Shining under the spotlight

How metallic effects can best be achieved in UV curing finishes

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The challenges of achieving a good metallic finish in UV-curable coatings are assessed. Aqueous systems provide the best compromise between visual and performance properties. To achieve effective cure despite the UV-reflection of the pigment, the pigmentation level must be optimised for the application and pigment grade.

The attainment of highly brilliant metallic effects in UV-curable coating systems is a task with many aspects. Current investigations reveal how formulations can be optimised for this purpose.

Solvent-free, conventional or aqueous: in what system can the advantages of UV technology be combined with attaining highly brilliant effects? As a rule, the following factors must be considered to attain metallic effects with ideal flop characteristics in coatings:

» Correct pigment selection and formulation;
» Coating production;
» Application as well as drying and curing.

Visual criteria as well as the particle size distribution or particle structure and the stability of the aluminium pigments are crucial for pigment selection. For UV coatings in particular, it must be noted that aluminium has a catalytic effect on the radical curing reaction. This catalysis leads to a gelling of the coating after only a short storage period [1].

In aqueous UV formulations, the pigment must also be protected against water. The use of encapsulated aluminium pigments is therefore recommended, as these provide maximum resistance to gassing and gelling in comparison to additive-stabilised types.

In addition to the dispersion, drying is especially important for the orientation of aluminium pigments. High film shrinkage and rapid physical drying favour parallel alignment of the pigments. This is not available in the case of high solids and 100 % solids systems, which thus leads to less effective flop characteristics.

In UV systems, the effect attainable therefore essentially depends on the type of formulation. Aqueous, conventional or solvent-free systems consequently pose differing requirements for aluminium pigments and their processing.

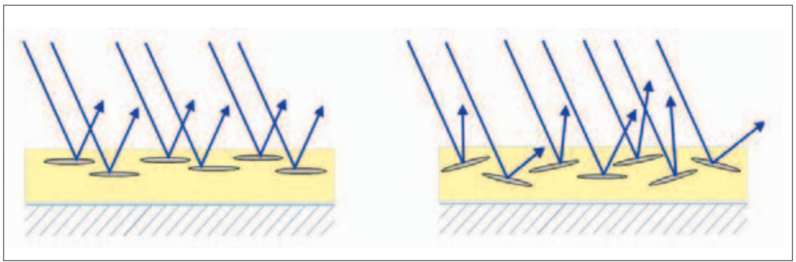

Figure 1: Schematic representation of the effects of metallic pigment orientation: optimal (left) and unfavourable (right)

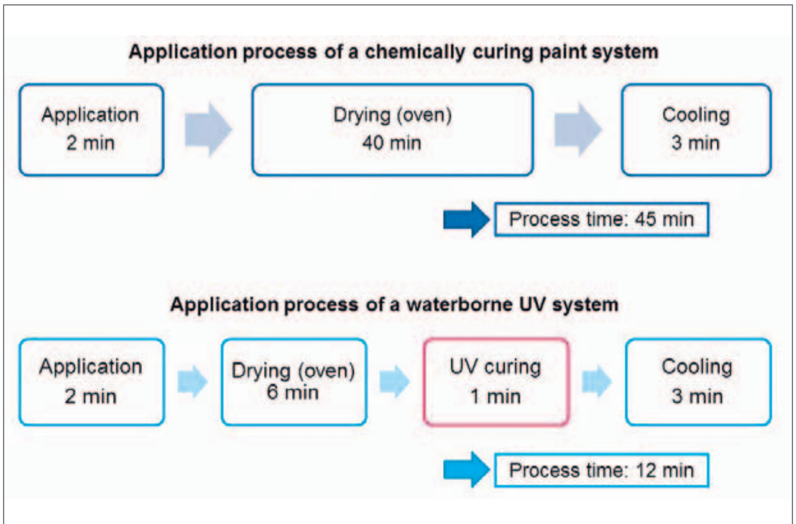

Figure 2: Comparison between application of an aqueous UV coating and a conventional chemically cured coating

Advantages and disadvantages of various approaches

What UV coating system represents the ideal solution for combining the desired brilliance with a high resistance? This question can only be answered definitively if the objective is clearly defined. The relevant requirements can range from purely visual applications through to functional purposes, including all conceivable combinations. The first step involves illustrating the fundamental advantages and disadvantages of the various approaches.

Solvent-free: moderate effects but best economics

Solvent-free systems represent the ideal case for the development of UV-curable metallic coatings. Only in the case of 100 % systems can the advantages of UV technology be utilised to the full. They allow curing immediately after application, leading to considerable savings – both in respect of space for paint spray lines as well as in respect of time and energy for drying and curing.

However, the coating formulation specialist soon encounters limits if brilliant metallic effects are required. 100 % UV systems dispense with the physical drying

stage mentioned above. Curing within seconds means that pigments are frozen into their position and do not have much scope to achieve an ideal alignment. This leads to reduced flop characteristics.
Coarser pigments usually have a more distinct bright-dark flop and therefore also still have a metallic effect, even with somewhat poorer alignment, while very fine pigments almost entirely lose their flop characteristics. *Figure 1* outlines the pigment orientation in diagrammatic form. In the optimum case of parallel alignment (left), the light reflection is directional – a highly metallic effect is attained. In the right-hand picture, on the other hand, the reflection is diffuse, which means that a metallic brilliance is not really obtainable.
In conventional and aqueous coating systems, the aluminium pigments are primarily oriented through the evaporation of the relevant solvents and the associated film shrinkage parallel to the substrate. This process is completely lost in a solvent-free system. The use of essential rheological additives means the viscosity increase resulting from the evaporation can be partially compensated for. The aim is as rapid a viscosity increase as possible after the application.
When selecting the pigments, the use of coated aluminium powder is recommended, so as not to introduce any solvents via a paste. The binding agents for these types of systems are distinguished by low viscosity. Nevertheless, reactive thinner contents of up to 50 % are sometimes necessary to allow processing [2].
The use of 100 % solids metallics is not recommended at present for applications in which the highest visual properties are required. These systems are an economical solution if moderate metallic effects are adequate, or specific mechanical and chemical resistance properties are paramount.

Conventional: VOC content determines brilliance

'Conventional' UV systems with solvents have the advantage that it is not the viscosity of the oligomers that plays a critical role in selection of the binding agent, but rather the property profile. The processing viscosity can be better controlled by using organic solvents. As the solvents are not incorporated in the film, they do not affect its properties, in contrast to reactive thinners.
Atomisation and final appearance improve, while solvent evaporation and film shrinkage favour parallel alignment of the pigments. During application and drying, this leads to an optimised viscosity profile, physical drying and ultimately more brilliant properties in the cured coating film.
The metallic brilliance is proportional to the amount of organic solvents used. From high solids via medium solids through to low solids, the VOC content increases in parallel to the improvement of the metallic effect.
In terms of coating technology, the 'solvent and UV' approach offers an interesting option for producing brilliant and resistant paints with high performance. However, the economic and ecological benefits of UV coating are mostly lost, as the solvent has to be removed by drying in the oven before curing and the resultant VOC emissions are very high in this respect. In Europe at least, conventional UV coatings are to be regarded as an interim solution and not as future-oriented alternatives, especially when it comes to new developments.

Aqueous: good results with an intermediate step

Aqueous UV technology represents a promising way to exploit the advantages of UV technology in the best possible manner while attaining brilliant effects at the same time. The only drawback is that a drying step has to be implemented upstream of the actual curing process.
It is necessary to remove water and cosolvents from the coating, which has a significant effect on the finished coating. A time saving nevertheless results as, in comparison to other chemically curing coatings, this prelimi-

Pigment	D10	D50	D90
Silver dollar 10 µm	5	10	10
Silver dollar 15 µm	7	15	26
Silver dollar 20 µm	10	20	32

Table 1: Pigments used, with average particle sizes in µm

Results at a glance

››› When comparing various approaches, aqueous UV metallic coatings provide the best compromise between visual and technical coatings properties.

››› The curing of aluminium-pigmented UV coatings is possible despite reflection. The coating formulation must be coordinated to the pigment used here.

››› The pigmentation level has a massive effect on the full hardening and the coating properties. Excess pigmentation is to be avoided.

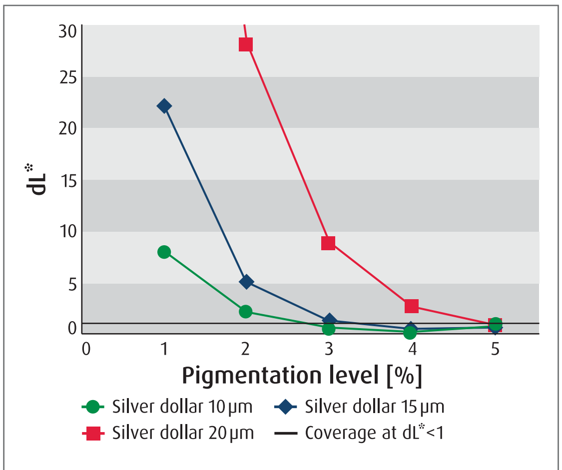

Figure 3: Development of covering power as pigmentation level increases, for three different sizes of aluminium pigment

nary drying only takes a fraction of the process time (see *Figure 2*).
Aqueous UV systems are free of monomers and can guarantee high resistance properties through the use of high molecular weight dispersions in combination with radical crosslinking [3]. The formulation is in principle similar to known aqueous metallic formulations.

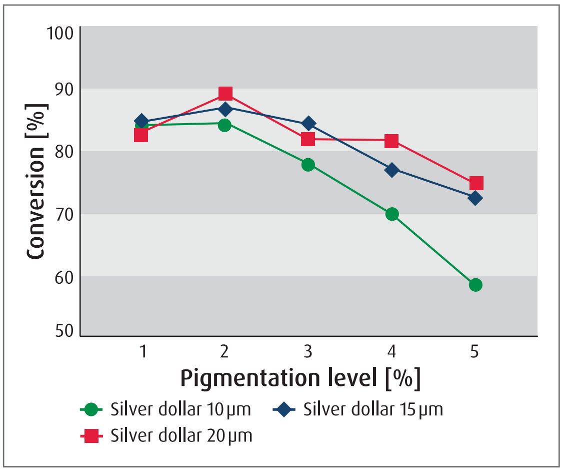

Figure 4: Double bond conversion at the underside of coatings, in per cent

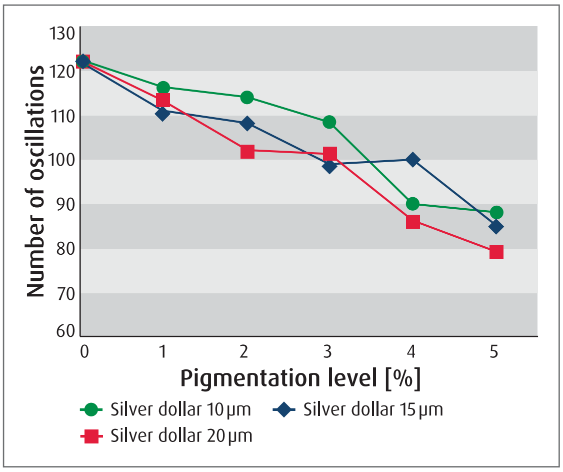

Figure 5: Results of the König pendulum hardness test

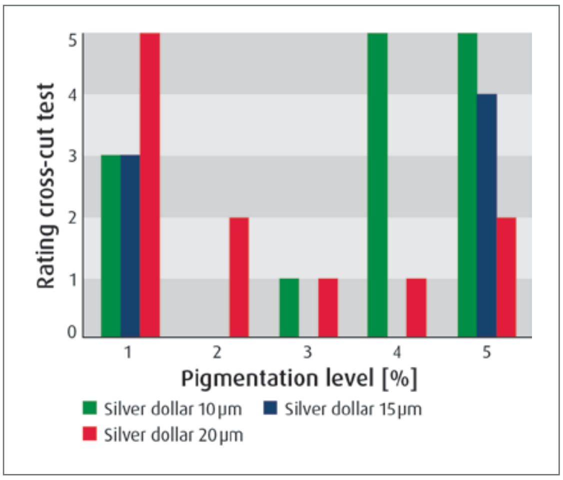

Figure 6: Results of the cross-cut tests

Essentially, the same adjustment techniques can be used to optimise the effect as for other aqueous metallic coatings, thus for example dispersing additives, thickeners or wax dispersions may be used. Owing to the high resistance properties that result from the crosslinking, an additional clear coating can even be omitted in some cases.

Water and UV curing: refining the best approach

This combination of waterborne systems and UV curing represents the best solution at present, in order to attain both metallic brilliance as well as high chemical resistance properties, especially in the area of single-layer coatings.
This insight led to extensive test series being conducted in an aqueous formulation based on a polyurethane dispersion suitable for UV cross-linking. These tests were to demonstrate what effect various types of effect pigments have on the properties of the coating.
Coated silver dollar pigments with an average particle diameter of 10, 15 and 20 µm were used for the tests (*Table 1*). The particle size distribution is approximately the same here. The pigmentation level was increased incrementally from one per cent (pigment solids) to five per cent.
Of all the finished coatings, the conversion of double bonds was determined using FTIR spectroscopy and the degree of coverage was measured. Further tests evaluated the hardness and adhesion.

Exploring the conflict between coverage and curing

The visual impression of a metallic coating results from light reflection and scattering by the aluminium pigments. The higher the component of reflected light, the more brilliant and appealing the coating appears.
In the case of a 'covering' coating, no light from the substrate reaches the viewer's eye, but instead it is reflected or scattered from the pigments beforehand. This can be measured by determining the colour values on a black and white substrate. If a colour difference of less than one unit occurs, this denotes a covering coating [4]. The finer the pigment, the lower the pigment level required to attain this value (see *Figure 3*).
For the production of UV metallic coatings, it is necessary for the highly energetic UV radiation to penetrate as deeply as possible into the coating layer so as to start the polymerisation reaction. This is in contrast to the desired light reflection of the pigments. In order to evaluate whether the complete conversion of the reactive double bonds is still ensured in the case of covering coating layers, their content was determined by FTIR spectroscopy.
The percentage conversion can be determined based on measurements on both the top and underside of the coating. No effect can be discerned at the coating surface –either in relation to the particle size or the pigmentation level. On the underside of the coating, however, it is clear that the conversion decreases as the pigmentation level increases (*Figure 4*). This is a logical consequence of the increasing reflection or scattering of the incident radiation.

This increasingly poor curing leads to a gradient in respect of cross-linking and hence also of hardness within the coating layer. This difference has an adverse effect on the properties of the coating. König pendulum hardness tests and cross-cut tests among others were carried out for the evaluation. These are standard tests for curing in the coatings industry.

Pendulum hardness test fails to correlate with curing

A decrease in hardness as the pigmentation increases can be observed in the pendulum hardness test. It is notable that the varying degrees of decrease in the cross-linking between the test series that can be seen in *Figure 5* cannot be found here. Rather, the aluminium pigments have a negative effect on the hardness of the coating film as the pigmentation level increases, irrespective of the particle size.
The pendulum hardness obviously depends more strongly on the aluminium content than on the degree of cross-linking and is therefore not a suitable test for evaluating the chemical cross-linking in this case.
The adhesion testing values reveal a similar picture. Here too, the compositions are significantly more complex and do not permit any clear conclusion in respect to the degree of curing determined by FTIR spectroscopy (see *Figure 6*). In the case of low pigmentation, the coating tends towards embrittlement and reduced adhesion, as a very close-meshed network can form.
The cross-linking density decreases as the pigment content increases. Nevertheless, this decrease cannot be observed in the conversion of the double bonds. At first, this leads to an improvement in the adhesion test (see *Figure 6*), but the values deteriorate further upon reaching the coverage limit. This return to a negative development can also be observed from the double bond density (*Figure 4*).

Formulation recommendations

The formulation must be precisely coordinated to the aluminium pigment for covering UV metallic coatings. Excess pigmentation results in less favourable coating properties. The ideal coating properties involve working precisely at the limit of coverage during the pigmentation. This limit should be determined via a test series for every type of coating or pigment.
These tests consider pigments with similar particle size distribution, which means the D50 value can be compared here. In general, the particle size distribution should be used for the evaluation of the pigment.
When selecting the binding agent, aqueous systems are recommended to satisfy high visual requirements. These can be formulated with relatively low solids, thereby ensuring a better orientation. Solvent-free UV metallic finishes are achievable, but contain a significant content of monomers in the case of spray application and only achieve moderate effects owing to the lack of film shrinkage.

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