Thermochromic Pigments in Leather Finishing

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Abstract

This study opens up a new issue concerning the potential usage of thermochromic pigment dispersions, which change color depending on temperature. The main objective was to investigate the applicability of thermochromic pigments as an alternative to conventional pigments used in leather finishing process. The thermochromic pigment dispersions were applied in leather finishing in order to obtain the color changing leathers with temperature in a controlled manner and to develop leather finishing recipes with these newly applied pigments. The color change and color-fastness properties of the thermochromic applied leathers were also determined. Accordingly, two thermochromic pigments, providing color change at 15°C and 31°C, were applied at different proportions in the base coat of finishing process. The color measurements of finished leathers – before and after rubbing fastness tests – were performed by Minolta CM-3600d spectrophotometer. The rubbing fastness properties of leathers were examined by Bally Finish Tester 9029 according to TS EN ISO 11640 standard.

Summing up the results, it was determined that the thermochromic applied leathers showed a significant color changing effect depending on temperature. Finished leather fastness properties were found to be adequate compared to conventional finished leathers. The findings suggest that the thermochromic pigments could be used as an alternative to conventional pigments in leather finishing according to leather fashion trends and different designs of leather products.

Keywords: Thermochromism, thermochromic pigments, color change, leather finishing, color fastness.

1. Introduction

The technological innovations and their adaptations in sector are one of the basic elements for achieving and maintaining the competitiveness in international markets. Companies, which realized the importance of technological knowledge, are active in innovations and take advantage from this situation. Today, market conditions are rapidly changing with globalization effect and to meet growing and ever-changing consumer demands becomes more complex. This situation is forcing companies to innovate more. Research and Development (R&D) is one of the most important operations that are required for innovation (Terzioğlu, 2008).

Generally, a competitiveness of the leather sector can be achieved in fashion, education, and technology. Together with the constantly evolving technology, the production of high value-added leather products is very important to ensure the continuity of the current export capacity. Nowadays, the high value-added manufactured leather products, as well as products in many other areas, are result of the R&D activities.

Dyes and pigments, which have the direct impact on the fashion and design, are used in various combinations together with various chemicals in leather finishing process. The variety of combinations can be provided on request with the desired changes and different designs can be developed. Color is an important visually detected element with the emotional impact and provides the background for esthetical experiments. It is obvious that color and pattern have the most significant effect on the original design in the leather production. Because the design has direct influence on competitiveness in the globalized world and, it is very important to create new designs for the latest fashions trends, which can respond to customer demands and can give various functional features to the leather.

In recent years, various commercial applications were performed with dyes that show significant color change, when they are exposed to a variety of external stimuli. This color change can be controlled and reversible. Such dyes are commonly called "chromic materials" and exist in a variety of types (Christie et al., 2007).

A thermochromism is a property when the object changes its color in dependence to the temperature (Periyasamy and Khanna, 2008). Numerous inorganic and organic compounds show the thermochromic behavior. Due to the occurrence of the color change in solution or at high temperatures, inorganic compounds are restricted for textile applications (Periyasamy and Khanna, 2008).

Generally two kinds of thermochromic colorants exist: liquid crystals and leuco dyes. The thermochromic liquid crystals have a limited range of color, a difficult adjustable thermal point for changing color and it is more expensive than other thermochromic dyes. Because of these properties it has limited usage in textile applications (Sen, 2001).

Thermochromic pigments usually consist of three main components: a color former (the leuco dye), a color developer (acid) and a low melting solvent. This system is encapsulated in order to protect itself in subsequent applications (Bamfield and Hutchings, 2010). For microencapsulation of thermochromic systems, two processes are used: complex coacervation and interfacial/in situ polymerization. The most common used systems for microencapsulation of thermochromic dyes are urea or melamine formaldehyde (Aitken et al., 1996).

The pigment is colored in the solid form of the material because in this state there is an interaction between the color former and the developer. Melting of the composite interferes with this interaction, leading to a negative thermochromic effect and to loss of the color (Bamfield and Hutchings, 2010).

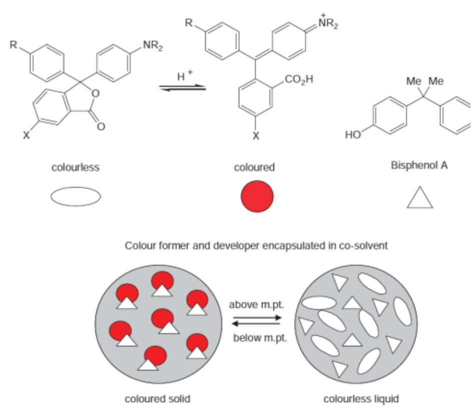

Fig. 1 Thermochromic pigment operation principle (Bamfield and Hutchings, 2010)

Because thermochromic pigments are usually applied in form of discrete solid particles, they are often identified as pigments instead of dyes (Christie et al., 2007).

In this study, the applicability of thermochromic pigments as an alternative to conventional pigments is investigated for leather finishing process. Thermochromic dyes have a considerable potential in area of new fashion leather product developments. In this sense, the usage improvement of thermochromic dye and pigment groups, as well as the traditional dyes and pigments used in leather industry, will give an innovative approach and a creative perspective to the leather industry. Moreover, the color change technology will enable to create unique and assertive design facilities.

2. Materials and Methods

Materials

In this research, crust metis sheep leathers were used and processed in accordance with the production of garment leather. For the color changing effect, a touch-activity (Magenta; TMC Hallcrest Company, UK) and a cold-activity (Blue; TMC Hallcrest Company, UK) thermochromic pigments, providing color change at 31°C and 15°C, were applied at finishing process of leathers.

Methods

In order to ensure the transition from one color to another within the finished products, leathers were dyed with a suitable base colors during dyeing process. Accordingly, one half of leathers were dyed yellow and another half was dyed red. This was performed in order to generate a more visible thermochromic effect.

The conventional pigments, which have same color as base colors, were mixed with thermochromic pigments to generate a more significant thermochromic effect and were applied to the leather in the base coat of the finishing process. In this mixture, three different proportions (25%, 50% and 75%) of thermochromic pigments were used in combination with conventional pigments.

In finishing formulations, the magenta thermochromic pigment was mixed with the conventional yellow pigment at specified proportions for the leathers dyed with yellow base color. When the temperature increases over 31°C under the influence of the body temperature transferred by touch, the thermochromic pigment becomes colorless. In this point, the leather is changing color from orange to yellow.

In addition, blue thermochromic pigment was mixed with conventional red pigment with the same mixing ratio to ensure more visible thermochromic effect for the leathers dyed with red base color. The base color (red) of the leathers appears at temperatures above 15°C due to the activation temperature of the thermochromic pigment. When the leather is cooled or leaved in a cool place (under 15 °C), the thermochromic pigment becomes active and the leather color are passing from red (base color) to claret red.

The color change effect acquired on the leathers has been proved by spectrophotometric measurements performed by Minolta CM-3600d spectrophotometer. Measurements were made according to the CIE Lab color system. These measurements were carried out separately for cold and touch activity leathers. Color effects in leather were observed in dependence to the concentration of used thermochromic pigments. Based on this, optimum doses were detected for the color change effect dependent on the temperature.

The rubbing fastness properties of leathers were examined by Bally Finish Tester 9029 according to TS

EN ISO 11640 standard (100 rubs in dry and 25 rubs in wet). In addition, color measurements were performed and the changes in color measurements were compared before and after the wet and dry rubbing fastness tests.

For the statistical analysis, IBM SPSS 20 package program was used and results were evaluated statistically by Duncan test in a significance level of $p \leq 0.05$.

3. Results and Discussion

The more pronounced color changes were obtained with increasing of thermochromic pigment ratio and therefore, the most obvious thermochromic effect was obtained using 75% of the thermochromic pigment. However, the significant thermochromic effect was observed also in case of 25% and 50% ratio. This observation was made and applies for both; touch-activity and cold-activity leathers.

Obtained color differences of thermochromic pigments in increasing concentrations were determined by calculating of ΔE value. This value has been calculated using Formula 1.

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

ΔE value represents a color difference which is obtained before and after the thermochromic effect. An increase of this value indicates the increase in color difference. Each thermochromic pigment ratio was represented by 3 samples. Three parallel experiments for each sample were carried out and finally all samples were measured in the 10 different regions. Table 1 shows color effects obtained in thermochromic leathers.

Table 1. Color effects obtained in thermochromic leathers

Concentration	**Thermochromic Effect with Touch Activity (ΔE)**	**Thermochromic Effect with Cold Activity (ΔE)**
25	15.71 ± 0.80^{a}	14.93 ± 1.76^{a}
50	24.61 ± 2.71^{b}	28.09 ± 2.07^{b}
75	35.72 ± 1.35^{c}	32.59 ± 3.86^{c}
Blank	0.00 ± 0.00^{d}	0.00 ± 0.00^{d}

Different letters in the same column is (a-d) represent significant differences between the groups ($p < 0.05$), n = 90

Based on obtained statistical data (for both; touch-activity land cold-activity leathers) after dry rubbing tests it was observed that the thermochromic effect significantly persists. This effect was partially reduced after wet rubbing tests, especially in case of cold-activity leathers (Table 2 and Table 3).

Table 2. Obtained color differences before and after dry-wet rubbing fastness test for touch-activity

Touch Activity Leathers When Thermochromic Pigments are in Inactive State		
Concentration	**Dry Rub (ΔE)**	**Wet Rub (ΔE)**
25	0.99±0.63[a]	1.06±0.50[a,b]
50	0.81±0.47[a]	1.20±0.75[b,c]
75	0.92±0.43[a]	0.91±0.74[a]
Blank	2.22±1.27[b]	1.37±0.84[c]
Touch Activity Leathers When Thermochromic Pigments are in Active State		
25	1.16±0.70[a]	1.37±0.87[a]
50	1.02±0.79[a]	1.43±0.97[a]
75	1.46±1.07[b]	2.35±1.39[b]
Blank	2.22±1.27[c]	1.37±0.84[a]

Different letters in the same column (a-c) represent significant differences between the groups ($p < 0.05$), n = 90

Table 3. Obtained color differences before and after dry-wet rubbing fastness test for cold-activity

Cold Activity Leathers When Thermochromic Pigments are in Inactive State		
Concentration	**Dry Rub (ΔE)**	**Wet Rub (ΔE)**
25	0.86±0.48[a]	1.61±0.91[a]
50	0.68±0.36[a]	1.73±1.01[a]
75	1.29±1.02[b]	3.02±1.96[b]
Blank	1.52±1.13[b]	2.14±1.18[c]
Cold Activity Leathers When Thermochromic Pigments are in Active State		
25	1.70±1.10[a]	5.43±2.75[a]
50	2.89±2.50[b]	11.65±5.98[b]
75	4.42±4.27[c]	15.38±8.45[c]
Blank	1.52±1.13[a]	2.14±1.18[d]

Different letters in the same column (a-d) represent significant differences between the groups ($p < 0.05$), n = 90

Figure 2 shows a practical test of the thermochromic effect in case of cold-activity leathers, where the change of leather color is caused by the glass of ice. In similar way, Figure 3 shows the thermochromic effect in case of touch-activity leathers, where the change of leather color appears after touching leather by hand.

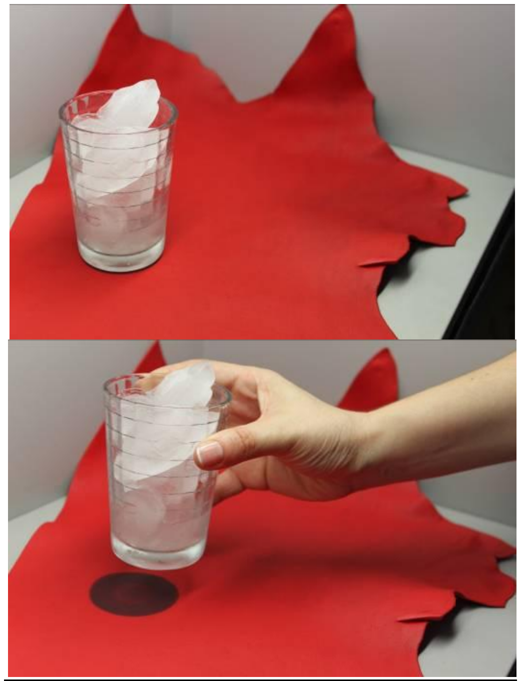

Fig. 2 Thermochromic effect in cold-activity leathers

Fig. 3 Thermochromic effect in touch-activity leathers

4. Conclusion

This research focused on the investigation of thermochromic pigments application as an alternative pigment for finishing process of leather industry. For this aim, applicability of two thermochromic pigments, with cold and touch activity was evaluated and the following conclusions have been drawn.

a) The thermochromic effect increased with increasing thermochromic pigment ratio.
b) The highest thermochromic effect was obtained from 75% application of thermochromic pigment.
c) The thermochromic effect significantly persisted after dry rubbing test.
d) This effect was partially reduced after wet rubbing tests, especially in case of cold-activity leathers.

These findings are strongly important in point of the applicability of thermochromic pigments in leather industry. This research brings to industry a high value-added product for producing a new fashion leathers and provides opportunities for use of the new pigment groups in the leather industry. However, the further development in the rubbing fastness of thermochromic pigments is needed and additional studies are necessary to examine other color fastness. The immediate implementation of these studies is that it enables the longer-lasting leather with the color-changing effect for the production.

5. Acknowledgement

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