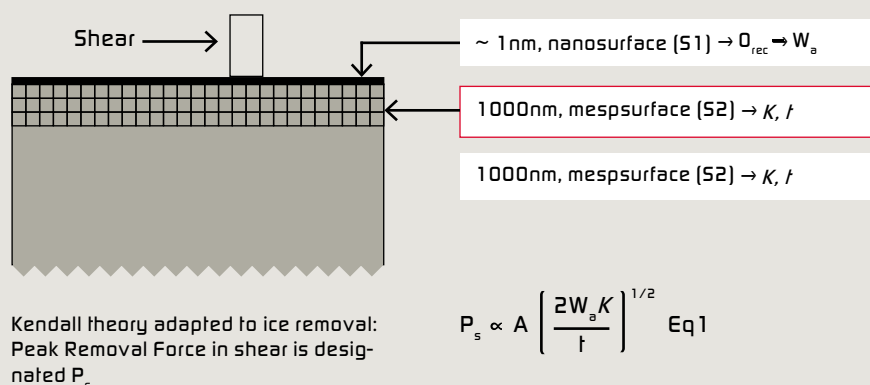
Ice build-up can lead to serious losses, damage or accidents in a range of industries. Some problems with current research into ice-release coatings are outlined. A new coating system adheres well to a range of substrates and shows low ice adhesion even after repeated ice-removal tests.

Ice accumulation is a serious problem for industries including aerospace, wind energy, power utilities, telecommunications, commercial fishing, transportation and others. Icing leads to material loss, property damage, reduced performance and interference with normal operations. Icing can precipitate injuries and, in some instances,

fatal accidents. Methods currently employed to combat icing and its effects include energy-intensive heating, labour-intensive mechanical removal and environmentally unfriendly chemical de-icing fluids. It is worth noting that these are all active methods; that is, they all require the intentional input of resources (chemicals and/or energies) as icing occurs.

Thus, a need exists for effective passive methods such as low ice-adhesion coatings that provide easy release of accumulated ice. However, current coatings have limited effectiveness. Some reasons for this and the formulation of an effective ice-release coating system are described below.

Figure 1: Release mechanism of rigid adherent on an elastomeric coating. Low modulus mesosurface contributes to the peak removal force P_s with two of the three parameters in Kendal's theory [1]: (1) work of adhesion (w_a), (2) modulus (K), and (3) thickness (t).



RESULTS AT A GLANCE

- Problems can be encountered with ice build-up in many different industries. Icing can lead to material loss, property damage, reduced performance and sometimes serious accidents.
- Current removal procedures are all 'active', requiring the application of de-icing compounds, heat and/or physical removal. A coating which will easily shed ice due to natural movement such as rotation or vibration of power lines offers considerable benefits.
- Current research often focuses on superhydrophobic coatings. However, the properties of ice and water are quite different, and the surface structures normally present in superhydrophobic coatings may be easily damaged by repeated ice removal.
- A tough and durable coating was developed that resists repeated ice removal, showing little change in properties after 20 test cycles. The coating shows good adhesion to a range of metals and to fibre-reinforced composite.

IS CURRENT ICE-RELEASE COATINGS RESEARCH MISGUIDED?

In pursuit of the goal of ice release, researchers have focused on the development of superhydrophobic or 'non-stick' surfaces. This approach, while apparently logical, can be misguided.

This is due to the fact that the physical properties of water in its solid state (ice) are significantly different from water in its liquid state; hence the interactions between water and a given surface are heavily dependent upon the physical state of the water itself. Superhydrophobic surfaces are designed to repel liquid water, and they excel at that task; once that water freezes, however, these surfaces can become a liability.

Many superhydrophobic surfaces rely upon delicate nanostructures to achieve their functionality. Not only do these nanostructures do little to prevent icing in some conditions [1], but they are also easily damaged and can actually reinforce ice adhesion to the surface, compounding any icing problems.

FACTORS AFFECTING ICE REMOVAL IN DIFFERENT INDUSTRIES

Because of the broad range of industry sectors affected, each with its own complexities, there is no universal solution to ice accumulation. Depending on the application, the desired outcome may be the prevention of ice *accumulation* through easy removal at an early stage of accretion by 'natural' forces including shear forces from air movement (wind and movement of surfaces), existing mechanical vibration, and/or centrifugal force.

Figure 2: a and b, PEG-RT-H ice-release testing system; c and d, PEG-G2-H ice-release testing system. e. A typical force-distance curve for a PEG LLC ice release surface.

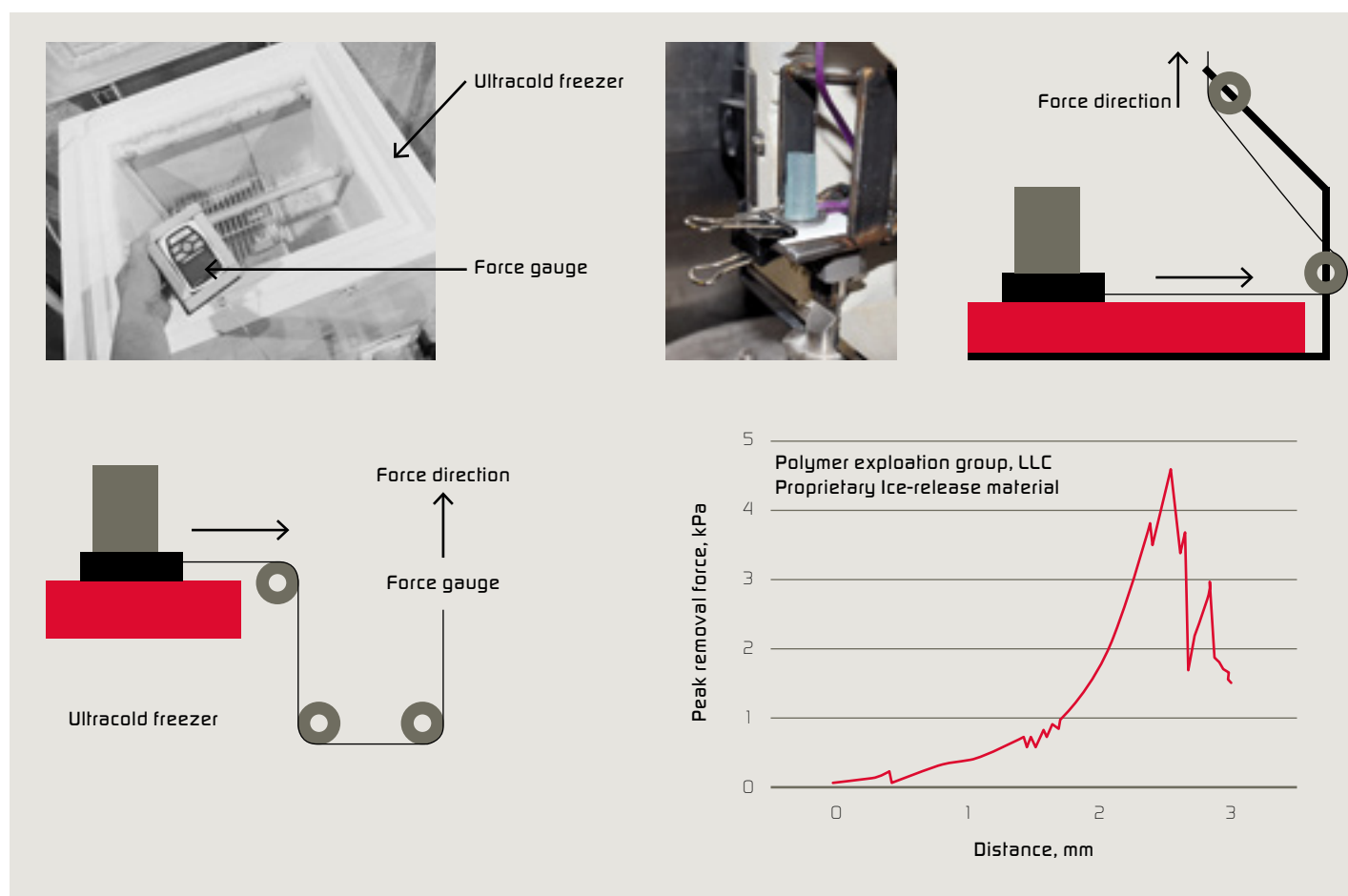


Figure 3: Comparison of peak removal force of ice on the same surfaces using G2-H and PEG-RT-H methods.

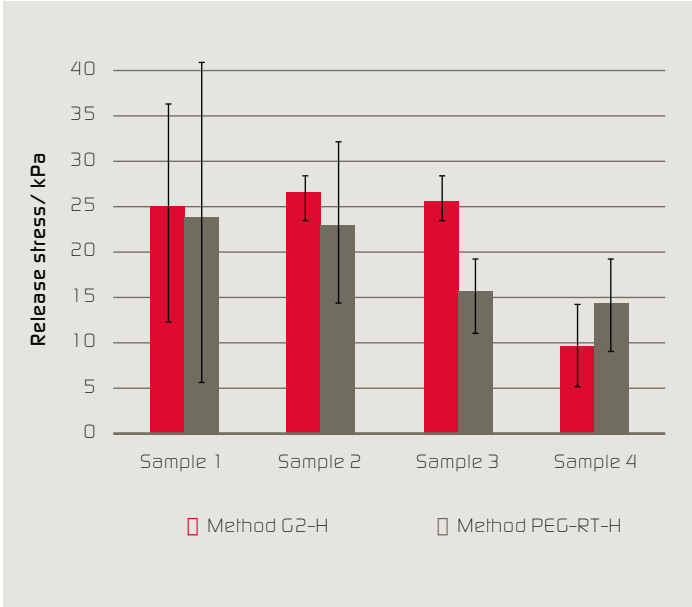


Figure 4: ER-Coat ice adhesion (peak removal force) from testing done at AERTS in the Aerospace Engineering Department at Penn State compared to PEG LLC in-house testing.

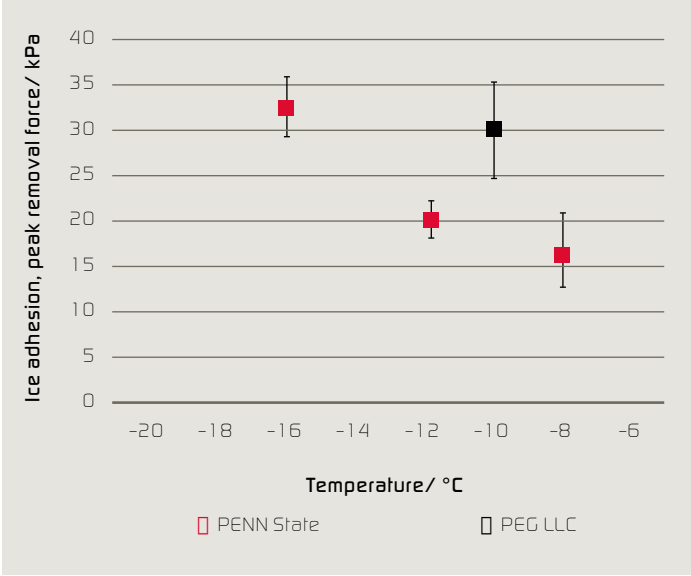
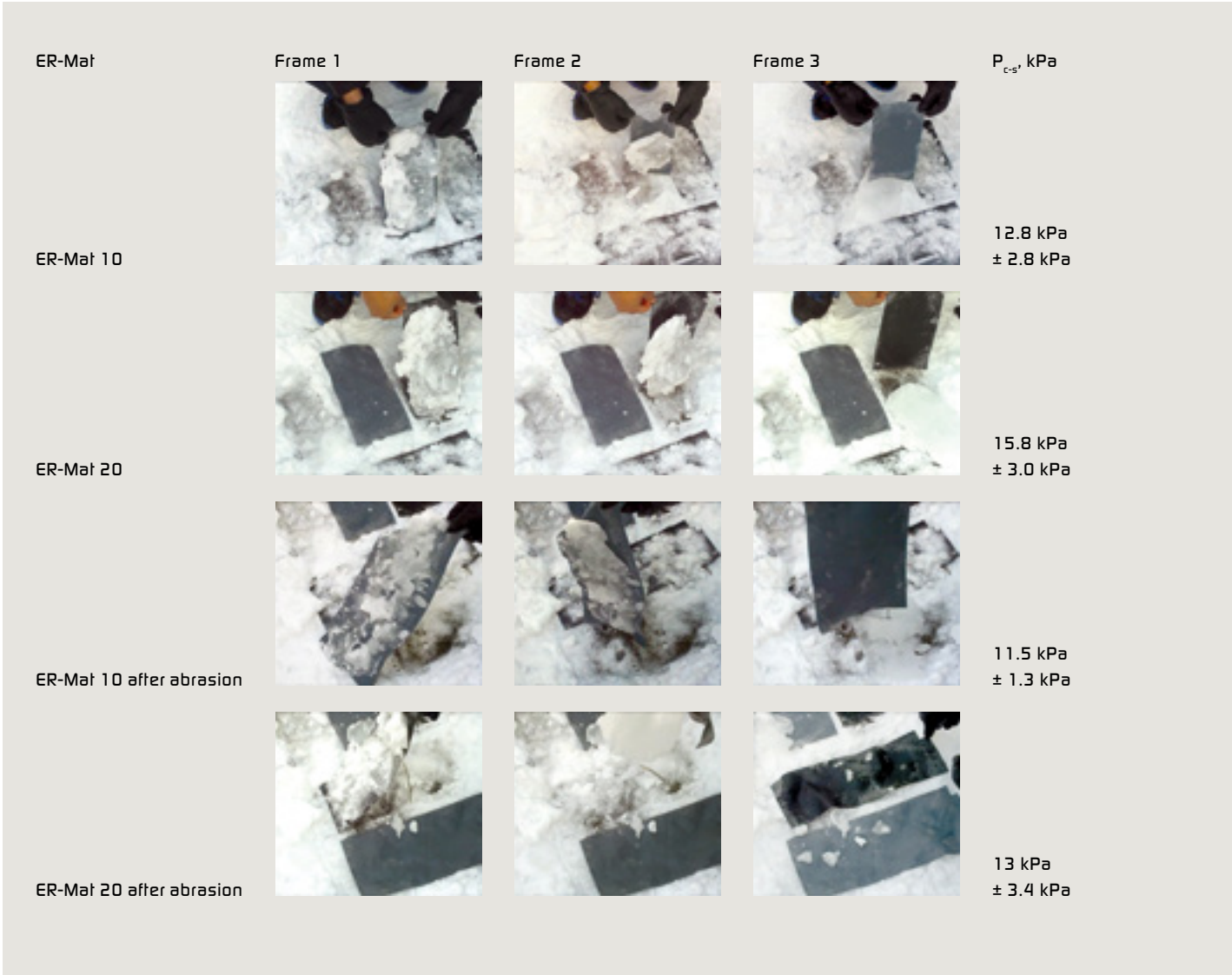


Figure 5: Ice release materials (ER-Mat) showing release by gravity phenomenon.



➤ The extent of accumulation that can be tolerated varies greatly, as does the degree to which ice can be removed from a surface by natural means. For example, a coating technology that seeks to remove ice by centrifugal force from a wind turbine blade must take into account that the blade close to the rotor hub moves more slowly than the tip of the blade.

Power and cable lines are fixed, but undergo flexing and vibration due to wind that can facilitate ice release with a suitable coating.

The most demanding application requirements are those of the aerospace industry. It is well known that aerofoil icing disrupts airflow, reduces lift and interferes with control. These applications have strict requirements for maximum tolerable mass and for uncompromised reliability.

Currently, the aviation industry generally employs active anti-icing (for example, heating, de-icing chemicals, rubber covers or a combination of multiple methods) to mitigate icing-related problems.

A NEW MODEL FOR ANALYSING ICE ADHESION PROBLEMS

Based on findings from an NSF funded study carried out in the Virginia Commonwealth University (VCU), a fundamentally different ice-removal model was established with considerations from multiple factors that contribute to ice adhesion.

It is important to note that VCU findings in soft surface science and engineering, which are being transitioned to the Polymer Exploration Group LLC (PEG LLC), depart from conventional thinking that focuses on water repellent superhydrophobic / low surface energy surfaces.

Rather, following Kendal adhesion theory for the force required to remove a rigid object from an elastomer (*Figure 1*) [2], fundamental studies provided the knowledge base for the development of a novel coating system that takes into account multiple contributions:

- Nanosurface work of adhesion, controlled by surface energy;
- Mesosurface (ca. 1,000 nm) that controls frontier mechanical properties;

➤ Bulk, that defines coating thickness and overall mechanical properties. This model has been previously published and is illustrated in *Figure 1*. Applying these new findings to commercial icing problems, the company has developed an inexpensive easy-release coating (ER-Coat) with commercially available engineering materials. This easily tailored coating also features good toughness and durability.

PRACTICAL BASIS OF ICE RELEASE TESTING PROCEDURES

In order to test the adhesion strength of ice to various surfaces, several high throughput methods were developed at VCU and at PEG LLC to measure the shear stress necessary to remove icing from a given surface. These methods, while distinct, share some fundamental similarities.

Each method makes use of a sample surface (the ice release performance of which is being measured), and an ice holder (an open ended prism with a known cross-sectional area). The sample is cooled to the desired testing temperature and the ice holder is placed upon it with the open cross-section facing down.

The ice holder is filled with a known quantity of water, which is then allowed to freeze and set for a specified time. The sample is clamped in place and a probe or 'sled' is then secured to the ice holder at the interface of the ice holder and sample. A force is applied to the ice via the probe in a direction parallel to the ice-sample interface.

The area of the interface, and the force required to remove the ice sample are recorded and used to calculate the shear stress (reported as peak removal force below) at interfacial failure.

Cohesive failure (the ice cylinder breaks rather than detaching from the surface) was occasionally observed, especially for control samples. But the accurate and delicate instrumentation employed to carry out the ice release test usually reaches its machine limit before causing cohesive failures and some adhesive failures.

It should be pointed out that a surface is not useful as an ice release ➤

Figure 6: Durability and longevity tests on ER-Coat.

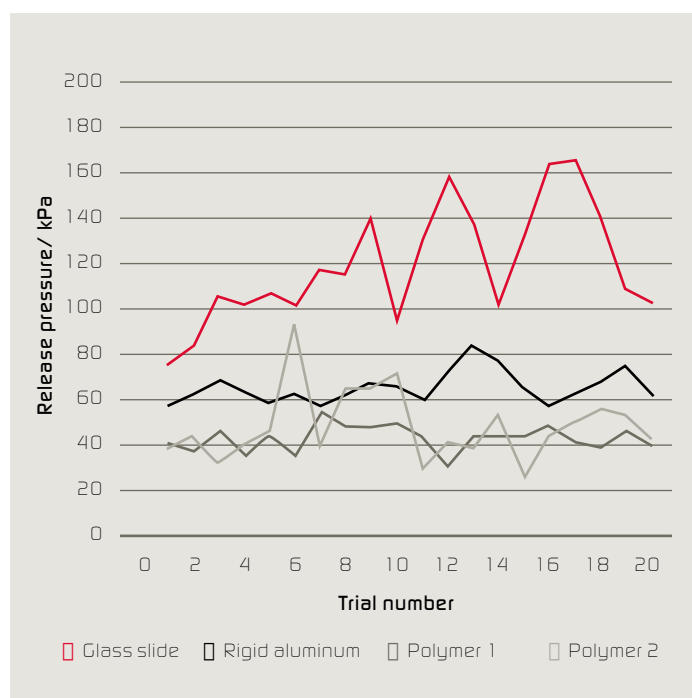
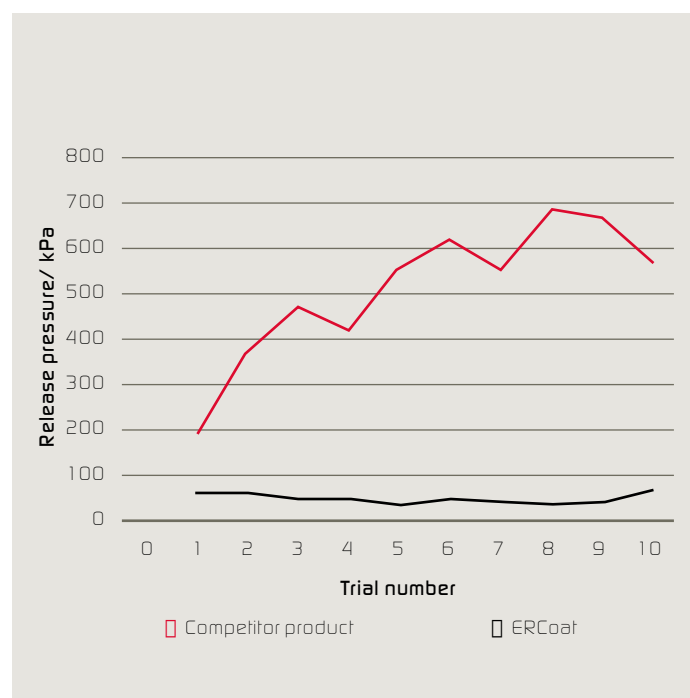


Figure 7: Ice release performance comparison of ER-Coat and an off-the shelf superhydrophobic spray-on coating with "ice-phobicity" claims.



- coating if cohesive failure is observed. However, because of the unknown values for the control samples where the instrumentation reached its maximum before causing interfacial/cohesive failures, the relative increase in ice release performance (ratio of the peak removal forces of the control surface versus that of the sample) may only be an estimated value.

TWO INDIVIDUAL TEST METHODS IN DETAIL

The first method (G2-V) is conducted using a commercial "RSA-G2" mechanical solids analyser from TA Instruments with a vertical sample holder. The icing sample is oriented vertically, and the probe arms/clamps are modified to apply shear stress to the ice impinging on the surface. This method is capable of testing rigid, square samples as large as 15 cm² (2.25 square inches).

This testing method and testing geometry is the same as that previously published [3-9]. It should be noted that the ice cylinders have to be formed in a separate freezer and then transferred to the testing chamber prior to testing. The force probe is also required to maintain a certain distance from the sample surface to prevent potential damage to the sample surface. This spacing between force probe and surface may cause non-shearing mechanical movement of the ice cylinder.

The second method (G2-H) is also performed in the same instrument, but employing a horizontal sample holder. This method uses a custom built sample mount which is placed in the non-mobile lower arm of the instrument. This mount facilitates the horizontal orientation of the sample in the testing environment.

This geometry, shown in *Figure 2d*, provides several advantages over the vertical arrangement of method G2-V. The horizontal sample ar-

angement allows for the testing of soft, flexible substrates (for which this method was initially developed) as well as allowing for in-situ freezing.

This in turn eliminates the possibility of thermal or mechanical shock during sample transfer (between the freezing chamber and the testing chamber) affecting the ice adhesion force. Additionally, this method ensures that the forces applied to the sample are true shear forces. This minimises the effects of forces other than shear acting on the ice.

SPECIAL METHOD DEVELOPED FOR TESTING LARGE AREAS

The third method (PEG Release Test Horizontal – PEG-RT-H) was developed to test sample areas as large as one square foot (around 0.09 m²). This large sample size required a larger testing environment than that of the standard instrument, so a commercial deep freezer was modified to facilitate ice release testing as shown in *Figure 2a* (picture of the apparatus) and *Figure 2b* (schematic of the working mechanism).

This method provides all the advantages of the horizontal sample orientation but also allows for the testing of multiple sites on a large sample as well as the testing of larger individual icing sites, which better approximate real world conditions.

Consistency between the modified commercial instrument for testing small samples (G2-H) and the in-house PEG-RT-H is observed, as shown in *Figure 3*. Within experimental error, these numbers are comparable, although the variance in the values recorded using method PEG-RT-H is typically larger than that in those recorded using method G2-H.

ROTARY TESTS CARRIED OUT AT EXTERNAL LABORATORY

Third party testing was performed at the Adverse Environment Rotor Test Stand (AERTS) facility in the Aerospace Engineering Department at Penn State University, depicted in *Figure 4*. The tests were carried out with coated test coupons mounted on the end of the test beam's leading edge.

Rotation is initiated up to 1,000 rpm after the room is cooled to the desired temperature. The tip speeds are up to 143 m/s (ca. 470 ft./s). After reaching the desired tip speed, a cold water mist is sprayed into the room. Water droplets freeze on the surface after impinging on the rotating sample and ice accumulates on the surface.

As the mass grows, the shear force at the interface of ice and test surface increases until the ice flies off. Measurements obtained from a strain gauge and torque sensor are used to calculate the numerical shear removal force.

This test was designed to reproduce natural icing conditions such as those on a helicopter rotor or airplane wing. However, because of the relatively low rotor speed, the test better simulates ice release from wind turbine blades. This forms a near-term targeted application for the company.

Of course, the Penn State test can stand alone as a valid general ice-release testing method without a specific targeted application [10-12].

GOOD PERFORMANCE OBTAINED OVER VARIOUS SUBSTRATES

With NSF Small Business Innovation Research (SBIR) funding, fast throughput in-house ice-release test methods and instrumentation (*Figure 2*) were used for the development of ER-Coat materials. Good adhesion of the ER-Coat on various substrates including aluminium, steel, polyethylene, PVC, and fibre-reinforced composite materials was achieved with or without primers and substrate surface treatments.

Table 1 lists the ice release performance on these substrates. Recent

Table 1: Comparison of ice-release performances of different materials and ER-Coat on different substrates.

Surface	Primer	Ice adhesion strength, kPa			
		Test 1	Test 2	Test 3	Average
Bare steel	None	588	785	788	720
Bare aluminium	None	523	811	1228	850
LDPE	None	>10 tests			345
ER-coat on PVC	None	29	31	16	25
ER-coat on PVC	None	26 kPa tested at Penn State			
ER-coat on MDPE	None	68	71	85	75
ER-coat on LDPE	None	>10 tests			59
ER-coat on glass fibre composite	None	55	27	90	58
ER-coat on glass	None	41	57	49	49
ER-Coat on primed metals	Primer A on steel	52	78	52	61
	Primer B on steel	582	537	539	552
	Primer C on Al	33 kPa tested at Penn State			
	Primer D on steel	156	172	169	166
	Primer D on steel	47 kPa tested at Penn State			

results indicate that an ice adhesion strength of 100 kPa is a critical value for any practical use. This force must be less than 10 kPa to remove ice from ER materials by gravity only.

Video evidence of this release by gravity was captured during a field test in Central Virginia region after a wintry storm. *Figure 5* shows the frame captures from this film alongside the ice adhesion values (measured using PEG-RT-H) associated with each sample. Third party testing has confirmed the results obtained from PEG LLC's in house testing findings (*Table 1* and *Figure 3*).

COATING FORMULATION OPTIMISED AFTER CONTINUED TESTING

Durability and longevity of the ER-Coat performance was studied during the last period of performance. To provide a measure of durability, as many as twenty ice release tests were performed on the same area. Increased ice adhesion (degradation of performance) was observed in one formulation series that had previously appeared optimum. Based on knowledge of results from a broad range of compositions, the formulation for ER-Coat was adjusted to a new range that has no degradation of performance over twenty ice release tests on the same area, as shown in *Figure 6*.

An off-the-shelf superhydrophobic spray-on coating with claims of "ice-phobicity" was purchased from a local hardware store. It was observed that this superhydrophobic coating delayed ice formation slightly during experiments. But ice release performance was found to be unacceptable.

In addition, the durability of this superhydrophobic coating is not comparable to ER-Coat. Ice adhesion force increased with the number of ice removal tests performed on the surface. It seems likely that part of the superhydrophobic surface is removed or damaged every time an ice sample is removed. Results are shown in *Figure 7*. 

ACKNOWLEDGEMENTS

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“Ice release and erosion protection properties can be combined in one product.”

3 questions to Wei Zhang.

Does the Kendall equation of Ice release state that in the future every aircraft passenger can rely on ice release on the aircraft wings as long as the coating is thick and elasticised enough? The simplified Kendall Equation is a tool to relate ice adhesion to the most important factors. By itself, it makes no such statement or prediction, however it is our belief that a material with the correct combination of properties could indeed provide reliable, passive icing protection. Such a material may prove ideal in aviation applications.

Does a highly elasticated, thick coating withstand the kinetic attack from rain and hail erosion on wing tips of rotor blades at wind mills? In short, yes. Kinetic energy must be absorbed by surface fracturing (erosion) or dissipated as heat by a resilient surface. Materials with high elasticity and resilience are used for erosion protection on wind turbine blades and airplane propellers. We believe that ice release and erosion protection properties can be combined in one product.

One term in the adapted Kendall equation is related to the top nano layer of the coating W_a . Could you describe what kind of surface structure will have a certain negative impact on that term and on the shear force to release the ice layer? The W_a term refers to the work of adhesion (surface energy) of the material. Any structure that minimises interfacial interactions such as intermolecular forces will reduce the value of the W_a term and thereby reduce the ice adhesion force. Many extant surfaces do this; the challenge lies in balancing this characteristic with other crucial factors.



DESIGNING FOR FREE FLOW

Testing low friction coatings for powder handling equipment. By Jamie Clayton, Freeman Technology and James Cooke, Curtiss Wright Surface Technologies (published in ECJ 7-8/2017).

Coatings applied to the surfaces of machinery and handling plant such as hoppers can reduce wear and corrosion, as well as improving handling by the control of friction. The frictional behaviour of coatings was studied in relation to powder flow. The application of the results to the design and specification of powder hoppers is discussed.

Specialised coatings can enhance equipment surfaces so as to control wear, reduce corrosion, protect against temperature change, increase lubrication and generally manage equipment deterioration over time. However, surface coatings will also have a direct effect on the friction between the equipment walls and the materials flowing through that equipment.

When used within processing plant, coatings have the potential to either slow or enhance the movement of a powder through pumps, pipes, valves or vessels such as hoppers. With a variety of coatings available, the ability to quantify this frictional effect by employing

robust, systematic tests in order to rank coatings can be highly beneficial to the operator, process engineer, manufacturer and equipment designer.

The criteria typically used to select equipment coatings can then be extended to include this data. This will ensure the coating used not only fulfils the original intention of extending the lifetime of the equipment but also does not impact detrimentally on performance, and indeed may even deliver improvements.

HOW COATINGS AFFECT POWDER FLOW

The way powders flow through any vessel is a result of interactions between individual particles in the powder, and between those powder particles and the vessel walls [1]. When designing plant, such as a hopper for example, engineers should consider wall friction as a flexible parameter, since wall coatings can be measured, understood and optimised relative to the characteristics of the powders that will be processed through the system.

Wall friction testing is a valuable method to measure the relative friction performance of various surface coatings. Assuming the materials being processed are predetermined and the powder properties are therefore fixed, the effects of different coatings on the magnitude of frictional interaction between hopper walls and powder flow can be used to rank each coating relative to its ability to ease powder flow through a process.

BASIC PRINCIPLES OF WALL FRICTION TESTING

A typical method to measure wall friction uses a consolidated powder sample. Consolidation causes a reduction in volume as the particles pack together more tightly under the applied stress, simulating how a powder stored in a hopper compacts under its own weight.

Figure 1 shows a typical apparatus for performing a wall friction test. A sample of the powder is first consolidated and a steady state is established where the sample has

RESULTS AT A GLANCE

- Coatings applied to the surfaces of machinery and handling plant such as hoppers can reduce wear and corrosion, as well as improving handling by the control of friction.
- For powder handling applications, wall friction can be measured by consolidating the powder and measuring the stress required to shear against it with a test disc.
- A range of different powders and low-friction coatings was evaluated with a powder rheometer using this principle. Significant reductions in wall friction (relative to uncoated stainless steel) were obtained, but both the friction values and the variability between coatings differed between the various powders tested.
- 'Slip-stick' behaviour, which can lead to unstable flow, was also evaluated and differed significantly between the coatings as well as the powders.
- The application of these results to the design and specification of hoppers to ensure free powder flow is discussed.

reached a repeatable, stable density relative to the applied compressive load.

During the subsequent testing stage, the stress needed to shear the test disc relative to the surface of the powder is measured [2]. Repeating the shear stress measurements for a range of different consolidation stresses generates a series of data points which can be plotted to create a wall yield locus, from which a least squares regression analysis is performed to determine a linear plot.

The slope of this plot then provides the wall friction angle (WFA, ϕ), as shown in *Figure 2*. The higher the wall friction angle, the greater the frictional forces between the surface being tested and the powder [2].

Different test surfaces, based on the wall materials and surface coatings under investigation, are then used to produce a set of comparable results. Tests with a single powder sample allow different materials and surface coatings to be evaluated, while comparing a range of powders allows a thorough assessment of a specific material/coating combination.

WALL FRICTION TESTING: A CASE STUDY

UK-based Curtiss Wright Surface Technologies (CWST) applies a continuous development strategy that includes the testing and characterisation of all new surface coatings. To extend its capabilities in the food and pharmaceutical sectors, the company sought to enhance its already considerable data bank of surface coating characteristics in or-

der to meet the stricter regulatory requirements within these sectors and respond to higher performance demands.

The applications of interest require rigorously specified corrosion resistance, wear profiles, and – of note in this case – frictional characteristics.

To assess a sample of proprietary coatings from its portfolio for food and pharmaceutical applications, CWST collaborated with Freeman Technology, a UK-based powder characterisation company. Using an "FT4" Powder Rheometer capable of robust dynamic flow, shear and bulk property testing (*Figure 3*), a study was undertaken to quantify the wall friction characteristics of various coatings using a range of powders.

TEST MATERIALS AND EQUIPMENT

Six coated stainless steels were evaluated, including four coatings proprietary to CWST and two competitive products. A standard brushed stainless steel was used as a baseline comparison. The coatings tested included three fluoropolymer-based coatings with different chemical properties and a medical grade low friction coating:

- "Flurene 611": low friction, high wear resistance, resin reinforced fluoropolymer
- "Flurene 177": low friction, high chemical and abrasion resistance, self-bonding fluoropolymer
- "Everlube 6102G": high wear, corrosion and chemical resistance, solid film lubricant fluoropolymer
- "Parylene": a low friction, high electrical insulation, moisture impermeable, medical grade bio-compatible lubricant
- Coating A: competitor product
- Coating B: competitor product
- Baseline control: brushed stainless steel at 1.2 micrometre Ra roughness.

Each of the seven discs was tested with five powders:

- "CRM 116": a grade of limestone produced as a reference material for shear cell tests
- "Respitose" and "FlowLac 100": pharmaceutical grades of lactose – a common excipient (i.e., inert addition to a pharmaceutical preparation)
- Skimmed milk powder (SMP) and cornflour: food ingredients.

All tests were carried out in duplicate to assess repeatability.

LEVEL OF IMPROVEMENT IS DEPENDENT ON POWDER TESTED

The results in *Table 1* show that the uncoated stainless steel generates the highest WFA values for all materials, despite being the standard material of construction in many food processes.

Figure 1: Wall friction test apparatus used to measure the effects of a surface coating on powder flow.

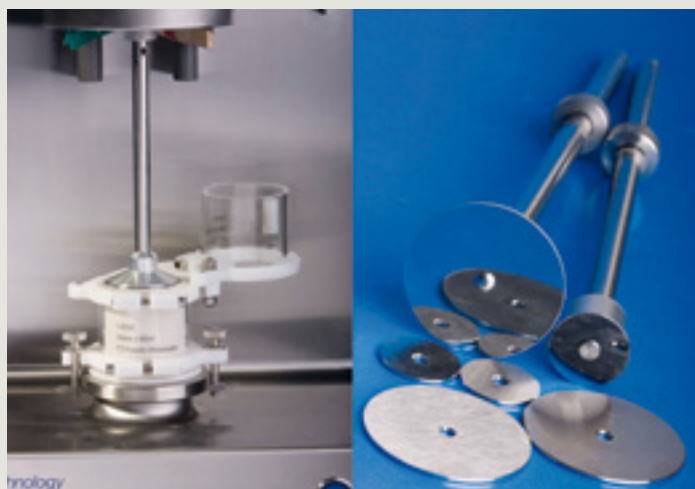


Figure 2: Wall friction test data for a single test surface and a consolidated powder sample under a range of normal stress levels.

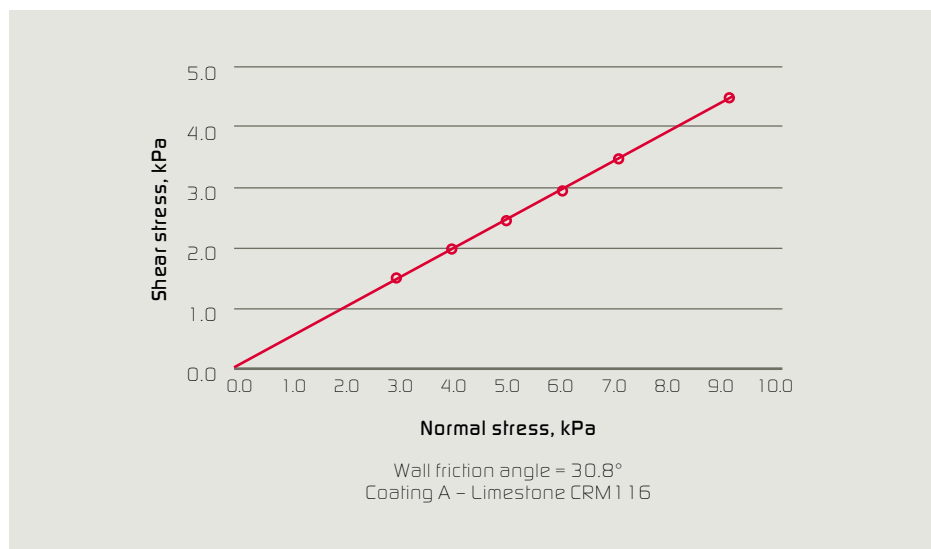


Figure 3: An “FT4” powder rheometer used to test wall friction between powders and surface coatings.



Figure 5: Variation in shear stress during pre-shearing, indicating the extent of slip-stick behaviour.

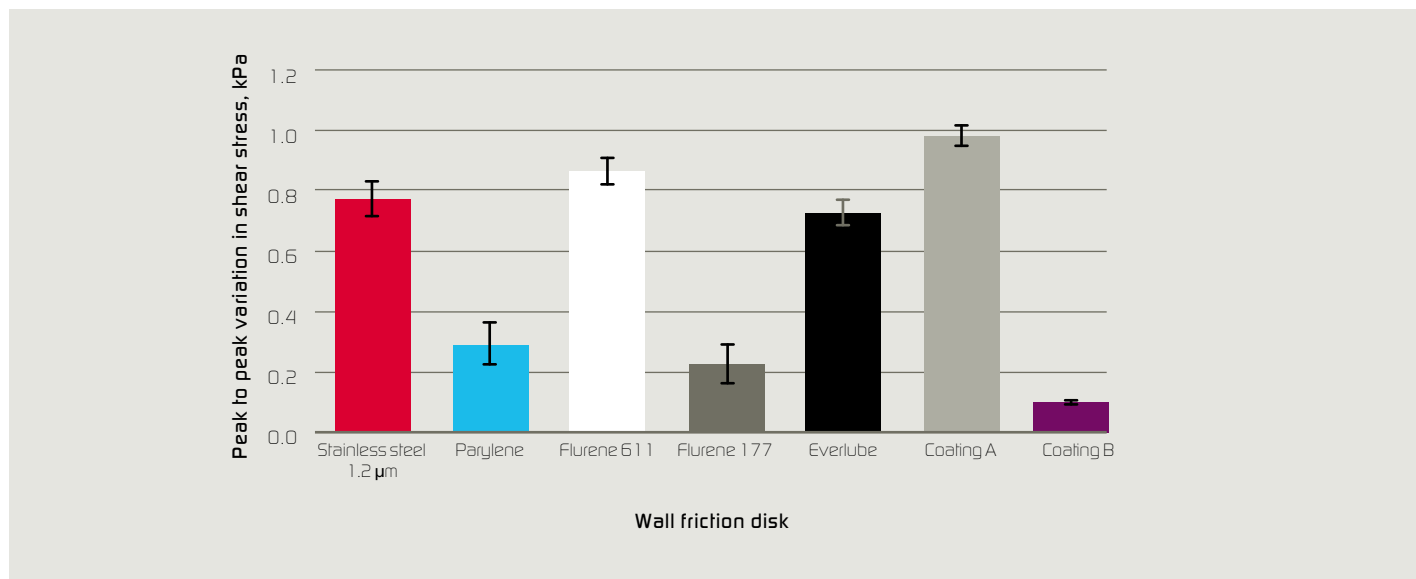


Figure 4: Analysis of wall friction data with SMP as test powder. Steel (red trace) and “Everlube” (grey trace), show slip-stick behaviour while “Fluren 177” (black) and Coating B (white) appear not to with this powder.

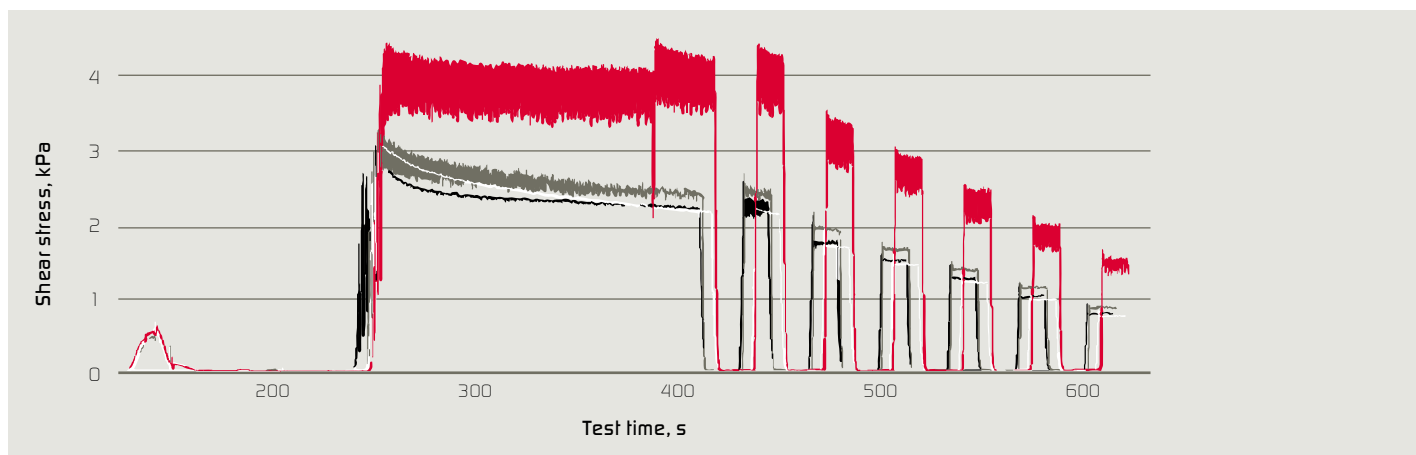


Table 1: Wall friction angles for six surface coatings measured using the “FT4” powder rheometer.

Disc	Respitose	Limestone	FlowLac	SMP	Cornflour
Stainless steel 1.2 $\mu\text{m Ra}$	31.4	34.7	18.8	23.3	28.5
Parylene	22.5	31.1	16.8	12.8	17.3
Flurene 611	23.7	32.7	16.7	12.4	26.3
Flurene 177	20.4	30.5	15.7	12.6	19.9
Everlube	27.2	32.2	16.6	13.7	24.7
Coating A	27.4	30.8	16.9	14.1	23.9
Coating B	30.1	27.5	18.1	14.0	23.2

The data also shows the limited variation exhibited by limestone when it is tested against the different coatings, although Coating B does generate a lower WFA and “Flurene 177” provides better performance than the other coatings from CWST.

SMP generates the lowest WFA values with all test coatings and for this powder, all coatings show significant improvement when compared to the uncoated stainless steel. The CWST coatings provide performance comparable to Coating A and Coating B and in certain cases, such as with “Respitose” and SMP, even outperform the competitor products.

ANALYSING THE PROBLEMS OF ‘SLIP-STICK’ BEHAVIOUR

Further analysis of the raw data from the experiments above reveals ‘slip-stick’ behaviour for certain materials. ‘Slip-stick’ occurs when a powder initially flows under applied stress but then stops due to reorientation and repositioning of the particles. This can result in unstable, pulsatile flow and contributes to erratic and undesirable process performance.

Figure 4 shows the shear data recorded during wall friction tests with SMP. Slip-stick behaviour is particularly evident when using steel (red trace) and to an extent with “Everlube” (grey trace), while the “Flurene 177” (black) and Coating B (white) trace suggest that these coatings do not exhibit this issue with SMP.

Cornflour is also known to exhibit slip-stick behaviour. Analysis of the data for all surface coatings with cornflour revealed that all but Coating B suffered from slip-stick, although the issue also was significantly reduced with the use of “Parylene” and “Flurene 177”.

For any given combination of powder and surface coating, the extent of slip-stick behaviour can be quantified by assessing the variability in shear stress measurements during the pre-shearing process (see Figure 5).

APPLYING COATING RANKINGS TO HOPPER DESIGN

In addition to the selection of wall material and surface coatings, hopper performance relies heavily on geometric design. Specifically, the gradient of the hopper outlet, relative to the vertical sides of the main vessel (the hopper half angle, α) and the size of the outlet opening (B), as detailed in Figure 6, have major effects on performance.

Systems designed to accommodate less free-flowing powder/coating combinations, i.e. those with high wall friction angles, typically require steeper hoppers ($< \alpha$) and optimised outlet sizes (B).

Figure 6: Hopper design: half angle α and hopper outlet size B .

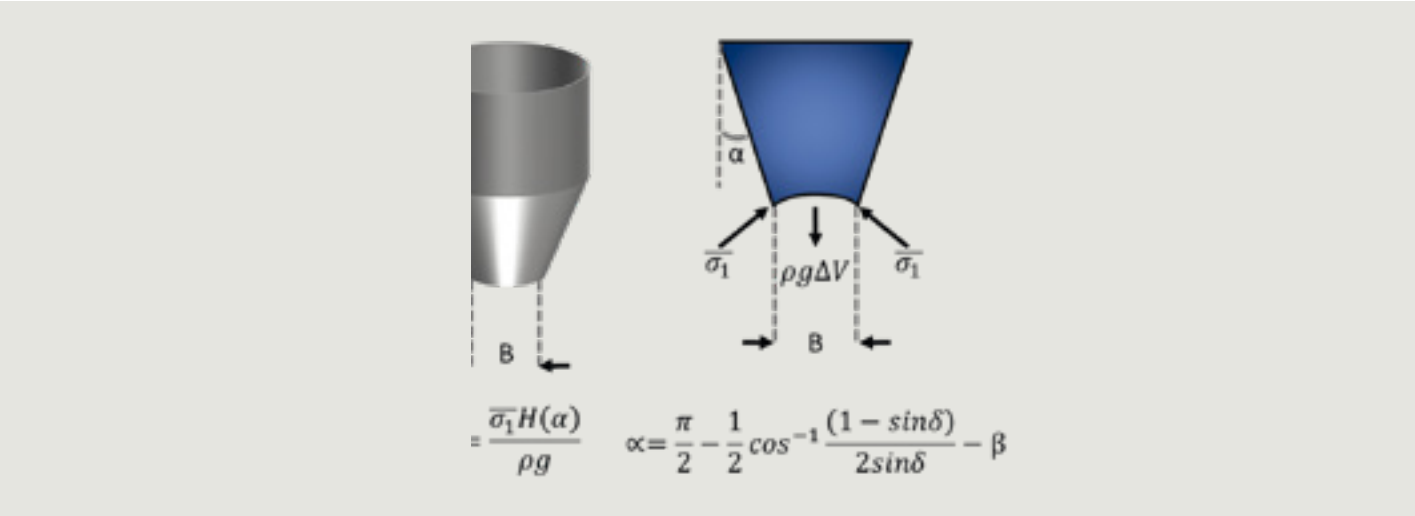


Figure 7: WFA, hopper half angle and outlet size indicate variations in performance for a range of coating/powder combinations.



“With the right coating, powders that exhibit ‘slip-stick’ properties flow smoothly.”

3 questions to James Cooke

How have the surface coatings been applied? All the coatings were applied by HVLP spray guns giving a dry film thickness of 8-15µm, with the exception of “Parylene”, which is applied by Physical Vapour Deposition (PVD) at the dry film thickness of 2-5µm.

Can you say something about the durability of the coatings? This is all dependent on the specific application, the environmental conditions and most importantly what material is wearing against it. The high molecular weight polymers will be most wear resistant and have the potential to last for years under low stress conditions. The coating with the lowest durability would be “Parylene”, as this has limited wear properties, as it is typically used for medical application, such as stents and guide wires.

What are the major challenges associated with the selection of a suitable coating in order to ensure optimum powder flow and achieve high levels of productivity? This is really a balance of frictional properties, wear resistance, cost, environmental conditions (temperatures, humidity, chemistry - either in the air or in direct contact) and the ‘slip stick’ performance. Unfortunately, no one coating stands out as offering the greatest properties in each field. This really highlights the importance of partnering the coating choice with accurate laboratory data using instrumentation like the “FT4”, as each combination of powder and coating will show different wall friction performance. One of the real highlights of this study is showing that with certain powders that exhibit ‘slip stick’ properties, if partnered with the right coating will actually flow in a smooth and more predictable manner.



James Cooke

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Using the data collected during this study, the effect of surface coating on hopper geometry can be assessed. The results are presented in Figure 6 and demonstrate how this information can be applied to identify the most appropriate combinations of surface coating and geometry when designing powder handling equipment.

For example, a plant handling SMP could specify an axially symmetric hopper with a half angle of around 30° and an outlet of approximately 0.6 m combined with any of the six coatings. In contrast, designing a hopper to handle cornflour would require a more detailed consideration of the coatings and

geometry. A half angle of around 25° and an outlet of some 0.75 m may be suitable if “Parylene” is used whereas Coating B is likely to cause blockages due to the lower half angle (steeper slope) required for this product.

USING RESULTS TO GENERATE COMMERCIAL ADVANTAGE

This study illustrates the importance of selecting suitable coatings in order to optimise process performance and demonstrates how the most appropriate coating will depend on the powders being handled. Design engineers should select coatings according

to the requirements of each individual unit's operations in order to ensure optimum powder flow and achieve the highest levels of efficiency and productivity. 

REFERENCES

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