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Spectrophotometric Evaluation of Urethane Acrylate Based Pigment Colour Stability

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Abstract

The aim of the paper is to analyse the influence of violet and green pigment concentration on acrylate coating colour stability with increased temperature and in UV light. A set of coating formulations were generated with different pigment mass concentrations (0, 1% to 5%) and coating colour change were evaluated at room temperature, at 50°C and in direct sunlight over a 28 day period. After application and UV cure, the samples were examined using spectrometric methods. Spectrometric colour difference measurements were performed using colour system CIEL*a*b* to evaluate their stability over time. It was found that increasing pigment concentration improves the colour stability.

Introduction

Colour stability is crucial quality parameter for decorative coatings, where pigments are added to enhance aesthetic properties [1,2]. Different methods of optical microscopy and spectroscopy using the whole range of electromagnetic radiation are applied in routine examinations of paint samples. Infrared spectrometry provides information about polymer binder and fillers, Raman spectrometry is used to anlayse pigment and dyes, and Thin Layer Chromatography (TLC) can be also used not only for colour examination but also in the identification of organic pigments [3-5].

The initial criterion used for paint samples comparison is an estimation of the similarity of their colour. Micro spectrometry in the visible range MSP-Vis (combination of optical microscopy and spectrometry) is an objective way to compare colour. This method is often used in the examination of colour [6].

A quantitative colour description based on the colour theory accepted by the CIE (Commission Internationale De l'Eclairage) is an important method for evaluating the colour property of polymer coatings when exposed over time to water, heat, UV etc. [3,4,6]. CIE is accurate and sensitive for detecting the colour changes of a coating, often caused by uptake of UV radiation, temperature and during its degradation; therefore it is a very useful tool for predicting the lifetime of coatings [6].

One of colour spaces is CIEL / a / b / space characterized by axis: L – for lightness, a – green–red, b – blue–yellow colour-opponent dimensions. Colour coordinates are calculated from the Vis spectra. Its superiority to the visual method of colour comparison has been discussed in many papers [3-9].

The aim of this paper is to assess whether the pigment concentration in the polymer binder has significant influence on the coating colour stability under conditions of increased T and in direct sunlight.

Experimental method

Materials and methods

Two sets of paint samples were prepared. Violet (CI 77742, ammonium manganese (III) pyrophosphate from Kromachem) and green (CI77288, chromium oxide from Kromachem) pigments were incorporated in urethane acrylate base. Di-HEMA Trimethylhexyl Dicarbamate from Sartomer was used as oligomer, Hydroxyethyl Methacrylate from Esstech was used as monomer, and Ethyl Trimethylbenzoyl Phenylphosphinate from IGM was used as photoiniciator. Pigments were incorporated in the mixture in 4 mass concentrations: 0,1%, 0,2%, 1% and 5% table 1. The composition with 5% green pigment wasn't

Table 1: Coating formulation

Formulation name	Pigment	Pigment conc. %	Oligomer conc. %	Monomer conc. %	Photoiniciator conc. %
G-0,1	green	0,1	64,9	30	5
G-0,2	green	0,2	64,8	30	5
G-1.0	green	1	64	30	5
V-0,1	violet	0,1	64,9	30	5
V-0,2	violet	0,2	64,8	30	5
V-1.0	violet	1	64	30	5
V-5.0	violet	5	60	30	5

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evaluated as it doesn't cure in UV light due to the high pigment concentration. Paper test panels were obtained from BYK Additives & Instruments.

Coating application

The green and violet pigments were dispersed in urethane acrylate base by stirring for 4 min at 1800 rpm in Dispermill KK 250. The coating was applied by a BYK film applicator onto BYK paper test panels. Before applying coating, the panels were rinsed with acetone. The wet film thickness was 200 µm. All coating samples were cured in UVLED lamp (KP800LED, luminous intensity of 130 mw, λ = 405 nm from YI Liang Electron Technology Co, China) for 30 s. To avoid oxygen inhibition activity on the curing in coating surface, it was coated with transparent PE film with thickness 50µm. After curing, the PE film was removed [10].

Test methods

The first coating of each composition was applied on BYK paper test panels and cured under UV light. These coatings were used as reference samples for colour tests. One more application from each composition was kept in direct sunlight for 28 days. The other composition was divided into 2 jars and one of them was kept in room temperature and another one in 50°C for 28 days. Compositions were evaluated after 2 days, 7 days and 28 days. Applications were made from these compositions and used for colour evaluation.

The spectrophotometer measured the colour of prepared pigment coatings on the applications. It measured the colour on both the white and black parts of the application sheet. The first colour measurement became the reference for which, in the course of the study, a comparison of the pigment colour with light-curable urethane acrylate mixture was compared. The resulting applications were stored in the dark.

The colour evaluation was performed on a Data colour DC200 spectrophotometer using Colour match Plus software. On the base of spectra the colour parameters (chromaticity coordinates) and colour difference parameter ΔE were calculated using the following formula [6]:

$$\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2} \quad (1)$$

Where L_1^*, a_1^*, b_1^* and L_2^*, a_2^*, b_2^* are the CIE Lab values obtained for 2 samples labelled as 1 and 2, where 1 is the reference sample and 2 the tested sample after aging conditions. Colour is a subjective response of the eye and brain to incident radiation that illuminates an object. To eliminate the subjectivity of human perception, colour coordinates are calculated from the VIS spectrum. The mathematical distance between two points in colour space (ΔE) is a numerical description of a difference in colour.

Results and Discussions

In the field of gel coating production, colour stability is an essential criterion for high quality coatings. Therefore, it is important to understand the colour changes of the pigment both in liquid form and as a coating on the substrate during their life time [2, 3]. This research allows the prevention and reduces the production of poor quality products and unstable coatings.

In this study we evaluated manganese violet and chromium (III) oxide green pigments in urethane acrylate composition. The colour stability of the pigmented coating was analysed at room temperature, at 50° C, and in a direct sunlight for 4 weeks.

Pigment dispersion

The degree of pigment dispersion has a critical effect on coating property [6]. For all the pigmented coatings, the pigments were uniformly distributed in the coating matrix without any aggregates or agglomerates.

Colour stability

UV light causes photo-degradation of polymers therefore colour can change in time. The absorption of UV energy induces chemical reactions between polymer and oxygen [6]. The chemical reactions result in physical changes of coatings, such as colour difference, loss of gloss and thickness, and cracking and chalking [4,6,7]. The colour difference can be evaluated according to the CIELAB colour system, which describes colours in three dimensions mathematically. The colour difference before and after UV exposure is determined by analysing the change in L*, a*, and b*, where L*, a*, b* represents lightness, redness-greenness, and yellowness-blueness, respectively. The equation for CIELAB colour difference (ΔE*) is represented in formula (1) [6].

Figure 1A reports the colour difference of all samples as a function of UV exposure time. For most of the samples, the ΔE values increase with the increase of the UV exposure (sunlight) time. From G-0,1 to V-5.0, the ΔE values decrease with the increase of pigment concentration. The highest colour difference (lowest colour stability) is obtained for formulations, which is a urethane coating with 0,1% of green and violet pigments. The lower ΔE values are obtained for other formulations with the highest pigment concentrations: G-1.0 (1% of green pigment) and V-5.0 (5% of violet pigment). According to DIN 55987 [6], this stability of coatings is considered acceptable and sufficient if ΔE ≤ 2. In this work, after UV exposure of 28 days, ΔE value of all formulations, where formulation contain more than 01 % of green pigment and 0,2% of violet pigments, are less than 2. It indicates that all these formulations have a good UV stability.

The UV region of sunlight can be classified into three parts: UVA (315–400 nm), UVB (280–315 nm), and UVC (100–280 nm) [6]. UVC is only found in outer space. UVA and UVB are responsible for the most damage from UV radiation on the earth. The UV stability of coating is mainly due to the reflection and absorption of UV light by pigments. Organic pigments can absorb UV energy and convert it into thermal energy, which is harmless to coatings [6,8,9]. The good UV stability for the pigmented coating is because these pigments can absorb UVA and UVB light. The UV/Vis spectrum of the pigments tested demonstrates that those pigments are good UV absorbers with promising potential to protect coatings from the damage of UV radiation.

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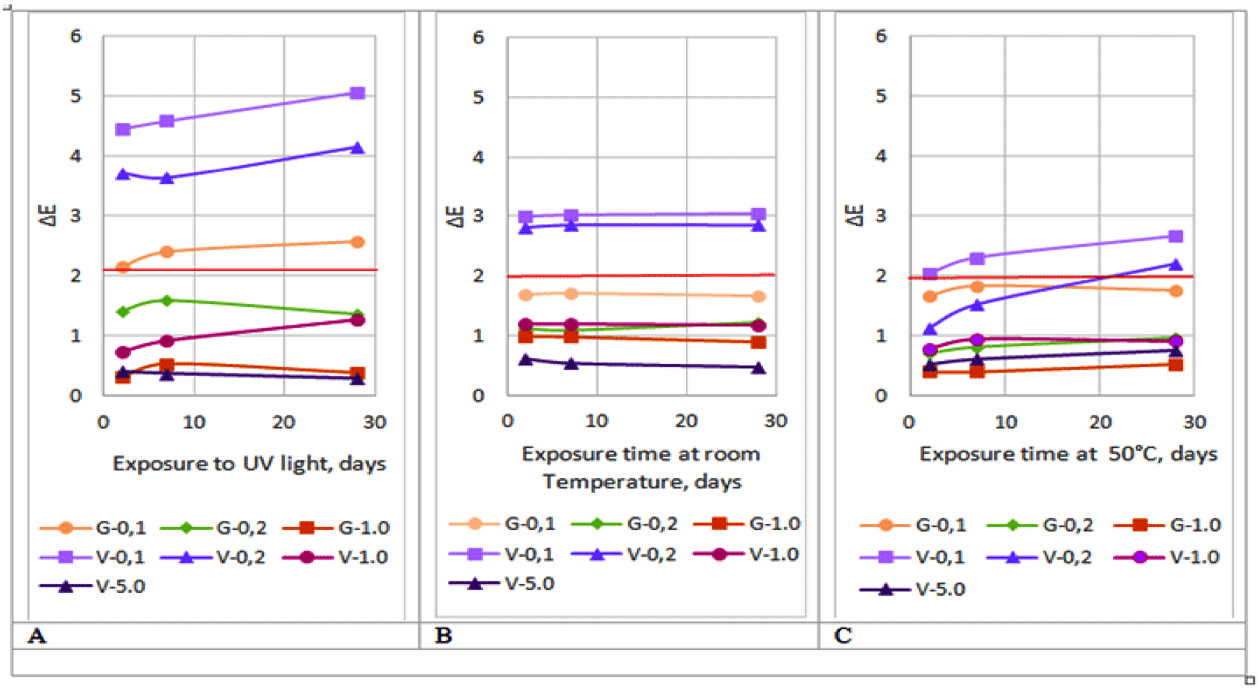

Figure 1: Colour difference (ΔE*) change of coating samples: **A-** as a function of time exposed in the UV light (from sunlight) under the continuous exposure; **B-** as a function of time exposed at room temperature; **C-** a function of time exposed at 50°C. G-0, 1 to V-5.0 refers to different pigment concentrations as listed in Table 1.

Figure 1B shows the colour stability of coatings in time at room temperature. Most of the pigment systems tested had the same colour change after 2 days and after 28 days. ΔE fluctuates within the error range. These results will allow the group to reduce the colour stability testing time from 28 days to 2 days in a future.

Also, there is a correlation between ΔE and pigment concentration: higher is the pigment concentration – more stable is the colour (smaller ΔE).

Figure 1C shows the colour stability of coatings over time at increased temperature (50°C). There can be seen the tendencies as in room temperature test, only compositions with 0,1 and 0,2% of violet pigment shows the difference of ΔE after 2 days and after 28 days. There also is a correlation between ΔE and pigment concentration: higher is the pigment concentration – more stable is the colour (smaller ΔE).

For all of the coatings tested, ΔE at room temperature is higher than in increased temperature. This can be explained by sample contact with UV light, as these results show the same tendency as do samples that were kept in direct sunlight.

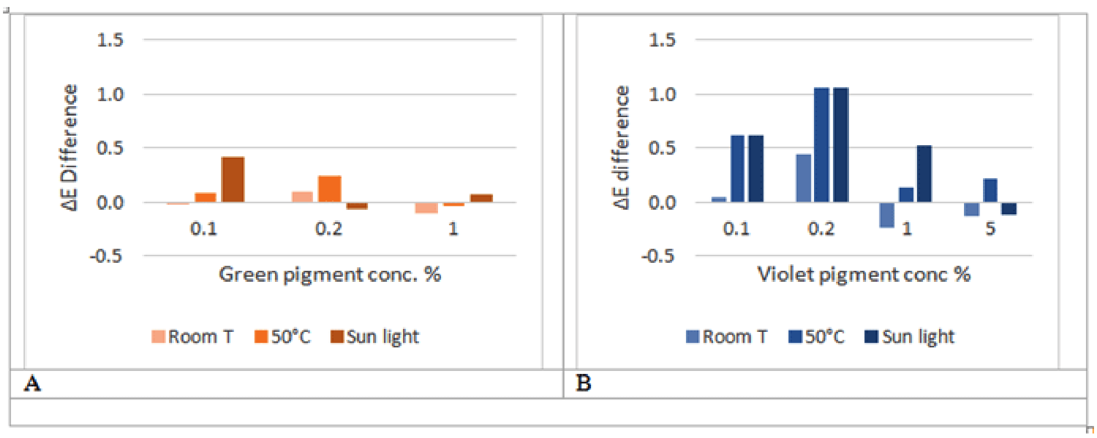

Figure 2: Colour difference (ΔE) between second day and 28th day as a function of pigment concentration: **A–** for coatings with green pigments; **B-** for coatings with violet pigments.

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We compared the colour difference (ΔE) between the second day and 28th day as a function of pigment concentration. It can be seen from figure (2A,2B), that systems with green pigment are more stable than systems with violet pigment. These figures very clearly show that the pigment concentration correlates with ΔE. There is a border for each pigment, where ΔE starts to decrease. For green pigment this border is between 0,1% and 0,2% of pigments, but for violet pigment the border is between 0,2% and 1,0% of pigment.

Conclusions

In this study, dispersion the colour stability of violet and green pigments was evaluated by incorporating them into UV light-curing urethane acrylate coatings. Assumption, that pigments can prevent coatings from UV damage was confirmed. Two sets of paint samples: one containing violet and another one green pigment were prepared. Each set consisted of 4 samples differed gradually in the concentration of pigment. After application and UV cure the samples were examined using MSP-Vis method with CIEL/a/b. The colour of samples were compared after 3 aging tests (at room temperature, at 50°C and in sunlight) in 28 days period according to colour theory. It was found that coating stability increases with increasing manganese violet and chromium (III) oxide green pigment content.

The colour difference ΔE of the samples stored at room temperature, 50° C and in the sunshine after 2 days is mostly equivalent to a 1-month result, so it can be concluded that the pigments in the urethane acrylate composition are stable over time.

The ΔE values for coatings containing more than 0,2% of pigments are acceptable and within tolerances, as evidenced by the professional team of paint chemists who could not observe any changes in colour.

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References

1. Milinavičiūtė A, Jankauskaitė V, Narmontas P. Properties of UV-Curable Hyperbranched Urethane-Acrylate Modified Acrylic Monomer Coatings. Mater Sci. 2011;17(4):378-383.
2. Grigale-Sorocina Z, Kalnins M, Simanovska J, Vindedze E, Birks I, Brazdauska E. Additives in UV-activated urethane acrlylate polymerization composite coatings. Proceedings of the Estonian Academy of Sciences. 2015;64:88-93.
3. Johnson BW, Mcintyre R. Analysis of test methods for UV durability predictions of polymer coatings. Progress in Organic Coatings. 1996;27(1-4):95-106.
4. Erznožnik H, Razboršek T, Gunde MK. Characterization of orange pigments in decorative outdoor coatings and their weather fastness. Progress Organic Coatings. 2016;99:47-54.
5. Jose S, Prakash A, Laha S, Natarajan S, Reddy ML. Green colored nano-pigments derived from Y2BaCuO5: NIR reflective coatings. Dyes and Pigments. 2014;107:118-126.
6. Weixiu Z, Qixin Z, Haichang Z, Xiaoning QI. One-coat epoxy coating development for the improvement of UV stability by DPP pigments. Dyes and pigments. 2018;151:157-164.
7. Trzcinska B, Kowalski R, Zieba-Palus J. Comparison of pigment content of paint samples using spectrometric methods. Spectrochim Acta A Mol Biomol Spectrosc. 2014;130:534-538. doi: 10.1016/j.saa.2014.03.099
8. Gao Q, Wu X, Fan Y. Solar spectral optical properties of rutile TiO2 coated mica-titania pigments. Dyes and Pigments. 2014;109:90-95.
9. Bierwagen G, Tallman D, Li J, He L, Jeffcoate C. EIS studies of coated metals in accelerated exposure. Progress in Organic Coatings. 2003;46(2):149-158.
10. Grigale-Sorocina Z, Kalnins M, Gross KA. Influence of monomer on structure, processing and application characteristics of UV curable urethane acrylate composite coatings. IOP Conference Series: Materials Science and Engineering. 2016:111.

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