The Influence of Pigments on Rheological Properties and Spectral Selectivity of Solar Paints

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ABSTRACT

The effect of different ratio between large Al flakes and small inorganic oxide pigments in Thickness Insensitive Spectrally Selective (TISS) paints was studied regarding rheological properties and spectral selectivity. In order to prepare coloured TISS coatings blue, green and black pigments were incorporated into polyurethane resin binder. Rheological properties of liquid paints were examined under destructive and non-destructive shear conditions, while spectral selective properties of dry coatings were determined from spectroscopic measurements. In order to determine colour strengths, metric chroma values *C** and lightness *L** were calculated from the reflectance data in visible spectral region.

INTRODUCTION

Thickness Insensitive Spectrally Selective (TISS) paints consist of absorbing pigments (mixed inorganic oxides), providing high solar absorbance, and metallic flakes which act as reflectors of the infrared radiation and are therefore responsible for low emittance. High solar absorptivity ($a_s > 0.90$) and low thermal emissivity ($e_T < 0.25$) characterize high spectral selectivity, which is in the observed material a result of different processes, such as intrinsic absorption, interference in double layer (reflecting–absorbing tandem), interference effects of alternating dielectrics and metals, geometrical trapping by surface roughness, and the size of metal particles in an insulating matrix.[1] Metal flakes are added in TISS paints in order to change the optical properties throughout the solar and thermal region and therefore influence spectral selectivity, i.e. solar absorbance and thermal emittance of dry coating. Due to incorporated metal flakes, the benefit of TISS coatings is that they could be applied on substrates other than metal and they still provide high spectral selectivity. However, the large difference between the metallic and inorganic oxide pigment particles poses a problem for paint application in a well reproducible manner, necessary for attaining high difference between solar absorptance and thermal emittance values (i.e. spectral selectivity) of the applied coatings. The effect of spectral selectivity therefore strongly depends on the microstructure of all pigments in the dry coating, especially on the position and orientation of metal flakes.[2,3]

The highest solar absorptivity is achieved with black pigments, but the production of non-black selective surfaces is more and more desirable because of their decorative property. Good examples of their use are façade solar absorbers, passive cooling systems or military applications. Coloured spectrally selective TISS paints, prepared by adding low-emitting metal flakes to ordinary paints, has been extensively tested in our laboratory over the past years.[4,5] When aluminium flakes are added into the paint, the initial colour of the pigmented paints lightens, the a_s values decrease, while the values of e_T increase. A certain improvement of colour and lightness can be achieved by adding black pigment to coloured paints, which increased both a_s and e_T values. Nevertheless, colours other than black are highly desired, even if a lower efficiency would have to be accepted.

In the present work a complex multi-phase structure of black TISS coatings consisted of large Al flakes (> 50 μm) and small black and coloured inorganic oxide pigments (< 500 nm), embedded into the polyurethane resin. The influence of pigment size on rheological properties and spectral selectivity was studied with black TISS paints, prepared by various concentrations of large Al flakes and small black inorganic pigment. The influence of pigment colour was studied with blue and green TISS paints, for which the colour strength was expressed by chroma values *C** and lightness *L**, determined from the reflectance data in visible spectral region.

EXPERIMENTAL

Rheological measurements

Rheological characterization was performed with controlled rate rheometer Physica MCR 301 (Anton Par) equipped with a cone and plate sensor system (CP 50/2°). Standard rotational flow tests were performed with a triangular method by changing the shear rate from 0 to 500 s^{-1}. Oscillatory stress sweep tests at constant frequency of oscillation (1 Hz) were used in order to determine the linear viscoelastic range (LVR). Frequency tests were performed at constant small deformation in LVR by decreasing the frequency from 20 to 0.01 Hz. In addition to standard rotational and oscillatory tests, time tests were performed in order to simulate the 3 steps to which the paint is subjected: storage in the container, deposition on the substrate and the formation of dry film. In the 1st and the 3rd step the paint is subjected to the conditions with no shear at constant small deformation in LVR, while in the 2nd step – during the application, when the paint is subjected to high shear - a high shear rate (100 s^{-1}) was applied. All rheological tests were performed at constant temperature T = 23°C, which was also the temperature at which the paints were sprayed on the substrate.

Spectral selective properties

The spectral selective properties of the paint coatings were determined from the infrared (IR) reflectance spectra. Reflectance in the visible (VIS) and near infrared (NIR) range were measured on a Perkin Elmer Lambda 950 UV/VIS/NIR spectrometer with an integrating sphere (module 150 mm), while the reflectivity spectra in the middle IR spectral range were obtained on a Bruker IFS66/S spectrometer equipped with an integrating sphere (OPTOSOL), using a gold plate as a standard for diffuse reflectance. Solar absorptance (a_s) and thermal emittance (e_T) values were determined from the reflectance spectra using a standard procedure[6].

The colorimetric parameters were calculated from the reflectance data in visible spectral region using CIELAB color space, under D65 illumination and 10° standard observer. Lightness *L** represents the difference between light (*L** = 100) and dark (*L** = 0). Color differences were calculated using the color difference formulas[7]. Chroma values *C** were calculated from Eq. 1.

$$C^*_{ab} = \sqrt{(a^*)^2 + (b^*)^2}\,, \qquad (1)$$

The preparation of TISS paint coatings

The paints were prepared using a standard procedure with large Al flakes (> 50 μm), serving as reflectors and enabling low emittance, and much smaller (< 500 nm) black, blue and green pigment, respectively, providing high solar absorbance. Pigment dispersions were prepared by mixing the pigments with the polyurethane resin binder in specific proportions and grinding in a ball mill.

Table 1. The amounts of pigments in the prepared Blue/Green TISS paints.

	Blue /Green	Black	Al flakes
17:0	17	0	10.6
14:3	14	3	10.6
12:5	12	5	10.6
10:7	10	7	10.6
7:10	7	10	10.6
5:12	5	12	10.6
0:17	0	17	10.6

Table 2. The amounts of black pigment and Al flakes in the prepared black TISS paints.

	Al flakes	Black
17:0	17	0
14:3	14	3
12:5	12	5
10:7	10	7
7:10	7	10
5:12	5	12
0:17	0	17

In order to determine the influence of different pigments on rheological and solar properties the paints were prepared with different ratio of the pigments and Al flakes, respectively (Table 1, 2). Two sets of paints were prepared: (i) coloured blue and green with variation of black and blue/green pigment with the same concentration of Al flakes; (ii) black paints with variation of the ratio between black pigment and Al flakes.
The paints were deposited on aluminium substrates by a Sata jet 1000 B RP spray gun with an operating pressure of 2 – 2.5 bar.

RESULTS AND DISCUSSIONS

Rheological measurements of solar paints

Flow curves of black TISS paints with the variation of black pigment and Al flakes are presented in Fig. 1. All examined TISS paints exhibited shear thinning behaviour with detected time dependence and yield stress. A progressive increase of shear thinning behaviour was detected when the amount of Al flakes was increased on the account of decreasing amount of black pigment. The paint with only the black pigment and no Al flakes (17Black : 0Al flakes) exhibited a gentle decreasing of the viscosity with shear stress in a wide range of shear stresses, while the paint with high amount of Al flakes and low concentration of black pigment (3Black : 14Al flakes) exhibited a steep decrease of the viscosity in a narrow range of shear stresses (Fig. 1). Moreover, also the values of the viscosity and yield stress depended on the amount of Al flakes. When no Al flakes were added to the paint, the viscosity and yield stress were the lowest indicating good flow properties but tendency towards sedimentation. On the other hand, when high concentration of large Al flakes was added, the values of yield stress increased, indicating a more stable dispersion with lower tendency towards sedimentation. However, high yield stresses could lead to decreased ability of proper flow during the application and good levelling after the application of the paint on the substrate.

The influence of the ratio between the black and coloured pigment on the flow properties was studied with blue and green TISS paints. Flow curves for blue TISS paints with different concentrations of black and blue are presented in Fig. 1B. Similar results were obtained also for the green TISS paints. Due to similar sizes of black, blue and green pigments different concentrations of the pigments had almost no effect on the flow properties of coloured TISS paint.

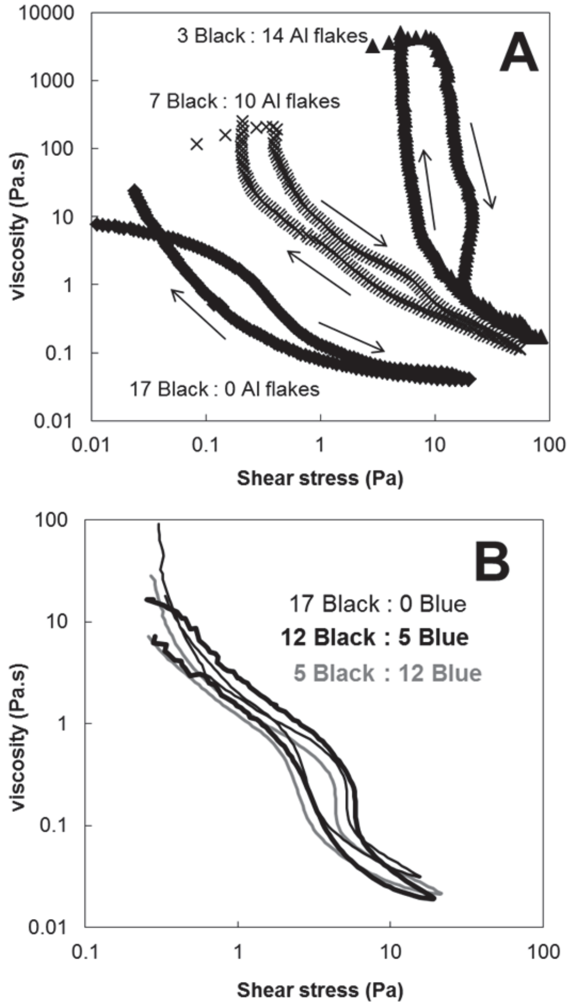

Figure 1. Flow curves for TISS paints: the effect of different ratio between A) black pigment and Al flakes; B) black and blue pigment.

Similar results with minor impact were detected also when comparing flow properties of blue and green TISS paints, prepared with the same amount of Al flakes and the same ratio of coloured vs. black pigment (Fig. 2). As expected, due to similar sizes of blue, green and black pigments, the colour of the pigment had almost no effect on the flow properties of blue and green TISS paints, respectively.

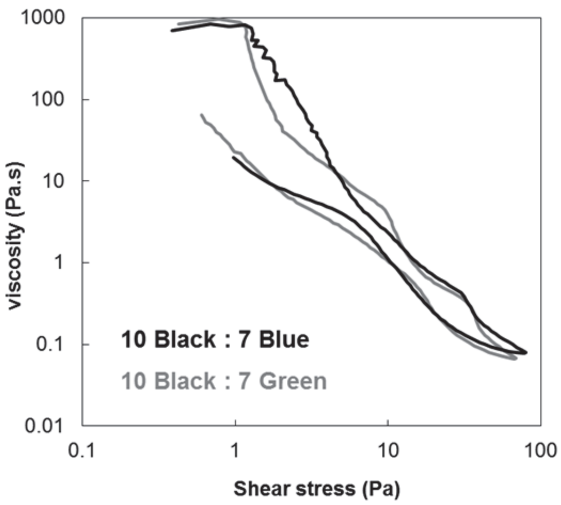

Figure 2. Flow curves for blue and green TISS paints with the same ratio of black pigment.

As mentioned above, in order to simulate the conditions to which the paint is subjected during storage, application and formation of dry coating on the substrate, 3-step time tests were performed for all TISS paints. When the paint was prepared with no Al flakes (17Black : 0Al flakes, Fig.3), the paint during the storage (low deformation, Fig. 3) exhibited liquid-like properties with low values of dynamic moduli and slight prevalence of loss modulus *G''* over the elastic one *G'*. Due to high shear during the application, the values of viscoelastic moduli *G'* and *G''* dropped according to flow curves (Fig. 1). After the application when the paint was again subjected to small deformation, the viscoelastic moduli slowly recovered to initial values. In this step the prevalence of the viscous modulus *G''* over the elastic one *G'* increased, indicating low consistency and more liquid-like properties of the paint after the application. TISS paints with no addition of Al flakes exhibited liquid-like viscoelastic properties before and after the application, suggesting strong tendency towards sedimentation at rest and occurrence of possible small defects during the formation of dry coatings. The addition of Al flakes changed the consistency and viscoelastic properties of the paints. At rest the dynamic moduli exhibited higher values with elastic moduli *G'* prevailing over the viscous one *G''*. After drop of the consistence during the application, dynamic moduli very slowly started to increase in the 3rd step of time tests (Fig. 3). Prevalence of elastic modulus *G'* over the viscous one *G''* in the 1st and 3rd step indicates a stability of the paint towards sedimentation, however, high consistency of the paint could lead to problems during the application.

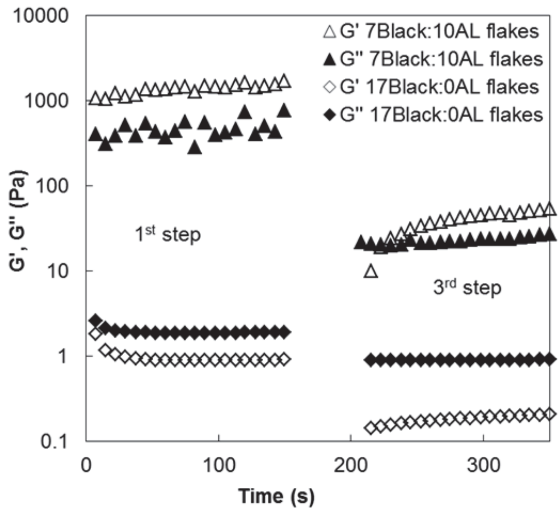

Figure 3. 3-step time tests for TISS paints: the effect of different ratio between black pigment and Al flakes.

<u>Spectral selective properties of dry coatings</u>

After thermal treatment of dry coatings, spectral selective properties were determined for black and coloured TISS paints. As expected the Al flakes and black pigment had major impact on the spectral selectivity, i.e. thermal emittance e_T and solar absorptivity a_S values (Fig. 4 and Fig. 5), while the differences between green and blue pigments were minor. For black TISS paints, the higher concentration of Al flakes resulted in lower values of thermal emissivity e_T, but also in lower values of solar absorptivity a_S. On the other hand, higher concentrations of black pigment increased solar absorptivity, but then again thermal emissivity increased too. For coloured TISS paints with the same concentration of Al flakes the spectral selectivity depended on the amount of black pigment, which increased solar absorptivity and thermal emissivity. The difference between blue and green colour was small, however for all concentrations of added pigments the green TISS paints exhibited slightly higher a_s and e_T values.

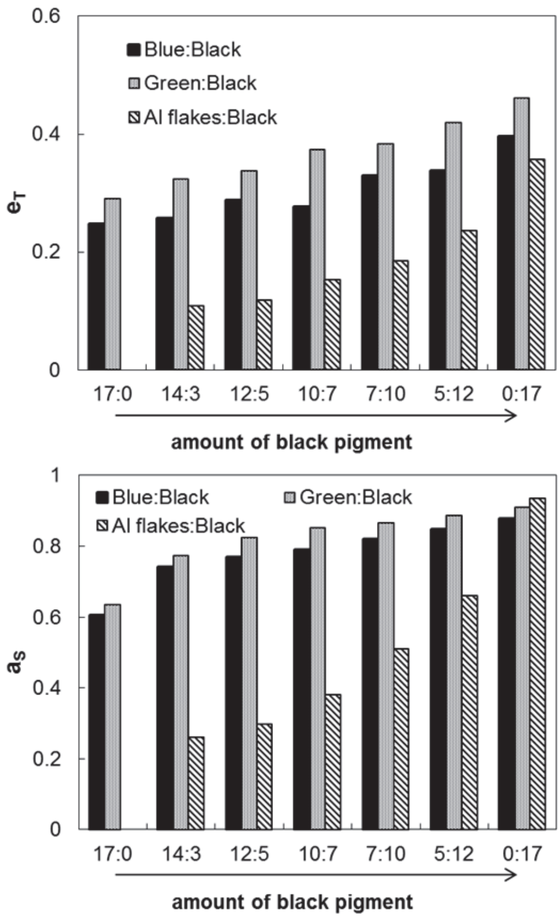

Figure 4. The influence of black pigment on thermal emissivity e_T and solar absorptivity a_S.

As mentioned above, the spectral selectivity is the best when the difference between solar absorptivity and thermal emissivity is the highest. The comparison of the spectral selectivity between black and coloured TISS coatings, used in this study (Fig. 5), shows that the concentration of the ratio between large Al flakes and small black pigment has a great impact on spectral selectivity. The values of a_s - e_T exponentially increased with decreasing concentration of Al flakes and increasing amount of black pigment. The best spectral selectivity (the highest difference between a_s and e_T values) was achieved with the highest concentration of black pigment and no addition of Al flakes. However, this paint exhibit very poor thermal emissivity, as the e_T exceeded the value of 0.45.

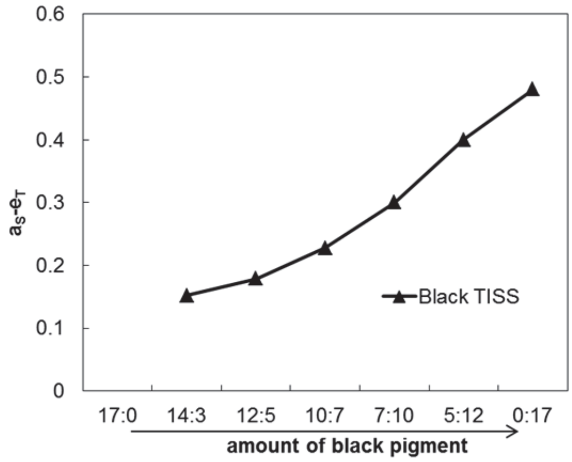

Figure 5. Spectral selectivity (a_s - e_T) for black TISS paints, prepared by different ratio of Al flakes and black pigment.

<u>Colour strength</u>

Lightness *L** and chroma *C** values were determined for coloured TISS paints in order to evaluate the influence of black pigment on the colour of dry coatings. Coloured TISS coatings exhibited high chroma values ($C^* > 40$) when small concentration of black pigment was added to the coloured pigment. However, for these coatings the lightness was the highest ($L^* > 40$) and the corresponding a_S values were too low to impart the corresponding paints sufficiently high spectral selectivity. Lightness decreased with increasing concentration of black pigment, but at the same time the colour of the coating decreased too and the chroma values fell to the values below 10. As a result TISS coatings became dark with less pronounced blue and green colour.

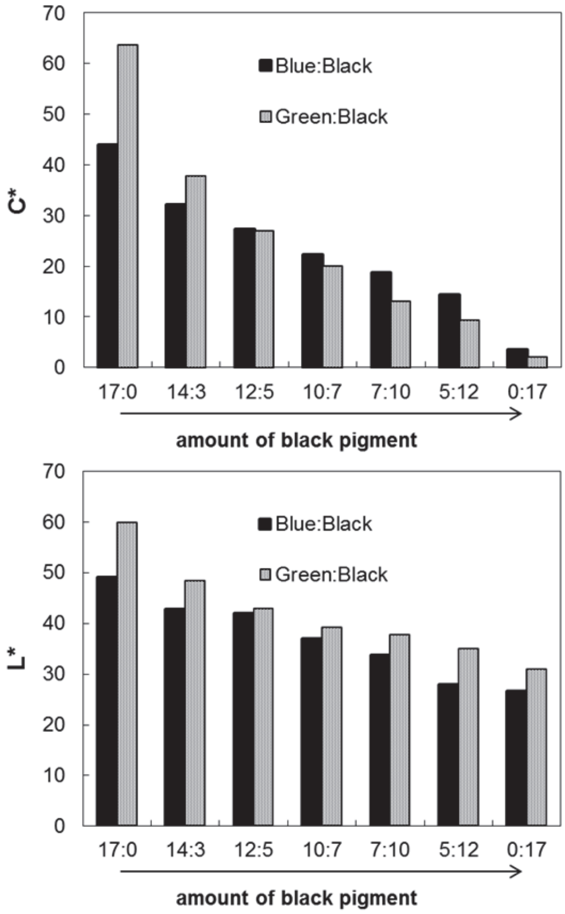

Figure 6. Chroma values for green and blue TISS paints prepared by different ratio of added pigment particles.

CONCLUSIONS

The results showed that the ratio between large Al flakes and small coloured pigments has a great impact on the rheological properties of liquid paints and only the proper balance between the pigments leads to high spectral selectivity and high colour strengths of coloured TISS paints, expressed by lightness *L** and chroma values *C**.

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