

## Article

# Behaviour of Thermochromic Coatings under Thermal Exposure

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**Abstract:** Interactive thermochromic coatings based on Leuco dye are most commonly used in research for building cooling applications. The coatings developed by the authors are primarily aimed at industrial applications on metal substrates, mainly for safety reasons. Thanks to a higher transition temperature associated with a significant change in shade, they have the potential to prevent burns and can be used as an element of active protection in exposed areas. Interactive thermochromic materials with different base matrices and two dispersion methods have been monitored and tested over the long term to gain an overall impression of their behaviour and applicability. The monitoring of colour characteristics helps to understand the behaviour of the thermochromic pigment in different primer matrices. The values of  $L^*$ ,  $a^*$ , and  $b^*$  and the spectral curves measured by a spectrophotometer were compared. Colour differences between the cold and heated conditions were also evaluated.  $\Delta E^*$  values for acrylate polyol reached up to 39. For waterborne paint, they varied according to the method of dispersion—when using a saw tooth stirrer,  $\Delta E^*$  was 23, and when mixing with a rotor-stator device, up to 56. Similarly, for the polyurethane matrix:  $\Delta E^*$  went up to 39 for stirring with a saw tooth stirrer while  $\Delta E^*$  was 64 for the rotor-stator. From the measurement of the behaviour of the coatings during temperature exposure, it can be concluded that most of the samples show a decrease in the transition temperature. Monitoring the behaviour of coatings during cooling is important for choosing a suitable base matrix that will ensure the long-term functionality of the coating and declare the temperature range of its use for safety applications.



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**Keywords:** thermochromic coating; leuco dye; colour characteristics; spectral curves; interactive coating

## 1. Introduction

Leuco dye pigment is a special composite consisting of three components—chromogenic dye, developer, and an auxiliary solvent [1–4]. As a dye, the compound most commonly used is crystal violet lactone (CVL) [5–7], and as a developer, bisphenol A (BPA) [8] or lauryl gallate (LG) [9,10]. The choice of auxiliary solvent (most often alcohol-based) can directly influence the transition temperature [6,7,11]. During production, the thermochromic pigment is encapsulated in a polymer microcapsule [12–14], which acts as a protective element and without which faster degradation would occur. The working principle of the leuco dye pigment is the interaction between the dye and the solvent [9]. When the solvent is in a solid state, the interaction between the dye and the developer is maximal—the complex is coloured. When the temperature increases and the solvent is liquefied, the interaction between the dye and the developer is broken, resulting in negative thermochromia [3,8,14,15]. Interactive coatings with Leuco dye pigment, which function on the basis of chromism, are currently being investigated mainly in facade paint and cement applications [16–18]. Recent research has also considered the application of metallic [19] or natural [20,21] materials. Some authors have investigated the possibility of combining thermochromic pigments with other additives for a synergistic effect, for instance [22,23].

However, the application of LD pigments in coatings [20,24] is limited by the lack of information on the interaction of the pigment with the coating matrix and the effect of the dispersion method. In most of the available studies [15,25,26], the pigment is mixed only by hand, using a magnetic stirrer [24] or a centrifuge [27].

Thus, the authors tried to follow the manufacturer's guidelines, which declared the high sensitivity of thermochromic pigments to mechanical stresses. However, the manual dispersion method does not guarantee the homogeneity of the coatings produced or the possibility of continuous production. Within the framework of the research, three basic matrices were used, and two methods of thermochromic pigment dispersion were investigated. The formulated coatings (designated IP02, IP03, IP04) containing conventional and thermochromic (TCH) pigments were produced in two batches. The difference in these series is due to the different methods of dispersion for the TCH pigment, i.e., the first series—the saw tooth stirrer, the second series—and the rotor-stator-type mixer [28]. The method of dispersion was chosen to verify the functionality of the thermochromic pigment under increased mechanical stress.

Mechanical properties [29] and colour characteristics [30], including the influence of the base matrix and dispersion for the formed coatings, were investigated. For a comprehensive view, the samples were monitored for a long time, and their characteristics were evaluated.

The hypotheses for this research are presented in the following text. The acrylic polyol may contain components that can disrupt the polymer envelope and thus change the properties of the pigment. It is possible that the functionality of the pigment is reduced, where it loses the ability to “re-colour”, which can lead to a change in the shade after cooling. Waterborne acrylic should be non-reactive in its composition, and the primer should not damage the pigment envelope. The prerequisite is the maintenance of the functionality of the pigment in the entire range and the temperature ranges specified in the technical sheet. Polyurethane has such a composition that it should not fundamentally disturb the polymer coating of the pigment. Possible interactions may occur with the epoxy primer.

## 2. Materials and Methods

### 2.1. Components for Preparation Thermochromic Paints

The following components were chosen for the production of thermochromic paints: a thermochromic pigment APEX TH50 with a temperature transition of 47–52 °C, red, from ChemoxPound (Farnborough, UK), a conventional pigment P.Y. 74 from Synthesia (Pardubice, Czech Republic) and primer Setalux 1182 SS-55 from Nuplex (Bergen op Zoom, The Netherlands), which is an acrylic polyol with 1.8% OH, Viton HAE 30 (České Budějovice, Czech Republic) as a self-curing waterborne coating and Viton PD 53 (České Budějovice, Czech Republic) as a two-component polyurethane in combination with an epoxy base (Viton ZG13—České Budějovice, Czech Republic). An S6006 thinner for synthetic resins from Colorlak (Staré Město, Czech Republic) was used to dilute IP02. The composition of the coatings is defined in Table 1.

**Table 1.** Composition of coatings.

Coating Designation	Thermochromic Pigment	Conventional Pigment	Generic Name of Base Matrix	Base Matrix
IP02			Acrylic polyol	Setalux 1182 SS-55
IP03	5% APEX TH 50 RED	10% P.Y. 74	Waterborne acrylic	Viton HAE 30a
IP04			Polyurethane	Viton PD 53

## 2.2. Dispergation Parameters

In particular, the pigment was added to the final coating (already pigmented with a conventional yellow pigment) as the last component to minimise stress. Two dispersion methods were used: a 50 mm diameter saw tooth stirrer (INOXPA S.A.U., Banyoles, Spain), and parameters (Table 2), and a rotor-stator mixer (IKA T25 Digital with SR-25G stirrer, IKA<sup>®</sup>-Werke GmbH & Co. KG, Staufen, Germany) parameters (Table 3). The objective was to verify the applicability of the thermochromic pigment under normal production conditions.

**Table 2.** Process parameters using a saw tooth stirrer.

Coating Material	Base Matrix	Dispergation Time [Min]	Mixer Speed [Min <sup>-1</sup> ]
IP02	Acrylic polyol	5	3000
IP03	Waterborne acrylic	2	3000
IP04	Polyurethane	3	3000

**Table 3.** Process parameters for rotor-stator applications.

Coating Material	Base Matrix	Dispergation Time [Min]	Mixer Speed [Min <sup>-1</sup> ]
IP02	Acrylic polyol	2	10,000
IP03	Waterborne acrylic	2	10,000
IP04	Polyurethane	2	10,000

When using a saw tooth stirrer, the mixing of individual paint materials was approached individually, and their behaviour was checked during the process. The dispersion of the IP03 and IP04 systems took place without any problems, and with the IP02 system, it was necessary to mix longer due to the imperfect dispersion of the pigment in the paint. Dispergation with the rotor-stator device was successful for IP03 and IP04. The IP02, which was prepared last, degraded almost immediately and unexpectedly. This process could probably be reversed by controlling the cooling of the coating or by shortening the dispersion time.

The resultant coating formulation, therefore, had an orange colour at normal temperatures (around 20 °C); at increased temperatures, the red thermochromic pigment discoloured, and the coating remained yellow. After visual evaluation, it was found that this dispersion method affected the colour characteristic of the resulting coating, which was darker compared to IP03 and IP04 1st series.

## 2.3. Marking of Samples

For clarity, Table 4 shows the method for marking the samples. VP18 was in its original state while VP18\_PTL was in a condition from three years after its application (i.e., samples placed in a normal indoor environment without significant corrosion load, without increased humidity (up to 60%) and with access to normal (not direct) daylight). The VN21 samples were created from original paint materials (in a liquid state) that had been stored for three years. The original paint materials in a liquid state were stored at temperatures of +10 to 20 °C in the original packaging. There are two exceptions with an added index—VN21\_IP02Ř and VN21\_IP03Č. For VN21\_IP02Ř, a thinner (S6006 from Colorlak, Staré Město, Czech Republic) was added to the paint to improve its application properties. However, the general appearance of the coating changed, probably due to the reaction of some hydrocarbons, which were present in small quantities in the used thinner. These samples were presented separately from VN21\_IP02. Samples VN21\_IP03Č, without thermochromic pigment, were used in the work as a colour standard after heating.

**Table 4.** Prepared samples.

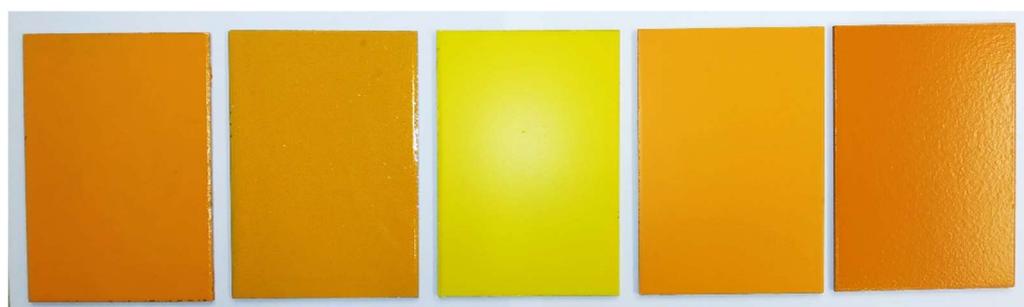
Designation	Significance
1VP18_IP02	method of dispergation: saw tooth stirrer
2VP18_IP03	method of dispergation: rotor-stator mixer
1VP18_IP02	original state
1VP18_IP02_PTL	after three years of exposure
VN21_IP03	comparator, created by original painting material in liquid state
IP02, IP03, IP04	describes the name of the coating material, generic name is shown in Table 1

#### 2.4. Sample Material and Pretreatment

For the experimental work, test panels were created using the newly formulated coatings IP02, IP03, and IP04 in different configurations. All coatings were applied to a steel substrate (S235 JR) with a defined size of  $100 \times 150 \times 4$  mm. For samples 1VP18 and 2VP18, corundum blasting and degreasing in technical alcohol was conducted, and for samples of VN21, steel shot blasting and degreasing with Viton CL07 solvent formulation was chosen.

The first batch of IP02, IP03, and IP04 thermochromic coatings was applied using an applicator (Baker film applicator, Elcometer, Manchester, England). Thickness was measured by the device Positector 6000 (DeFelsko, NY, USA), with average values of  $133 \pm 10$   $\mu\text{m}$  for 1VP18\_IP02,  $117 \pm 7$   $\mu\text{m}$  for 1VP18\_IP03, and  $119 \pm 1$   $\mu\text{m}$  for 1VP18\_IP04. The second batch of coatings IP02, IP03, and IP04 was applied using pneumatic spraying to make the application method as close to industrial use as possible. The average thickness was  $77 \pm 1$   $\mu\text{m}$  for 2VP18\_IP03 and  $105 \pm 6$   $\mu\text{m}$  for 2VP18\_IP04.

To evaluate the applicability state of the coatings, comparative samples were made after three years (Figure 1). The original coatings IP02, IP03, and IP04 from the first series (dispergation by saw tooth mixer) were used. Pneumatic spraying was chosen for the application. Previous measurements of the mechanical properties showed that it would be advantageous to increase the thickness of the coating. The average thickness was  $168 \pm 13$   $\mu\text{m}$  for VN21\_IP02,  $116 \pm 8$   $\mu\text{m}$  for VN21\_IP02Ř,  $170 \pm 12$   $\mu\text{m}$  for VN21\_IP03,  $134 \pm 9$   $\mu\text{m}$  for VN21\_IP03Č and  $232 \pm 17$   $\mu\text{m}$  for VN21\_IP04.



**Figure 1.** Comparative samples of the original coating systems. From the left: VP21\_IP02, VP21\_IP02Ř, VP21\_IP03Č, VP21\_IP03, VP21\_IP04.

After the application of the coating material, the drying took place at a temperature of  $18$   $^{\circ}\text{C}$  and relative humidity of 50%. After drying to the touch, the samples were placed in the laboratory at a temperature of  $21$   $^{\circ}\text{C}$  and a relative humidity of 48% to fully develop the properties of the coating. Testing was carried out after thirty days of storage.

#### 2.5. Methodology for Measuring the Behaviour of Thermochromic Coatings under Thermal Loading

A ThermoScientific Haratherm OMH 400 drying oven (Thermo Fisher Scientific, Waltham, MA, USA) was used for heating, and a BYK Gardner Spectro guide spectropho-

tometer (BYK—Gardner, Wesel, Germany) was used for measurement. Spectrophotometer was performed with colour geometry 45/0, illuminants D65 a 10° observer. The repeatability Colour was 0.01  $\Delta E^*$  (10 consecutive measurements in white), and the reproducibility Colour was 0.2  $\Delta E^*$  (average of 12 BCRA tiles). Continuous monitoring was carried out using an Ahlborn Therm 2420 thermometer (AHLBORN, Holzkirchen, Germany).

Boundary conditions for measuring the cooling behaviour of thermochromic coatings:

- The temperature exposure of the samples was performed in a temperature-controlled oven with an accuracy of  $\pm 0.5$  °C;
- The samples were exposed to a temperature 25 °C higher than the defined transition temperature (Table 5) and were then cooled naturally;
- The time of temperature loading was dependent on the dimensions of the sample, and consistent heating throughout the volume had to be guaranteed;
- The heated sample had a temperature at least 5 °C higher than the first measurement value before starting the measurement;
- The temperature was continuously sensed by an appropriate method, i.e., a thermometer;
- Colour measurements were made using a spectrophotometer in the heated state and at an appropriate interval during cooling.

**Table 5.** Defined measurement temperature values for the specified transition temperatures.

Defined Pigment Transition Temperature [°C]	Exposure Temperature [°C]	Temperature Measurement in the Heated State [°C]	Temperature When the Coating Is Defined as Cold [°C]
20	45	25–40	10–15
30	55	35–50	15–20
40	65	45–60	20–25
50	75	55–70	20–25
60	85	65–80	20–25

All of the compared samples were heated in an oven at 75 °C. Their temperature was continuously sensed using a thermocouple and a non-contact thermometer. At set intervals of  $5 \pm 1$  °C, the colour hue was measured with a spectrophotometer. Measurements were made for fixed temperatures of 60, 55, 50, 45, 40, 35, 30, and 25 °C. All spectral reflectance curves were recorded in graphs so that it was possible to observe the behaviour as the samples gradually cooled. For a better orientation, a panel representing the average colour at a given temperature (by converting the measured coordinates) was created using a coordinate converter. The cooling rate depended on the ambient temperature. Note: the transition temperature was given in the technical data sheet of the product [31].

## 2.6. Evaluation of Measured Data

In the CIELAB colour space, the  $a^*$  and  $b^*$  coordinates were derived from the primary values. Coordinates  $a^*$  define the colour on the red-green axis, while  $b^*$  defines the colour on the yellow-blue axis. The parameter L defines the lightness. The colour difference  $\Delta E^*$  can be defined mathematically as follows [32,33]. See Table 6 for the evaluation.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where  $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$  are the coordinate differences of the compared colours.

This can be seen where:

$L^*$  is the lightness parameter;

$a^*$  specifies the position on the a-axis where the colours green to red are located;

$b^*$  determines the position on the b-axis where the colours blue and yellow are located;

**Table 6.** Colour difference evaluation.

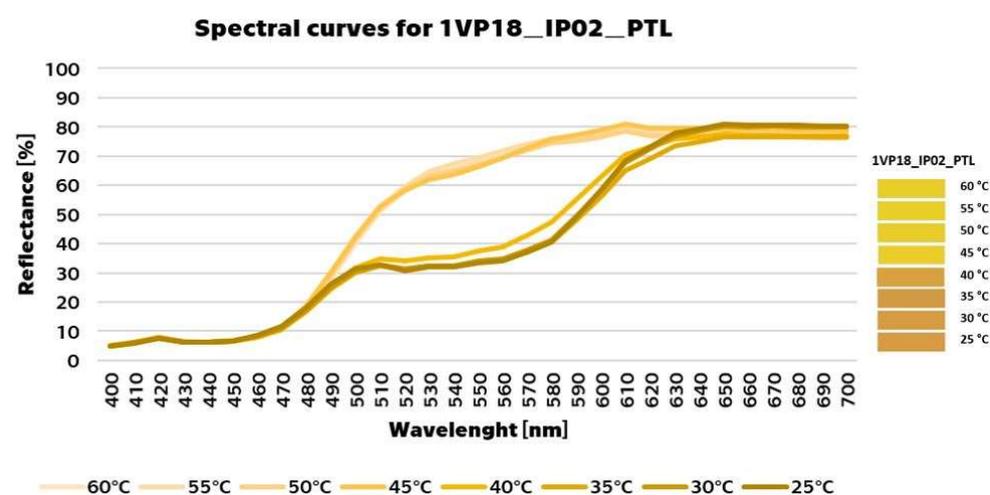
$\Delta E^*$	Verbal Evaluation of the Difference
0–0.2	Imperceptible
1.5–3	Clearly perceptible
3–6	Medium
6–12	Distinctive
12–16	Very marked
More than 16	Distracting

#### Method of Evaluation

- The  $L^*$ ,  $a^*$ , and  $b^*$  coordinates and values for the determination of spectral reflectance curves were evaluated;
- Changes in the colour characteristics were evaluated by both calculating the colour difference  $\Delta E^*$  between the limit states, the differences in individual coordinates, and evaluating the spectral reflectance curves, which clearly showed the overall change;
- The shift in the individual curves between the two edge states (i.e., heated and cold) determined the colour behaviour during cooling. From the position of the individual curves, it was possible to define the behaviour of the coating;
- The evaluation of the colour difference between the cold and heated coatings was bounded by a minimum value greater than  $\Delta E^* = 20$ . This colour change should be easily and safely readable for most of the population. Here, the rule of thumb is that the greater the colour change, the more it is observable to the human eye.

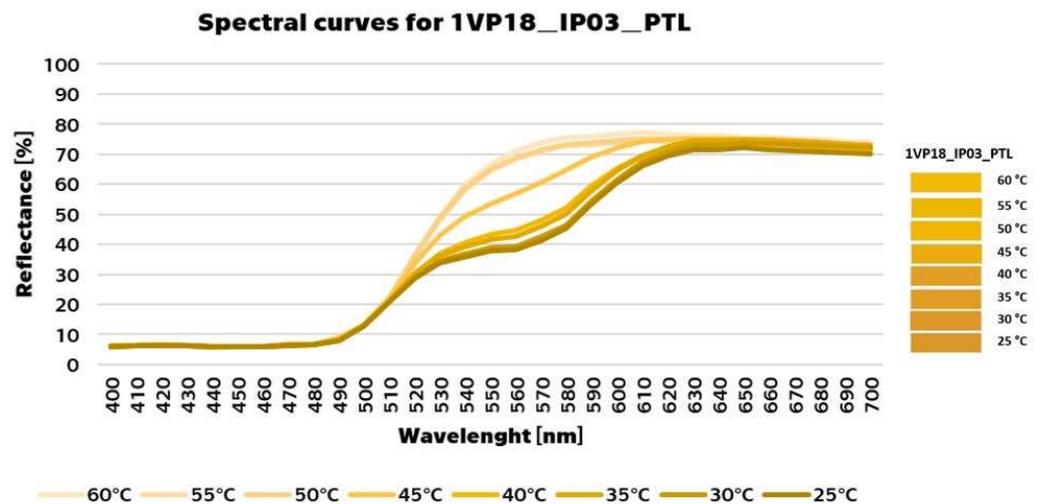
### 3. Results

In Figure 2, the behaviour of samples 1VP18\_IP02\_PTL is monitored, i.e., in the state after three years of exposure. The greatest colour difference can be observed when the samples were cooled to 40 °C. The colour change is easily recognisable; the colour difference between the cold and heated states is  $\Delta E^* = 33$ . This value is more than sufficient to read the colour change without any problems, as shown in Figure 2.



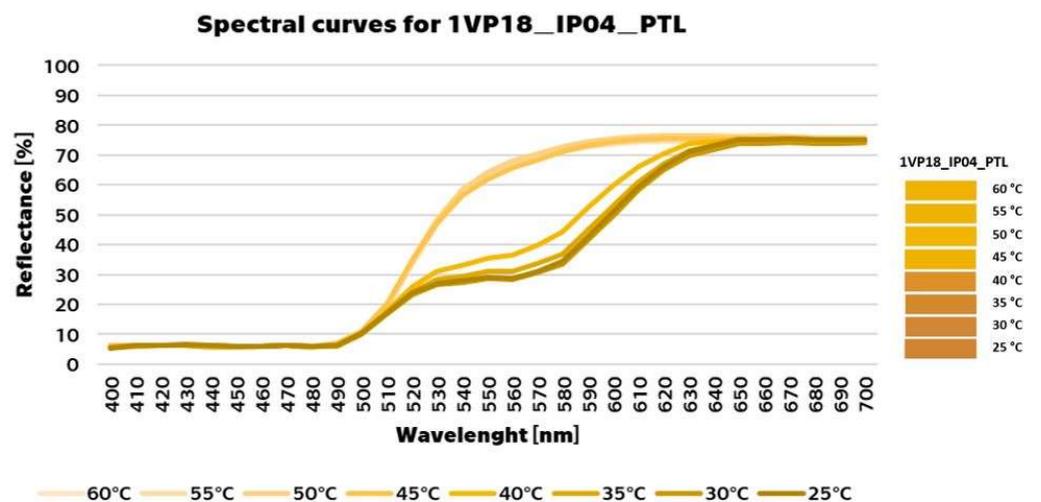
**Figure 2.** Spectral curves of the temperature drop of 1VP18\_IP02\_PTL samples (after three years of exposure) and a visual representation of the colour change.

Figure 3 shows the spectral reflectance curves for the 1VP18\_IP03\_PTL samples. They are characterized by the very gradual visibility of the red thermochromic pigment, with the largest colour difference visible in the 40–35 °C interval. Afterward, there was a slight deepening of the orange hue. This shade has a different characteristic curve compared to IP02 and IP04 and is also the yellowest (on the  $b^*$  axis). The colour difference, which reaches  $\Delta E^* = 23$ , is significant but is the lowest compared to the other samples.



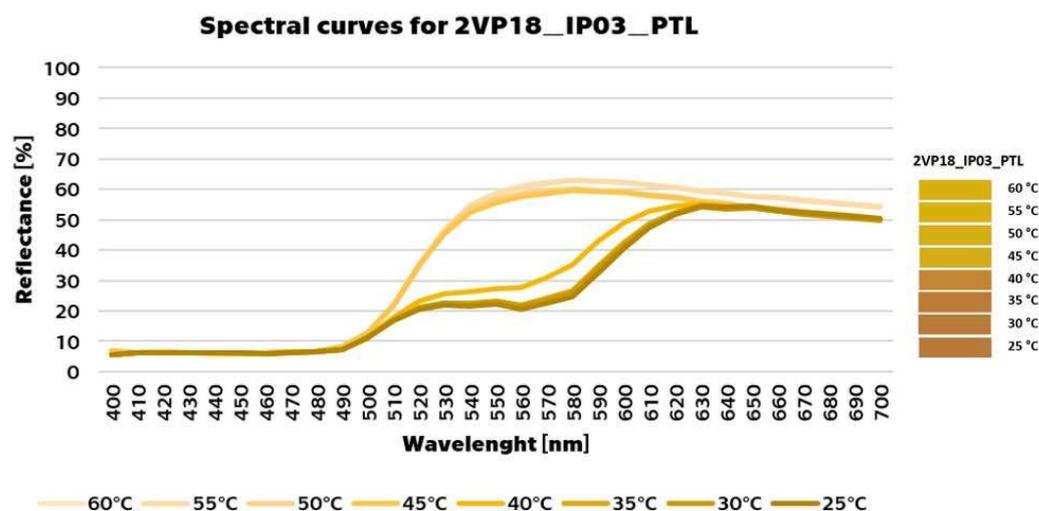
**Figure 3.** Spectral curves of the temperature drop of the 1VP18\_IP03\_PTL samples (after three years of exposure) and a visual representation of the colour change process.

The measurements show that the largest colour difference toward the orange shade can be also observed in the 1VP18\_IP04\_PTL samples (Figure 4) when cooled to 40 °C. This sample behaved stably and had a well-read colour change. In the temperature interval from 45 °C, the colour was characteristically yellow, which detected an elevated temperature. The colour difference is defined by  $\Delta E^* = 31$ , which shows a marked difference between the cold and heated states.



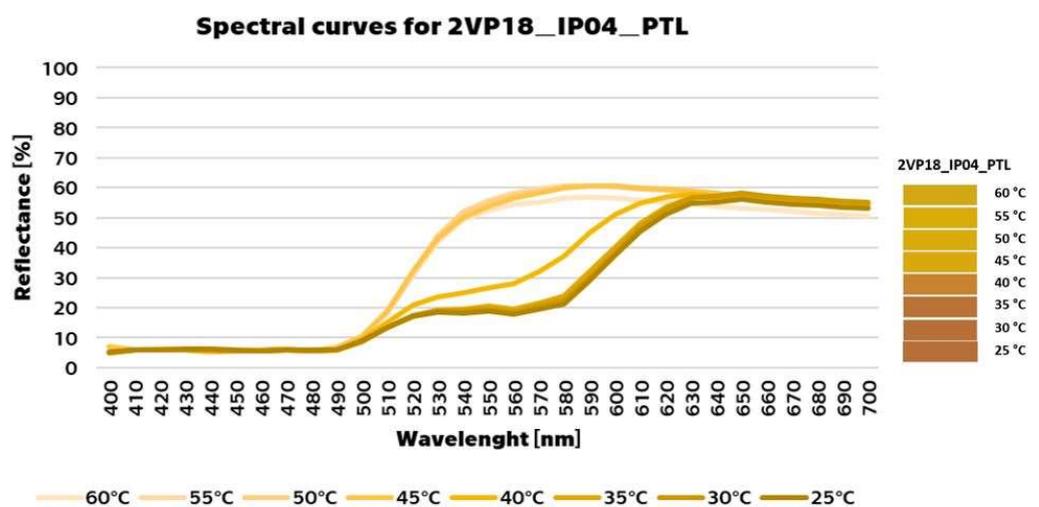
**Figure 4.** Spectral curves of the temperature drop of the 1VP18\_IP04\_PTL (after three years of exposure) samples and a visual representation of the colour change progression.

Figure 5 shows spectral curves for sample 2VP18\_IP03\_PTL. At a temperature of 25 °C, this sample was fundamentally different from those of sample 1VP18. This is due to the coating dispersion method used. Therefore, when the sample was heated, a larger colour difference between the heated and cold samples could be observed ( $\Delta E^* = 37$ ), which contributed to the better readability of the colour change. The transition from yellow to the characteristic brown-orange colour occurred again in the 40 °C range. There was a deepening of the hue afterward. In these samples, we observed a stepwise decrease, in contrast to 1VP18\_IP03\_PTL, where the decrease was gradual. This behaviour change could be attributed to the dispersion method.



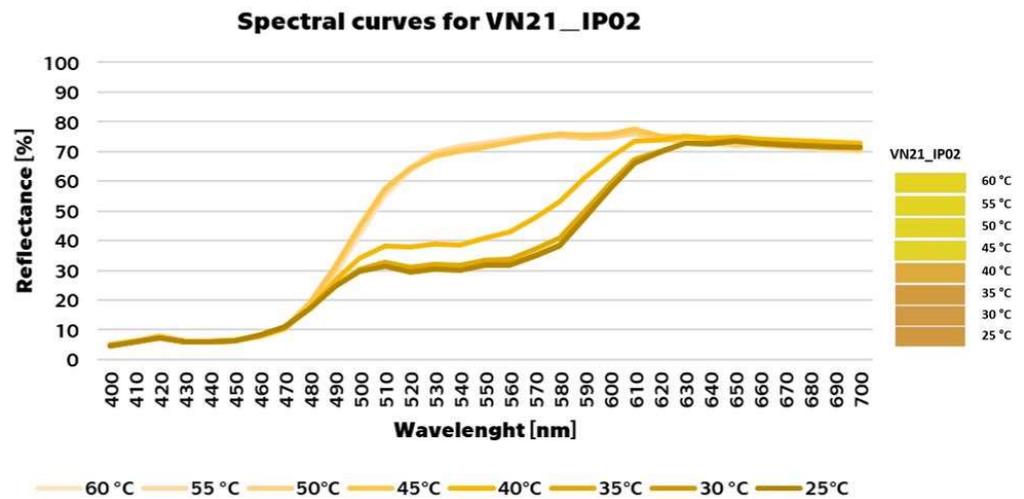
**Figure 5.** Spectral curves of the temperature drop of 2VP18\_IP03\_PTL samples (after three years of exposure) and visual representation of the colour change process.

The character of the curves for the 2VP18\_IP04\_PTL samples (Figure 6) was very similar to the 2VP18\_IP03\_PTL samples with a few minor differences. The colour pattern for 40 °C was redder on the  $a^*$  axis and yellower on the  $b^*$  axis for 2VP18\_IP04\_PTL samples than for 2VP18\_IP03\_PTL samples. The colour difference between the heated and cold states reached values of  $\Delta E^* = 39$ .

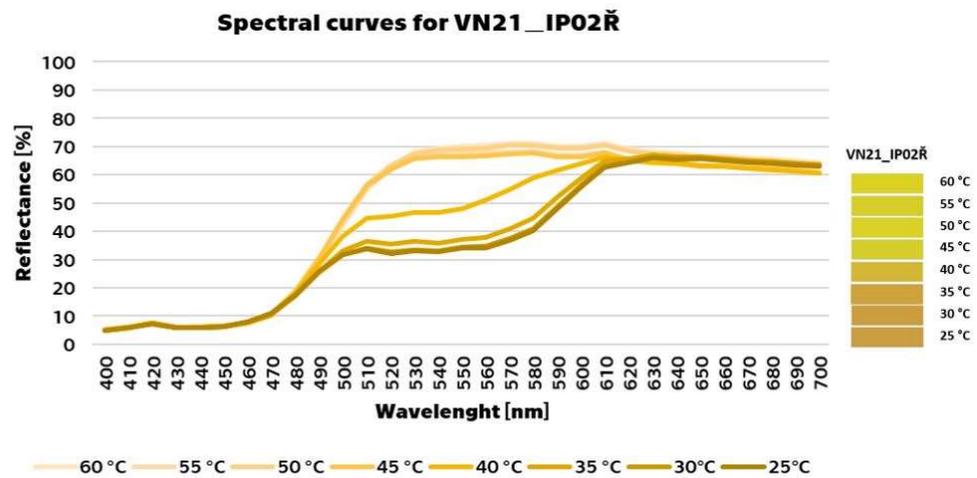


**Figure 6.** Spectral curves of the temperature drop of 2VP18\_IP04\_PTL samples (after three years of exposure) and visual representation of the colour changes.

The spectral curves for samples VN21\_IP02 (Figure 7) and samples VN21\_IP02Ř (Figure 8) were similar in shape at 60 and 25 °C, except that the heated VN21\_IP02Ř sample, which was greener on the  $a^*$ -axis and bluer on the  $b^*$ -axis. The major colour drops in VN21\_IP02 samples toward the original orange hue were evident in the 40 °C temperature curve. However, in the VN21\_IP02Ř samples, the greatest colour difference was only evident at 35 °C. This indicates that the diluent used had a major effect on the regeneration ability of the pigment. Some hydrocarbons could probably disturb the shell of the pigment and damage some components of the thermochromic pigment. It was obvious that there was a large colour difference in cooling, namely at  $\Delta E^* = 39$  for VN21\_IP02 samples and at  $\Delta E^* = 34$  for VN21\_IP02Ř samples.



**Figure 7.** Spectral curves of the temperature drop of VN21\_IP02 samples (resin stored for 3 years) and visual representation of the colour change progression.



**Figure 8.** Spectral curves of the temperature drop of VN21\_IP02R samples (resin stored for 3 years) and visual representation of the colour change process.

Figure 9 shows the spectral curves for VN21\_IP03 samples. The gradual visibility of the red thermochromic pigment during cooling represented a more gradual transition to orange. The largest colour changes to orange occurred at the 40–35 °C interval, but the overall colour difference was not very marked. The characteristic shape of the curve for 25 °C was different from that of VN21\_IP02 and VN21\_IP04, indicating a different (largest difference on the  $b^*$  axis) orange hue. Despite this finding, it can be concluded that the colour difference at  $\Delta E^* = 23$  between the cold and heated states was sufficient.

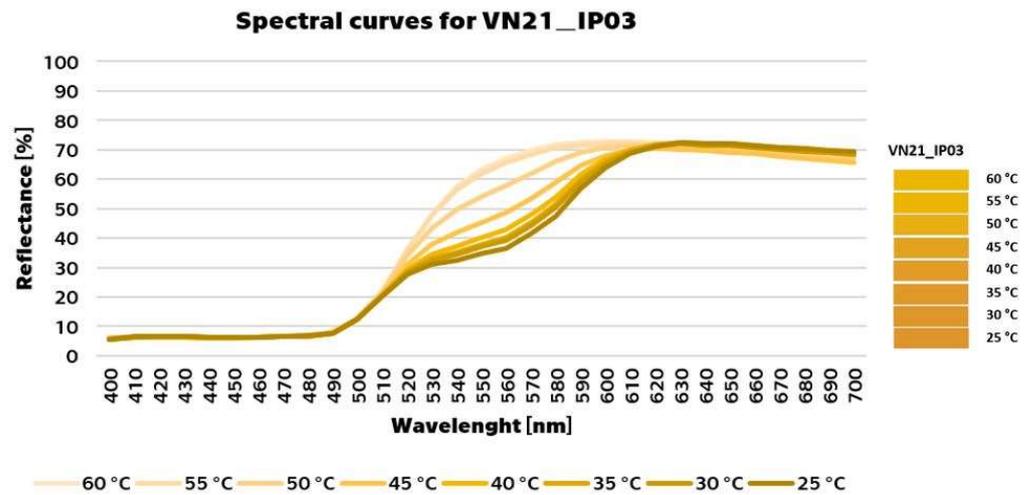


Figure 9. Spectral curves of the temperature drop of VN21\_IP03 samples (resin stored for 3 years) and a visual representation of the colour change process.

In Figure 10, the spectral reflectance curves for the VN21\_IP03Č samples are almost identical for all measurements; these samples are only yellow pigmented (i.e., without thermochromic pigment), so their colour hue does not change. They were included in the measurements mainly to monitor the resistance of the classical pigment at elevated temperatures. The colour difference takes the value  $\Delta E^* = 1$ , which is absolutely minimal and almost imperceptible to the human eye.

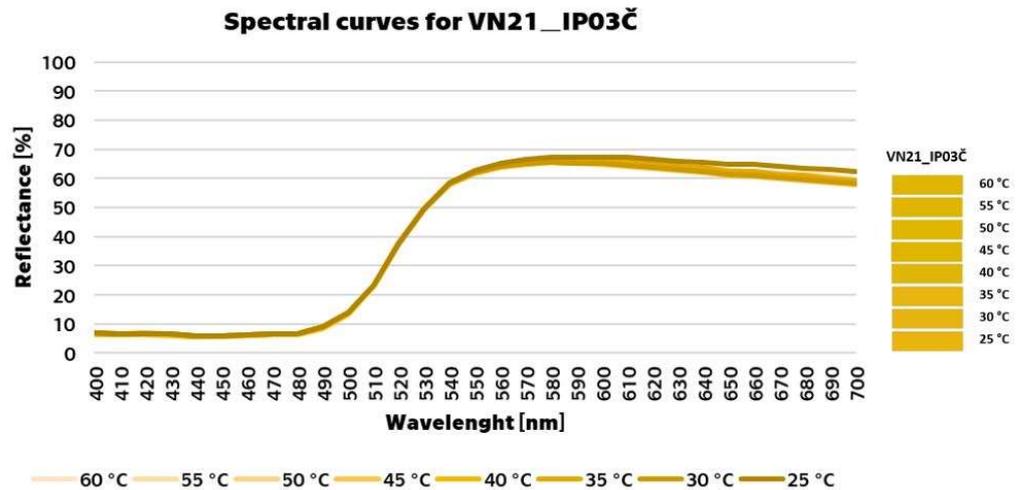
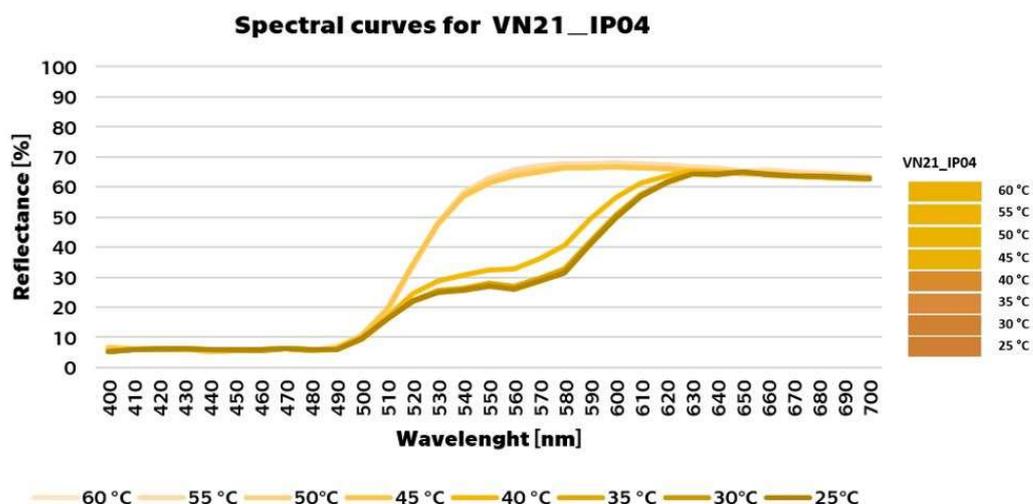


Figure 10. Spectral curves of the temperature drop of VN21\_IP03Č samples (resin stored for 3 years) and visual representation of the colour changes.

In Figure 11, the spectral curves of the VN21\_IP04 samples show a similar trend to the VN21\_IP02 samples, especially in terms of the marked colour difference, which reached  $\Delta E^* = 34$ . The colour change is greatest for the curve that describes the behaviour of the sample at 40 °C. With further cooling, the orange hue deepened.



**Figure 11.** Spectral curves of the temperature drop of VN21\_IP04 samples (resin stored for 3 years) and visual representation of the colour change progression.

#### 4. Discussion

In this work, the behaviour of coatings with thermochromic pigments with a transition temperature in the 47–52 °C range was investigated. A higher transition temperature was chosen for safety applications [29,30], where the shade change must warn against elevated temperature and thus prevent burns. Other research work has looked at pigments with lower transition temperatures, most commonly in the range of up to 28 °C [18,22,24] or 31 °C [16,25,26]. An exception to the higher transition temperature experiments was reported in [5]. For lower transition temperature applications, where there is no risk of burning, it is not required to monitor the curves between the two limit states of heated and cold. In our case, however, it is important to know at what real temperature the transition to the “safe colour” occurs.

The graphical evaluation of the spectral reflectance curves was inspired by the paper [24], where the authors monitored the behaviour of a thermochromic pigment in an epoxy coating. Through a simple representation of the progression of the curves and a visualisation panel that was created by converting the measured coordinates, it was possible to evaluate at which temperatures the coating returned to its original orange hue. In the datasheet, the manufacturer declared the transition temperature of the thermochromic pigment at 47–52 °C. However, measurements showed the greatest colour change in the 40–45 °C interval. These measurements show that the paint matrices used affected the behaviour of the thermochromic pigment by lowering the transition temperature. The dispersion method had no significant effect in this case, and the transition temperature remained similar for both the dispersion methods tested.

This method of measurement is very close to this research [5,20,21], and the results obtained will be compared and discussed. Identical to the result of [5,21], the Lab coordinates of sample VN21\_IP03C (without thermochromic pigment) fluctuated very slightly, while the colour difference between the heated and cold states was not significant. It could also be agreed that the colour difference increased with the increasing temperature and did not change anymore after reaching the transition temperature. The authors [5,20,21] evaluated samples with different contents of the thermochromic pigment; while in this work, the pigment content was stable (5%), the basic coating matrix and the dispersion method changed. While [5] considers that at a thermochromic pigment content of up to 10%, the colour difference is not very marked (up to approximately 8), the authors of [20] evaluated  $\Delta E^*$  for a thermochromic component concentration of 5% with a value of 106, and 110.5 at 10% content. In this work, the colour differences of the coatings in the original state (1VP18, 2VP18), their state after three years of exposure (1VP18\_PTL, 2VP18\_PTL), and comparative samples created from the original coatings (VN21) that were stored in

the liquid state for three years were evaluated. The  $\Delta E^*$  values were in the range of values analysed by both authors [5,20]. The type of coating matrix used was likely to be the main influence, with [5] probably using an alkyd matrix while [20] used a waterborne base. By evaluating the calculated colour difference between the heated and cold samples in all states for IP02 (acrylic polyol), i.e., the original (1VP18\_IP02), after three years (1VP18\_IP02\_PTL) and the new samples (VN21\_IP02), the ratio of  $\Delta E^*$  values was determined to be 34:33:39. Thus, the colour difference decreased slightly with time exposure to the coating, while it increased with storage in the liquid state. These changes were probably due to the ongoing interaction between the individual components of the coating and the thermochromic pigment, while in the liquid medium, these processes occurred with greater intensity. The colour difference for IP03 (waterborne matrix) was in the ratio of  $\Delta E^*$  values 22:23:23, so it increased very slightly. Compared to the second series, where the pigment was dispersed by a rotor-stator device with  $\Delta E^*$  values of 56:37 (2VP18\_IP03: 2VP18\_IP03\_PTL), this difference was very slight. It should be noted here that the method of dispersion by the rotor-stator changed the shade of the coating, which was darker. The colour difference values for IP04 (polyurethane) were in the ratio  $\Delta E^*$  39:31:34 for samples 1VP18\_IP04: 1VP18\_IP04\_PTL: VN21\_IP04. Therefore, there was a decrease in the difference compared to the original state, but this did not affect the legibility of the colour change. The ratios for the second series of coatings took on  $\Delta E^*$  values of 64:39, and a similar trend to that of 2VP18\_IP03 could be observed. Here, it was evident that, in addition to the thermochromic pigment content, the resulting colour difference was influenced by the base matrix used and, above all, by the dispersion method, which could fundamentally change the colour shade and, thus, the overall difference.

Hypothesis: The behaviour of acrylic-based matrix coatings, such as Polyol (IP02), is interesting. The formed coating behaves uncharacteristically from the beginning, which leads to the idea that there are interactions between the matrix and the pigment and, consequently, that the pigment is degraded by a certain component of the base matrix. When heated above the transition temperature, VN21 (a coating formed from three years of stored liquid paint) showed a clear change in discolouration—it was lighter and greener than the standard. The colour difference value also increased due to this phenomenon. The reversible behaviour was slower than the other coatings. It can be demonstrated here that degradation processes took place in the liquid medium when this matrix was used. From the measured spectral reflectance curves, it is usually possible to observe the moment when a leap change in colour occurs. In the case of IP03, which was prepared using a saw tooth stirrer, the graph shows that there was no leap change, and the colour difference was not significant. A gradual colour change is not desirable in this case. Compared to the original hypothesis, i.e., that this matrix would be non-reactive, it can be concluded that some reaction did occur, and the thermochromic pigment did not show a reliable behaviour. The reason why a similar change did not occur in the rotor-stator method of dispersion cannot yet be satisfactorily explained. The IP04 coatings are the most stable and have a large colour difference, which ensures a trouble-free reading of the cold-warm state. No degradation processes have been observed that would fundamentally alter the behaviour of the coatings.

## 5. Conclusions

The measurement of the colour behaviour of thermochromic coatings is one of the fundamental characteristics observed, and it is important for understanding the influence of the underlying coating matrices and their interactions with the thermochromic pigment. Mapping the behaviour over long-time scales allows for a broader insight into the behaviour of these coatings and, through comparison, allows us to better predict the lifetime of a given coating system. For coatings that are stored in a liquid state for a long time and then applied, the observed fluctuating trends depend directly on the coating matrix used. Acrylic polyol (IP02) shows a base matrix–pigment interaction that increases the colour differential and also changes the overall hue in the heated state. Waterborne acrylic (IP03)

is essentially non-reactive. In the polyurethane matrix (IP04), the thermochromic pigment also reacts, with a slight decrease in the overall colour difference.

For thermochromic paints used for safety purposes, it is particularly important to have a sufficient colour difference between the cold and heated states to allow the change in state to be read without problems. This condition was fulfilled for all of the coatings produced, with a greater colour difference for the coatings prepared by the rotor-stator mixer dispersion method.

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