Spectrophotometric evaluation of pigmented urethane acrylate coating colour stability

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Abstract. The research was carried out testing two red pigment dispersion colour stability in UV light-curing urethane acrylate composition. The given urethane acrylate composition was pigmented with a pigment content of 0.1% to 5%. Coating colour change was evaluated at room temperature and at 50°C over a 28-day period. For all prepared pigment samples, spectrometric colour difference measurements were performed using CIEL*a*b* and CIEL*C*h* colour systems and FTIR-ATR to evaluate their stability over time. The colour stability was improved with increasing pigment concentration. There was found the difference between tested red pigments and can be concluded that one of them are more stable for use in pigmented coatings.

1. Introduction

The testing of thin coloured coatings based on urethane acrylate composition is a technologically advanced, highly specialized and complex process. For decorative pigmented coatings (construction coatings, electronic coatings and cosmetic coatings), colour stability is crucial quality parameter [1, 2, 3]. Optical microscopy and spectroscopy methods are used to test painted coatings. Different spectroscopy methods can give the additional information about the system changes in time. Raman spectrometry is used to analyse the changes of compositions in time. Infrared spectrometry provides information about polymer binder and fillers. Thin layer chromatography (TLC) can be also used not only for colour examination but also for the identification of organic pigments [4, 5, 6]. The main target of all those methods is to estimate the difference of the colour. The most objective way to compare the colours in the range of visible light is micro spectrometry. This method is most often used for the examination of colours [6].

There is polymer coating colour evaluation method accepted by CIE (Commission Internationale de l’Eclairage) which quantitatively describes the colour using colour theory. This method is important for evaluation of polymer coating colour over time and environment: water, heat, UV etc. [4, 6, 7].

It shows colour difference with measurable quantities, therefore it is a very useful tool for predicting the lifetime of coatings. Method is based on describing the colour coordinates: CIEL/a/b/ characterized by axis: L – for lightness, a – green – red, b – blue – yellow colour - opponent dimensions [8, 9, 10]. The aim of this paper is to compare two different red pigment dispersions and assess whether the pigment concentration in the polymer binder has significant influence on the coating colour stability under conditions of room T and increased T.
2. Materials and methods

2.1. Materials

Two sets of red - pigmented coating samples were prepared. Red #170 (CI 12475 from Kromachem) and Red #48 (CI 15865, from Kromachem) pigments were mixed in urethane acrylate base. As oligomer was used Di-HEMA Trimethylhexyl Dicarbamate from Sartomer, as monomer was used Hydroxyethyl Methacrylate from Esstech, and as photoinitiator was used Ethyl Trimethylbenzoyl Phenylphosphinate from IGM. Pigments were incorporated in the mixture in 4 mass concentrations: 0.1%, 0.2%, 1% and 5% (Table 1). Previous experience have shown that increased pigment concentration, improves colour stability, what should be proved.

| Formulation name | Pigment | Pigment conc. [%] | Oligomer conc. [%] | Monomer, conc. [%] | Photoinitiator conc. [%] |
|------------------|---------|------------------|-------------------|-------------------|-------------------------|
| R170-0,1         | Red 170 | 0,1              | 64,9              | 30                | 5                       |
| R170-0,2         | Red 170 | 0,2              | 64,8              | 30                | 5                       |
| R170-1           | Red 170 | 1                | 64                | 30                | 5                       |
| R170-5           | Red 170 | 5                | 60                | 30                | 5                       |
| R48-0,1          | Red 48  | 0,1              | 64,9              | 30                | 5                       |
| R48-0,2          | Red 48  | 0,2              | 64,8              | 30                | 5                       |
| R48-1            | Red 48  | 1                | 64                | 30                | 5                       |
| R48-5            | Red 48  | 5                | 60                | 30                | 5                       |

2.2. Coating application

Red pigments were dispersed in urethane acrylate base by stirring for 4 min at 1800 rpm in Dispermill KK 250. The coating was applied onto BYK paper test panels by a BYK film applicator. 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) for 30 s. Compositions were coated with transparent PE film with thickness 50µm to avoid oxygen inhibition activity on the curing coating surface. After curing, the PE film was removed [6, 11].

2.3. Test methods

The 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. 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 (as T where pigmented systems have been tested on sedimentation stability). Compositions were evaluated after 2 days, 7 days and 28 days. Applications were made from these compositions and used for colour evaluation [5, 6].

The spectrophotometer measured the colour of prepared pigment coatings. 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 [5, 6].

The colour evaluation were performed on a Datacolour DC200 spectrophotometer using Colourmatch Plus software. On the base of spectra the colour parameters (chromaticity coordinates) and colour difference parameter ΔE were calculated using the following formula [5, 6, 7]:

\[
\Delta E = \sqrt{(L'_1 - L'_2)^2 + (a'_1 - a'_2)^2 + (b'_1 - b'_2)^2} \tag{1}
\]
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 visible and infrared spectrum. The mathematical distance between two points in colour space ($\Delta E$) is a numerical description of a difference in colour [5].

Fisher Scientific, Nicolet 6700 was used to record coating spectra in the absorption area 650 cm$^{-1}$ to 4000 cm$^{-1}$, with the exception of 16 cm$^{-1}$. During testing, a method is adopted using ZnSe selection, where the incident light angle is 42o and the printing depth is 2.03 $\mu$m at 1000 cm$^{-1}$.

3. Results and discussions

3.1. Colour stability

Colour stability in time is essential criterion for pigmented coatings. Therefore, it is important to be able to predict the non-polymerized composition and cured coating colour change in time [2, 3, 5]. This research allows the prevention of poor quality products and unstable coatings in new product development and production.

In this study, we evaluated Red #107 and Red #48 pigments in urethane acrylate composition. As red pigments are one of the most often used, it is important to choose the most stable and most appropriate for urethane acrylate system. The colour stability of the pigmented coating was analyzed at room temperature and at 50°C for 28 days.

![Figure 1](image1.png)  
**Figure 1.** Colour difference ($\Delta E^*$) change of coating samples as a function of time exposed at room temperature; R48-0.1 to R170-5 refers to different pigment concentrations as listed in Table 1. Red line indicates acceptable colour change.

![Figure 2](image2.png)  
**Figure 2.** Colour difference ($\Delta E^*$) change of coating samples as a function of time exposed at 50°C temperature; R48-0.1 to R170-5 refers to different pigment concentrations as listed in Table 1. Red line indicates acceptable colour change.
Figure 1 reports the colour difference of all samples as a function of exposure time in room T. For both pigmented compositions, the ΔE values increase with the increase of the exposure time. Also there is the bright tendency – the highest the pigment concentration – lowest the difference in ΔE. The lowest ΔE values are obtained for formulations: R170-5.0 (5% of Red #170 pigment) and R48-5.0 (5% of Red #48 pigment), where ΔE ≤ 1.2. According to DIN 55987 [6], stability of coatings is considered acceptable and sufficient if ΔE ≤ 2.

Compositions with 0.1% and 0.22% of pigment Red #48 shows the highest ΔE increase in increased T: formulation with 0.1% after 28 days the ΔE value was increased to 18.05, but with the pigment content of 0.2% to 12.83. This difference is also observable with eyes: Figure 3 shows coating color before the test (figure 3. A) and after 28 days test (figure 3.B). Significantly, less ΔE growth was observed with a pigment content of 1.0% to 3.32 and 5.0% to 1.03, but still 1% pigment composition is not acceptable for use in coatings.

In this work, after exposure at room T for 28 days, formulations containing more than 0.2 % of Red #48 pigment and all formulations containing Red #170 pigments, ΔE value were less than 2. It indicates that all these formulations have a good stability at room T. Figure 2 shows that all pigmented systems tested containing Red#170 had the same colour change after 2 days and after 28 days. ΔE fluctuates within the error range. These results will allow reducing the colour stability testing time from 28 days to 2 days.

The increase of exposure temperature significantly increase ΔE values of all formulations, especially those containing pigment #48. All formulations with different concentrations of this pigment in 28 days reached ΔE values higher than 2. After this experiment, it’s clear that T increase noticeably increase colour change. This allows concluding, that pigmented systems should be tested not only at room T, but also at increased temperature regime.

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

3.2. Colour change detection with FTIR-ATR

Testing these two Kromachem pigments in urethane acrylate composition we can conclude, that acceptable formulations are with pigment Red#170 with concentrations above 0.2%.

![Figure 3. Colour change of coating samples R48-0.1: A- before test; B – after 28 days exposed at 50°C temperature.](image-url)
spectrometer. There was no correlation between the colour difference ΔE and the IR spectra. This is confirmed by figure 4 and figure 5: spectrum comparison of Red # 48 and Red # 170 with 0.1% content before and after testing at temperature 50°C. The value of the colour difference ΔE increased sharply during the test, the colour change was observed visually and using spectrophotometer but was not reflected in the IR spectrum (see Figure 4 and Figure 5).

![Figure 4. IR spectrum of red pigment #170 with 0.1% of pigment content before and after 50°C.](image1)

![Figure 5. IR spectrum of red pigment #48 with 0.1% of pigment content before and after 50°C.](image2)

4. Conclusions
In this study, colour stability of dispersions with red #48 and red #170 pigments were evaluated by incorporating them into UV light - curing urethane acrylate coatings. Assumption, that pigments can prevent coatings from colour degradation was confirmed. Two sets of paint samples: one containing Red #48 and another Red #170 pigment were prepared. Each set contains four samples with different concentrations of pigments. After application and UV cure, the samples were examined using MSP - Vis method with CIEL/a/b and FTIR - ATR. The colour was compared after two aging tests (at room temperature and at 50°C) in 28 days period. It was found that coating stability increases with increasing Red pigment content.

The colour difference ΔE of the samples stored at room temperature and 50 °C after 2 days is mostly equivalent to a 1 - month result, so it can be concluded that if the pigments in the urethane acrylate compositions have insignificant change in 2 days, that there will not be significant change also in 28days. The ΔE values for coatings containing Red #170 more than 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. Pigment Red #48 is not recommended to use for high quality coatings, as all concentrations showed ΔE values after experiments higher than acceptable.

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