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Matting Agent Concentration and its Effect on the Colour and the Rheology of Matted Coatings

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Abstract: Matting of polymeric pigmented coatings not only decreases the gloss of surfaces but also affects their colour and rheological properties. For this reason, it is important to study the changes in colour and rheology of coatings caused by adding a matting agent. Blue, green and white alkyd lacquers and pure silica as matting have been investigated regarding this purpose. The obtained results showed that after a saturation point, the alterations in colour and rheology change their direction. The optical processes effecting these alterations are discussed.

Key words: Coating, gloss, matting, silica, colour, rheology

INTRODUCTION

In the modern technology, the matting of pigmented coatings is largely used in order to decrease the gloss. The low-gloss coatings are popular when used for aesthetic and functional purposes. A surface with lower gloss hides surface imperfections in a way that is superior to the hiding provided by a higher gloss one. The application of a low-gloss coating might, therefore, be easier to achieve than that of a glossy one and be more cost effective. This is one of the reasons why matt finishes are produced.

The phenomenon of matting is commonly regarded as being due to a reduction in the amount of specular reflected light as a result of the surface roughness (Hunter and Harold, 1987). Indeed, the process of matting is linked to the optic phenomena that occur and notably the superficial scattering. When a coating film is opaque, the fraction of light that penetrates there is not transmitted but reflected out toward the outside as a scattering form. The phenomenon can be decomposed in several stages:

- Some amount of the incident light is reflected by the surface in a mirror type (specular reflection), i.e., the angle of incidence is equal to the angle of reflection. The more the light is reflected in this way, the greater is the impression of gloss (Simpson, 1987). Smooth and polished surfaces reflect a major part of the light in this way. This specular reflection doesn't give any information on the colour of the paint film (Dalal and Natale-Hoffman, 1999).
- The non reflected fraction penetrates more deeply in the coloured film, according to the opacity of this last. The microscopic inhomogeneity in the structure of the film provokes a scattering of the light to several directions. When the diffusion is perfect, the luminance is constant whatever the direction of observation is, the distributor is then said Lambertien. The majority of surfaces are not of Lambertien type and the scattering occurs preferentially in the neighbouring directions of the one of specular reflection.
- During its optic path in the coloured film, the light is absorbed in a selective way. The spectral composition of the radiance scattered by the film is then different of the one of the incident radiance. The scattering light carry then the message of the colour of the applied film.

Thus, the total reflectance index measured by spectrophotometer can be expressed as (Zvonkina and Indeiken, 2001):

$$R_{total} = R_{front\ surface} + R_{scattered} - I_{pigmented\ coating}$$

where, R_{total} is the total reflectance measured by the spectrophotometer, $R_{front\ surface}$ is the specular component of

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the front surface reflectance, $R_{scattered}$ is concerned the light flux scattered by the pigmented surface of the coating and $I_{pigmented\ coating}$ is the relative amount of the light penetrated into the pigmented coating.

Several techniques are known to produce liquid-based coatings with lower gloss finishes. One of the most convenient ways is to add an additive of non-soluble particles to their composition. This agent is spilled in the film while provoking a micro heterogeneity in the surface after loss of solvents and condensation products. Thus, a diffusely reflecting micro-textured surface is formed (Braun, 1991; Braun and Fields, 1994) that leads to an increase of $R_{scattered}$ relatively to $R_{front\ surface}$ Different inorganic compounds such as the precipitate silica, the kaolin, the bentonite or others are used as matting agents.

Another method to receive matt coating consists in adding some incompatible substances to the polymeric composition (Shitova *et al*., 1982). These additives float to the upper part of the coating. The matting is in this case dictated by the difference in the refractive index of the upper and lower parts of the coating and by some non-uniformity at the coating surface that affects a growth in the light scattering in the film.

Finally, the matt aspect of paint also depends on its formulation and more precisely of its Pigment Volume Concentration (PVC). More the PVC is raised, more gloss is decreased.

Silica gel matting agents are widely used within the coatings industry for matting purposes and are regarded as highly efficient in producing the type of surface roughness that is responsible for the appearance of mattness (Schneider, 1994; David, 2003). They are available in a range of particle sizes, pore volumes and surface treatments to suit specific application needs, they have a refractive index that is close to that of many binders, allowing clear matt coatings to be developed. The decrease in coating gloss is usually accompanied with changes in colorimetric properties (Zvonkina and Indeiken, 2001). Also, rheological problems may occasionally occur if matting is attempted by the use of high addition levels. This influence of matting process on the colorimetric and rheological properties has not been considered a lot in the literature. Thus, it is of interest to investigate it in order to be able to predict and control these properties of the matt coatings.

MATERIALS AND METHODS

In all research, blue, green and white mono pigmented alkyd lacquers with xylene as solvent were used. The pigment contents were fixed arbitrarily in taking into consideration their chemical nature and the difference in their specific areas and oil absorption (Table 1). Thus, 7% by weight was used for the blue and green organic pigments and 28% for the titanium dioxide. The matting agent used was pure silica supplied by Degussa. Its particle size varies between 20 and 50 nm.

Table 1: Properties of pigments used

Pigment	Colour	Specific area ($m^2\ g^{-1}$)	Oil absorption g $(100\ g)^{-1}$
Titanium dioxide	White	15	9
Copper phtalocyanine	Blue	36	35
Copper chlorophtalocyanine	Green	61	30

Varying addition levels of silica matting agent were dispersed for 20 min into the above lacquers by means of Grenier Charvet type disperser. Addition levels ranged from 0 to 6% by weight based on the wet paint.

Viscosity measurements on the wet paints were realized at 20°C with a Brookfield RVT type viscometer. A spindle n° 4 (diameter = 27.30 mm, thickness = 1.65 mm) was used for all measurements.

Coatings were applied to plates of glass by means of a 100 μm bar applicator so as to give dry film thickness ranging from 15 to 40 μm. The coatings were allowed to dry at room temperature for 1 day. The colorimetric parameters of the resulting paint films were measured with a Spectraflash 300 spectrocolorimeter supplied by Datacolor. The viewing conditions were 10° standard observer and D65 standard illuminating. The colour differences ΔE was measured relatively to non matted samples.

RESULTS AND DISCUSSION

Colour measurements: Initially, the changes in the optical properties of coatings with respect of matting agent concentration were studied through the reflectance curves. The spectra of the reflectivity for different concentrations of the matting agent were compared with that of the gloss sample for green, blue and white coatings.

For the green coatings, the curves (Fig. 1a) plotted for different concentrations going to 6% (weight to weight) of additive showed an increase of the reflectance compared to the non matted sample, which indicates an increase of the green colour intensity by matting. The maximum of intensity was, however, obtained at 4% concentration. Thus, we can expect this latter ratio of matting agent to be a turning ratio in the changes of the optical properties with matting. Similarly, the reflectance of the blue coating was observed to increase with respect of the matting agent ratio (Fig. 1b).

The white coatings are usually matted with matting additives in order to maintain their level whiteness very high. Otherwise, the paint film matted by increasing its PVC with fillers loose rapidly its whiteness and then, a

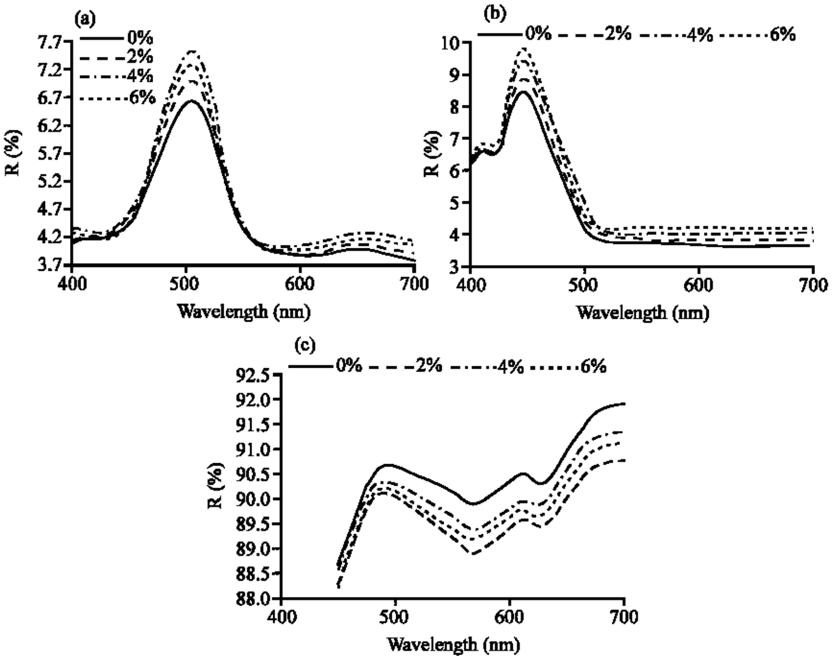

Fig. 1: The reflection spectrum of the gloss (a) green, (b) blue and (c) white coating compared to matted samples for various additive concentrations. The corresponded concentration (wt%) is pointed at the plot

yellowing of the film is usually observed in a few days after application. Contrarily of the green and blue paints, a reflectance decrease was observed for the white paint studied here after incorporating the additive matting (Fig. 1c). The decrease effect was found to be higher for 2% of the matting agent compared to the changes as the concentration of the additive grows. This change in the reflectance variation at 2% reflected a change in the surface state of the applied film and it may be connected with the effect of the light scattering, which starts working, after the heterogeneity appeared inside the polymeric coating.

The results obtained with the green, blue and white coatings highlights a wavelength-dependent character of the light scattering that leads to the changes in spectrum of the total light leaving the surface. This result is in good agreement with the Mie theory stating that if the particle size is smaller than the wavelength, the light scattering is inversely proportional to the value of the wavelength in some degree. Indeed, the particle size of the additive used in our study was relative but smaller than the wavelengths of the visible spectrum.

Another interesting result is that the influence of the light scattering on the optical properties is proposed to be reversed when the concentration of the additive achieve some point, so called saturation point. Indeed, as the lacquer composition gets saturated, the distances between the additive's particles become smaller and some growth of the amount of agglomerated particles can take place. An increase in the size of the particles is supposed to affect the reflection ability of the matting agent as well (Zvonkina and Indeiken, 2001).

By the data of the reflectance, the values of the colour characteristics were calculated in the so-called L*a*b* system recommended by the International Commission of Illumination (CIE) as universal standard. The letters L*, a* and b* refer to the three axes of the system, a lightness axis (L*) and two axes representing both hue and chroma, namely a red-green axis (a*) and a blue-yellow axis (b*). The angle h is a measure of the hue, e.g., h = 0° corresponds to a pure red, h = 90° to a pure yellow, h = 270° to a pure blue. The distance of a colour from the L* axis represents chroma which is, for a given lightness, a parameter describing the brilliance or purity of a colour.

The values of the chroma C*, the hue angle h° and the total colour difference ΔE in the CIE L*a*b* colour space were computed according to the known expressions (Judd and Wyszecki, 1975).

In present study, it was established that the changes in the optical properties of the white coating take place when adding the first portion of the additive; whereas for the blue and green coatings the most important changes in the properties occur only by reaching an additive concentration so-called saturation. We suggest this tendency to be connected with the effect of the light

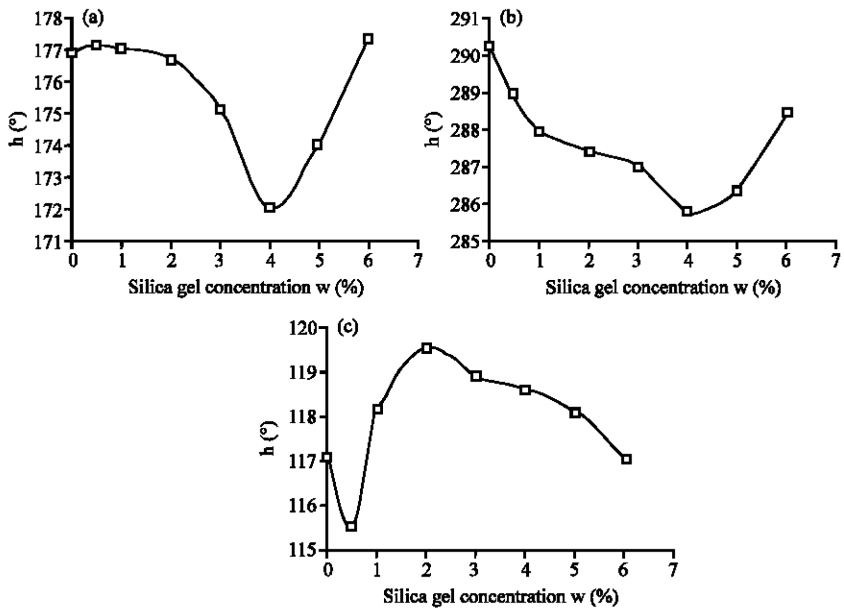

Fig. 2: The effect of the concentration (wt%) of the matting agent on the hue angle (h/°) for (a) green, (b) blue and (c) white coatings

scattering, which starts working, after the heterogeneity appeared inside the polymeric coating. When exceeding the saturation concentration, the alterations change the direction. Thus, the chroma and the hue angle start growing after decreasing.

In terms of the CIE L*a*b* colour space, the decrease of the hue angle till saturation (Fig. 2a, b) means that a colour vector connecting the origin with the point (a*, b*, L*) turns in the direction to the red region as the coating is saturated with the additive. The most changes in the hue are observed for blue coating compared with that for green one, which agrees with the influence of the wavelength-dependent character of the scattering. After exceeding the saturation point the vector turns in an opposite direction. At this stage, the hue is supposed to be affected more likely by the reflectivity of the filler and pigment particles rather than by the scattering in the film.

Two turning points were observed for the dependence of the hue angle of the white coating on the concentration of the additive (Fig. 2c). The first point is referred to the first portion of the matting agent added (0.5 wt%); the second one is the point of the saturation where the hue angle is maximum. This shift to higher angles at the saturation means a decrease of the yellowness index and then an increase of the whiteness of the coating.

An opposite character of the chroma C* was observed for the blue and green coatings. Its values make a slight growth as the first portion of the agent added, with further increasing with a growth of the concentration till the saturation point. Afterwards the chroma increase more rapidly for blue coating and decrease for green one (Fig. 3a, b).

In the case of the white coating as well (Fig. 3c), the chroma varies differently from the dependence of the hue angle on the concentration of the matting additive. In particular, after reaching the saturation point where it is minimum, the chroma slightly increase indicating the extinguishing of the effect of the light scattering by the growing influence of the additive's reflectance when exceeding the saturation.

The total colour difference ΔE^* was observed to grow as the concentration of the matting agent increases till the same value as in the previous tests for green and white patterns relatively and it slightly decreases afterwards, whereas it increases more rapidly after the saturation for the blue coating (Fig. 4a-c). In particular, the values of ΔE^* obtained for the white paint were all inferior to the unity, indicating a limited effect of the matting on the whiteness.

Rheological measurements: Rheological measurements on the wet paints were made for various concentrations of the matting additive. The obtained results show that the studied coatings have a pseudo plastic behaviour till some critical concentration of the additive. As an example, the Fig. 5 shows the green coating behaviour till 4% of

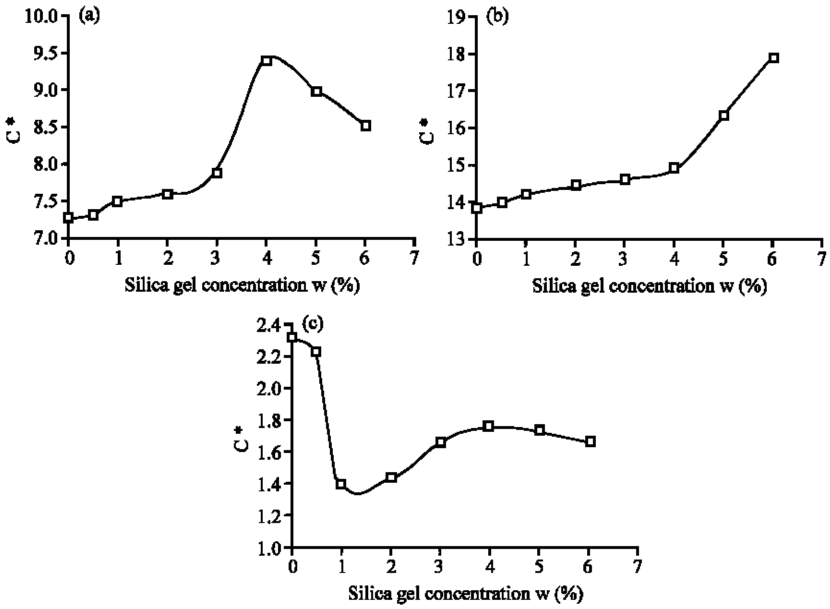

Fig. 3: The effect of the concentration (wt%) of the matting agent on the chroma (C*) for (a) green, (b) blue and (c) white coatings

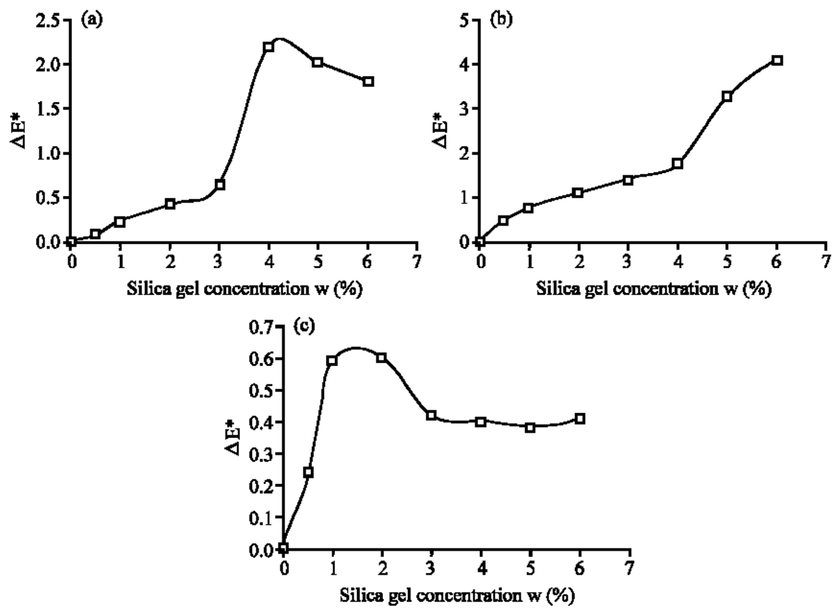

Fig. 4: The effect of the concentration (wt%) of the matting agent on the total colour difference referred to gloss sample (ΔE^*) for (a) green, (b) blue and (c) white coatings

the additive. As soon as the concentration of the matting additive reaches 5%, a viscosity increase and a change to a thixotropic behaviour were observed for the green coating (Fig. 6a). The thixotropy was deduced from the decrease of the viscosity with respect of time, which was verified for two spindle rates (10 and 50 tr. min^{-1}). A similar change was observed for the blue coating at 4% of the matting agent (Fig. 6b).

Interestingly, it was found that these changes in rheological behaviour were occurred almost at the same concentrations of the additive corresponding to the changes in the optical properties. Thus, the increase in the viscosities observed as the concentration of the matting agent exceeds the saturation is due to some growth of the amount of agglomerated particles. If this agglomeration is governed by weak forces, then a

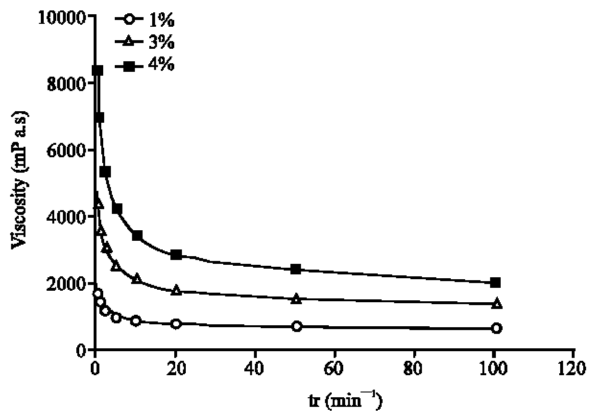

Fig. 5: Pseudo plastic behaviour of the green coatings before saturation. The corresponded concentration (wt%) is pointed at the plot

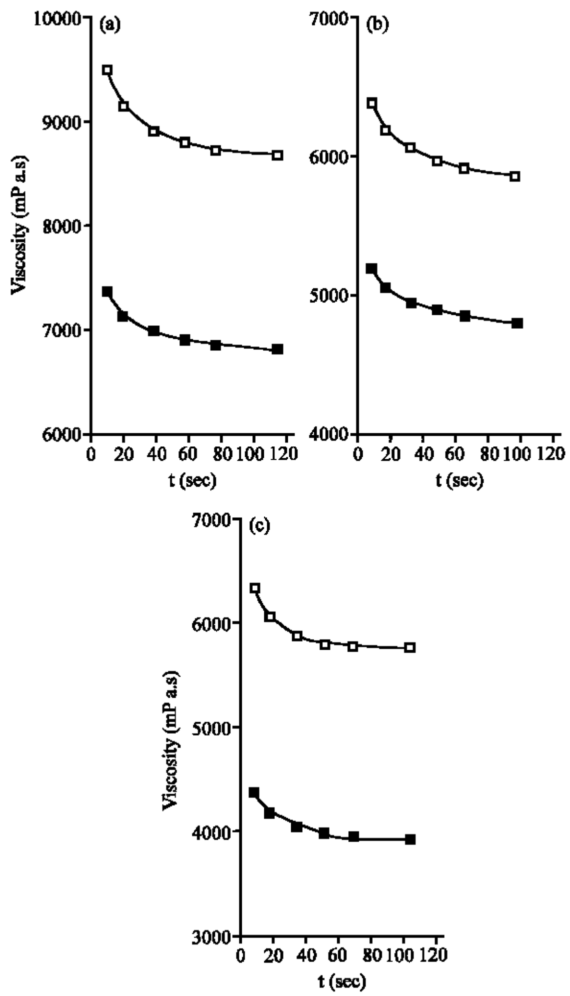

Fig. 6: Thixotropic behaviour of the coatings at the saturation: (a) green at 5 wt%, (b) blue at 4 wt% and (c) white at 5 wt%. (□) 10 t. min^{-1}, (■) 50 t. min^{-1}

controlled flocculation (Orr, 1996) of the paint dispersion is resulted which may lead to a weak thixotropy.

In the case of the white coating, the change to the thixotropic behaviour was found to occur at additive concentration higher than the saturation found in colour properties. This may be explained by the intrinsic rheological properties of the titanium dioxide of high dispersability that keep a pseudo plastic behaviour even at 4% of the matting additive (Fig. 6c).

The dependence of the coating rheology on the concentration of the matting agent has been theoretically studied by Fletcher (2002). The modelled equations stated the existence of a critical concentration at which the viscosity highly increases and goes to infinity. In present study, we confirmed experimentally this increase and we found that leads to a change in the behaviour and a tendency to a thixotropy.

CONCLUSION

The influence of the concentration of the matting agent added to the composition of gloss lacquers shows that the changes in the colour would be influenced by the light scattering inside the coating as the last one is getting filled till some saturation point. When the additive concentration exceeds the saturation point, an opposite direction of the changes in the properties was found to result because of the increased effect of the reflectivity of the additive. This tendency was found for the reflectance, chroma, hue angle and the total colour difference. The values of hue angle decrease at the first portions till the saturation point and grow after reaching the last mentioned value. The chroma and the total colour difference increase till the same point with further decrease when exceeding it; in the exception of blue coating where further increase of chroma and colour difference were observed. The most important changes in colour properties were observed for blue lacquers compared to green and white ones.

Besides the colour changes, an increase of viscosity was observed when adding a matting additive to the lacquer composition. Indeed, after saturation point the rheology of coatings became thixotropic. This saturation point coincides with that found in colour tests excepting in white coating where the thixotropy is delayed to higher concentration of the matting agent.

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