Getting the best effect pigment orientation

The selection of a suitable rheology additive is a decisive factor in the optimization of effect pigment orientation in waterborne effect pigment base coats. The additive should produce pseudoplastic flow characteristics, the required minimum viscosity and a sufficiently high degree of elasticity. Oscillatory evaluation of the viscoelastic behaviour is an effective test method for effect pigment orientation assessment.

Influence of rheology in waterborne paint systems
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Rheology additives are indispensable for good effect pigment orientation in waterborne paint systems. They help to optimize the viscoelastic properties of the paint. Rheology-modifying wax additives give particularly good results.
In many sectors of the paint industry, there is a clear trend toward environmentally friendly, waterborne coatings, particularly for the automotive industry. Paint developers are faced with new challenges due to the different physical and application engineering properties of waterborne compared to solventborne formulations. Metallic effects are obtained by the use of special-effect pigments. An optimum appearance requires a uniform distribution of pigments within the coating, so that they deflocculate and orient themselves parallel to the substrate (Figure 1). The metallic effect is the variation of perceived colour due to the differing degree of light reflection at various viewing angles (flip-flop) (Figure 2) [1].

Additive selection crucial
Effect pigments can have good orientation in solvent-borne base coats even without special rheology additives. The film dries so rapidly that the effect pigments are quickly fixed in a horizontal orientation. Rheology additives are primarily used to improve the stability in circulation systems by preventing settling of the heavier effect pigments. In contrast, in waterborne base coats, rheology additives have a considerable impact on the appearance. Selecting the right additive can be a decisive factor to achieve optimum effect-pigment orientation. This is because water evaporates much more slowly than solvents, thus extending the drying time. The applied paint is significantly "wetter" when it arrives on the substrate; therefore the effect pigments remain mobile for longer and may lose their initial orientation.

It is crucial for the selection of suitable rheology additives to know which properties have a positive effect on the orientation. The rheological requirements include resistance to settling of the pigments during storage. Furthermore, an appropriate application viscosity and a rapid increase in the viscosity after application are needed to obtain a uniform spray pattern. A pseudoplastic (thixotropic) paint fulfills these requirements, because the material undergoes significant shear thinning during application and the viscosity quickly returns to the initial level after application. However, thixotropic rheology additives have limitations with respect to the effect pigment orientation, because the viscosity of the paint initially remains at the lower level after shearing, with the result that the pigments can easily lose their initial orientation. Increasing the concentration of the additive can speed up the rise in viscosity and thus compensate for this undesirable effect.
The viscosity of the formulation (minimum viscosity) must be tailored to the application properties in order to obtain a homogeneous spray pattern. If the viscosity is too low, sag resistance is limited and may lead to edge crawling and cloudiness.
In addition to these parameters, the viscoelastic properties are also important. The elastic components, in particular, are crucial for good effect-pigment orientation. They must be at a higher level than the viscous components after spray application. The pigment particles are then fixed in a weak gel structure and cannot change their orientation during drying.
In contrast, it is more difficult to achieve good orientation in products with predominantly viscous properties. Although a high application viscosity can be obtained by controlling the dosage, thus reducing the mobility of the pigments in the wet film, compensation of the missing elastic component is not possible and the result is a compromise between orientation, leveling properties and edge crawling (Figure 3).
Viscoelastic substances are characterized by a combination of elastic and viscous properties. However, the term itself does not indicate which of the two properties dominates. Elastic substances store deformation energy under a shear load and release it when unloaded (a spring is 100 % elastic), whereas viscous substances lose this energy as frictional heat during the flow process (water is 100 % viscous) [2].
The viscoelastic properties are determined by carrying out oscillatory measurements with a rheometer. The measured rheological parameters are G' (storage modulus = elastic components) and G'' (loss modulus = viscous components), from which clear conclusions can be drawn with respect to an optimum effect pigment orientation (Figure 4).

Pseudoplastic and elastic properties in one
Although additives such as clays and acrylate thickeners are generally suitable for adjusting the viscosity (minimum viscosity) and for increasing the required elasticity, they are not easy to handle. Clays are difficult to disperse and frequently cause seeding, even if incorporated as a semi-finished product. Acrylate thickeners often result in greying of the base coat even though they are already pre-diluted and pre-neutralized to facilitate handling. PUF thickeners are usually easy to handle; however they show no appreciable elastic properties. A further disadvantage is their variable efficiency due to their associative behaviour with the binder. The effect of aqueous
polyamides, which are not widely used, is also very system-dependent and they are as challenging to handle as the clays. An entirely new class of additives for waterborne systems is now available: rheology-modifying wax additives (RM wax additives). They have been used successfully for many years in solventborne systems and they have now been adapted for use in waterborne materials. An RM wax additive has pseudoplastic flow behaviour and significant elasticity. The product is easy to use and shows a good compatibility. In contrast, conventional wax additives exhibit only very limited rheological effects in waterborne systems and thus have to be used in combination with rheology additives (Table 1).

Comprehensive tests of various rheology additives in a metallic base coat formulation, with detailed studies of the viscoelasticity, have demonstrated the influence of rheology and, in particular, the elastic components, on the effect pigment orientation (Table 1).

A good illustration of this is a comparison of a basecoat containing the RM wax additive with one with a PUR thickener, because these two types of additive differ the most with respect to viscoelastic behaviour. The viscoelasticity of the two differing base coats and a ‘blank’ sample without additive was evaluated using oscillation tests. The samples were subjected to a given frequency (1 Hz) at continuously increasing amplitude (deformation 0.1-100 %) (Figure 5).

Irrespective of the degree of deformation, viscous behaviour dominated in the blank sample (G'' && G'). The elastic components are negligible and are thus not included in the diagram. The base coat containing PUR thickener showed very similar behaviour, however, the viscous components were significantly higher. The elastic components were also well below those of the viscous components.

In contrast, the base coat with the RM wax additive behaved completely differently. The elastic components clearly dominated. This behaviour persisted over a wide range, even as the level of deformation increased. Structural degradation with a transition to more viscous behaviour only occurred at high levels of deformation (intersection of G' and G"). This essential difference in the measured results is reflected in the application performance; the aluminium flake orientation, homogeneity and edge crawling of the paint film were all significantly improved.

Influence of elasticity
The influence of elasticity on the effect-pigment orientation was studied with samples containing differing amounts of RM wax additive. The solids proportion (SP) of the samples was kept constant to avoid a further variable.

In practice, the base coat undergoes strong shearing during application. The elastic components then recover at differing speeds, depending on the amount of additive. This was simulated by using a step function with three intervals giving oscillation-rotation-oscillation (ORO). In the first interval, the unsheared sample was measured under oscillation to determine the initial level of viscoelasticity (G' and G")

In the second interval, the sample was subjected to brief but strong shearing to destroy the existing structures. In the third interval, another oscillatory measurement was carried out to evaluate the level of elasticity and the speed of structural recovery (Figure 6).

As expected, the elastic as well as the viscous components increased with the level of RM wax additive. The elastic components in this formulation dominated over the viscous components above a concentration of 5 %. Measurements in the third interval showed that the speed of structural recovery increased with the amount of additive.

For an application performance evaluation, the base coats were applied with an automatic sprayer under identical conditions and then finished with a clear coat. (The sample with 4 % RM wax additive was not included in the application performance tests, because its elasticity and viscosity were too low.) The application result was then measured optically using a Byk-mac, an instrument that measures the total colour impression of effect paints, changes of colour and the sparkle effect. Flip flop, homogeneity and intensity of the metallic effect were also evaluated. In addition, edge crawling along with the overall homogeneity of the paint film was assessed visually.

The rheological results correlated well with the application results. The orientation improved as the elasticity increased. The sample with 7 % RM wax additive gave the best result. Even higher amounts of additive increased the elasticity, however, they also increased the viscosity so that spray application was no longer practicable.

The results depended on the solids content of the formulation and on the type of binder. Thus, the optimum amount of additive is always system-dependent (Table 2).

Optimization by combining additives
The results clearly demonstrate that, based purely on flip-flop values, the largest light / dark difference occurs in a sample containing 5 % RM wax additive; however, the distribution of effect pigments and the coating film thickness are homogeneous for the sample containing 7 % of the additive.

Therefore, the next step was to check whether the use of a suitable combination of RM wax additive and a predominantly viscous additive (PUR thickener) can optimize the effect pigment orientation compared to a sample containing 7 % RM wax additive only. The combination tested was 5 % RM wax and 0.2 % PUR thickener. The amount of PUR thickener was selected so that both base coats had the same Brookfield viscosity (DVI, spindle 4, 50 rpm, 550 mPas).

The evaluation was carried out with the three-interval measurement (ORO) (Figure 7). In the first interval, the combination with the PUR thickener increased the viscosity and thereby the values of G' and G": the elastic components (G') dominated. In the third interval, directly after shearing, the viscous components initially dominated (G" && G'). Subsequently, the two curves intersected as the structure recovered and the elastic components quickly became most important (G" && G'). It is worth noting that the PUR thickener did not affect the speed of structural recovery.

Although the elastic components predominated immediately after shearing in the formulation with 7 % RM wax additive, at 5 % RM wax additive, the viscous components dominated for a short time. This also favoured an ideal effect-pigment orientation: the effect pigments can orientate even better directly after application if they are not immediately fixed in the elastic gel structure of the base coat. The decisive factor is that this structural recovery with a changeover to predominantly elastic components does
not last too long; otherwise the effect pigments can lose their initial orientation. The additive combination gave the best overall application result. The flip-flop effect is significantly better than the formulation with 7 % RM wax additive and there is no reduction in the homogeneity and intensity of the metallic effect (Table 3).

References:

Results at a glance
Suitable rheology additives are necessary for a good effect pigment orientation in waterborne base coats. Decisive factors for a good result are pseudoplastic flow behaviour, a suitable level of viscosity (minimum viscosity) and predominantly elastic components after spray application. A new class of waterborne rheology-modifying wax additives provides a very good effect pigment orientation. Combinations of additives can be optimized even further to achieve an ideal ratio between the elastic and viscous components.
Figure 1: Good (left) and poor (right) orientation of aluminum flakes in metal-effect paints (optical microscopy)
Figure 2: Ideal flip-flop and high brilliance are obtained when the flakes are oriented parallel to the surface in a uniform distribution and without agglomeration.
Figure 3: Viscosity and viscoelasticity of the paint formulation have a significant impact on the finished appearance.
Figure 4: Liquids with differing viscoelastic behaviour
Figure 5: Oscillatory measurements provide information on the viscous (G'') and elastic components (G') of the paint formulations containing an RM wax or a PUR thickener as the additive.
Figure 6: Effect of the RM wax additive concentration on the viscoelastic behaviour
Figure 7: Viscoelastic behaviour: base coats containing 5% and 7% RM wax additive compared to a formulation containing a combination of RM wax additive and PUR thickener.