Thermochromism for Smart Leathers

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Abstract

The Leather industry globally is poised for enhancing the unit value realization. With availability of raw material remaining more or less constant, conferring customer desired smart properties to leather enhances the value of leather. It is also quite possible that such new features would enable leather to enter unexplored territories such as those envisaged for smarter textiles. An innovation in visual stimulus creates immediate appeal and utility, leading to consumer perception of owning it. A survey of such stimulus-based innovations of immediate appeal to people indicated a preference to thermochromism – a reversible color change influenced by temperature. While such applications are predominantly associated with sensor applications, the same as a concept for leather has not yet emerged. This paper reports synthesis of a rare earth doped transition metal complex that had a color shift from pale pink to dark green in the temperature range of 200 – 210°C. This colorant could be applied through conventional finishing techniques on leather and is envisaged to have applications in safety products such as heat resistant gloves.

Introduction

Color has a huge impact on psychological and social aspects of humans. Leather is not an exception to its influence. Ever since the processing of leather began, color has become an inseparable quality of leather and acts as an enabler to enhance its aesthetic appeal. Chromism, a phenomenon associated with Chroma or color, involves reversible and irreversible changes. These changes can be of several types, commonly named after the stimulus causing the change.[1] For instance some of the chromism known to date include photochromism, ionochromism, electrochromism, gasochromism, solvatochromism, vapochromism, mechanochromism, chromicity through aggregation, thermochromism and other miscellaneous chromisms.[2] Chromism can extend its scope towards a visual stimulus; widening its applicable limit to greater technologies. Among the known chromism, thermochromism has in recent years attracted the attention of both fashion and safety markets. This is probably because of the fact that a heat-induced change of color has wider applications. This property can be incorporated into leather, as there are temperature-based applications in leather.

A chemical process, in which, a compound undergoes reversible or irreversible changes between two states possessing separate absorption spectra is broadly defined as thermochromism. The said compound can be a solid or solution.[1] Amongst the various thermochromic systems, the inorganic thermochromic systems have found applications in paints and crayons for indicating hot spots.[3] Current applications include incorporation into embroidery; weaving threads, transfer papers for thermal printing etc. Thermochromism is considered as a result of any one or several of the following temperature dependent changes: a) crystalline type, b) pH, c) loss of crystalline water from the substance, d) equilibrium movement of electrons between donor and acceptor, e) ring opening reactions in molecules etc.[3]

Based on these considerations, a survey of literature for available thermochromic materials was taken up. Though several options emerged, potential for altering the color values through the use of mixed metal isocyanates was found to be high. For instance, $[LnL_8][Cr(NCS)_6]$, where L is ε-caprolactum belongs to a class of binary complex salts formed from complex cations and anions.[4] One of the possible reasons for the use of caprolactum is the conformation ability of the seven-membered ring, leading to strong disordering of the ligand at room temperature.[5]

Experimental

Materials and Methods

Chrome alum ($KCr(SO_4)_2.12H_2O$), ε-caprolactum, lanthanum(III) chloride, praseodymium(III) chloride, potassium thiocyanate and other chemicals were procured from Sigma Aldrich, USA and used without further purification. For the standardization of the product, milli-Q water was used throughout for the synthesis.

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Synthesis of the Complex

Step 1: Synthesis of $K_3[Cr(NCS)_6]_4H_2O$

The complex was synthesized as per reported reaction given below

$$KNCS + 6KCr(SO_4)_2.12H_2O \longrightarrow K_3[Cr(NCS)_6].4H_2O + 2K_2SO_4$$

Briefly, 500 mg of $KCr(SO_4)_2.12H_2O$ and 584 mg of KNCS was dissolved in 5 ml of distilled water. The solution was stirred (400 – 600 RPM) under heating at 60°C for 2h. The resultant product was air dried placing the same on a hot plate. Obtained flakes were dissolved in ethanol, wherein $K_3[Cr(NCS)_6].4H_2O$ remained soluble in ethanol, while K_2SO_4 precipitated out of the solution, which was subsequently removed by filtration. Evaporation of the ethanolic mixture at 60°C resulted in powder form of $K_3[Cr(NCS)_6].4H_2O$.[6]

Step 2: Synthesis of $[LnL_8][Cr(NCS)_6]$

1 M equivalence of $K_3[Cr(NCS)_6].4H_2O$ from Step 1 was dissolved in 2 mL of distilled water and 8 M equivalence of ε-caprolactum dissolved in 2 mL of distilled water was added and the mixture stirred for 1 min. The pH of the solution was adjusted to 4 – 6. To this solution, 1 M equivalence of $LnCl_3$ dissolved in 1.5 mL of distilled water was added slowly and stirring continued for 5 min or till a semi-solid product was obtained. Though several trials on the variation of Ln by several lanthanides were carried out, this work reports the most successful (Ln = Pr, La). The semi-solid obtained was dried to powder form by treating in an air oven at 80°C and designated as **TP1** and **TP2** (1 for Pr and 2 for La).

Product Characterization

Methods of product characterization included differential scanning calorimetry (DSC) employing a TA Instruments TA-Q200 instrument employing Tzero aluminium hermetic reference pan. Protocol for the measurement was loading 5-10 mg of **TP1** in Al_2O_3 containers and heating it at the rate of 5°C min^{-1} from 0°C to 300°C in nitrogen atmosphere.

Visual assessment of the color change was not possible as easily viable instrumental techniques were not available at hand. An in-house method was developed by employing a custom designed glassware and an oil bath, operatable from RT to 250°C, with a precision of ± 1°C. Figure 1 provides the details of the technique employed. Briefly, a small quantity of **TP1** was uniformly spread on the surface of the glass container and placed inside the oil bath, with adequate care to ensure that hot oil did not penetrate into the glass container. With increasing temperature, the color change of **TP1** was visually monitored alongside recording the same in a high resolution DSLR camera.

For the evaluation of the leathers, change in color of the leather was evaluated by heating the leather surface on an embossing machine. A plain plate was employed in the embossing machine and the temperature was set for 210°C with a pressure of 100 lb f/in^2 for 2 sec. The color values, L, a*, and b* of the finished leathers before and after the heat treatment were determined using conventional CIELAB 1976 color coordinates method and tabulated. Same for **TP2** as well.

Application Trials

TP2 prepared in this study was added as one of the constituent in the finishing formulation and used for finishing of leathers. Chrome tanned undyed (white) goat crust leathers were used for the experiment. Finish formulation in presented in Table I. The formulation was applied on to the undyed crust by padding techniques for evaluation purpose. The leathers were dried and a top coat consisting of 1:1 lacquer emulsion and water was sprayed on to the leather surface in order to fix the formulation constituents to the leather surface. The leathers were dried and evaluated for the thermochromic effect both visually as well as through changes in the color coordinates measured as per the CIELAB 1976 method.

RESULTS AND DISCUSSION

TP1 was a pink colored powder, insoluble in water at room temperature, soluble in a mixture of water and organic solvents. The thermogram of **TP1** and **TP2** obtained from

TABLE I
Finish formulation employed for the study.

Material/Chemical	Quantity (g)	Remarks
TP2	100	Above ingredients were mixed well in water, homogenized and applied
Acrylic resin binder (commercial)	200	
Polyurethane binder (commercial)	100	
Protein binder (commercial)	50	
Plasticizer (commercial)	50	
Dispersing agent (commercial)	25	
Wax emulsion (commercial)	75	
Water	400	

Figure 1. In-house technique developed to understand color changes due to temperature.

differential scanning calorimetric analysis is presented in Figure 2. The thermogram obtained under nitrogen atmosphere present a phase change at around 225°C for **TP1**, while no such significant change was observed in the case of **TP2**. The cooling cycle (negative heat flow) indicated a complete reversibility of the process. The color change was monitored in the in-house designed apparatus as well. Compared to the calorimetric measurements these studies were performed under air atmosphere. The changes in color are presented in the form of color coordinates in Table II. A ΔE value of 47 before and after heating is indication of a complete change of color from pink to blue (as observed), which on cooling back returns to pink (ΔE= 13.1).

It is interesting to note that **TP1** and **TP2** are ionic compounds consisting of $[LnL_8]^{3+}$ cations and $[Cr(NCS)_6]^{3-}$ anions joined together through ionic interactions and NH ….. S hydrogen bonds. All the NH groups of L are likely to be involved in hydrogen bonding – four for NH …… O(L) intramolecular bonding, while the rest form interionic NH…..S(CN) such that each cation is joined to three anions and vice versa. Both La and Pr complexes demonstrated thermochromic properties and reversibly change from pale pink to dark green on heating in air, with complete reversibility observed on cooling. Unlike the case of the DSC measurements carried out in nitrogen atmosphere, under natural conditions the temperature of the start of thermolysis in air was 180°C for La and 200°C for Pr. No weight loss was observed during the process and the reversible color change is most likely due to structural changes in the crystals of the complexes on heating – attributable to the disorder in conformationally flexible seven membered cycles of the ligand.[5,6]

Application of Thermochromic Pigment in Finishing of Leather

TP1 and **TP2** were dried at 80°C to obtain the particles in powder form. In the present study, the prepared pigment was

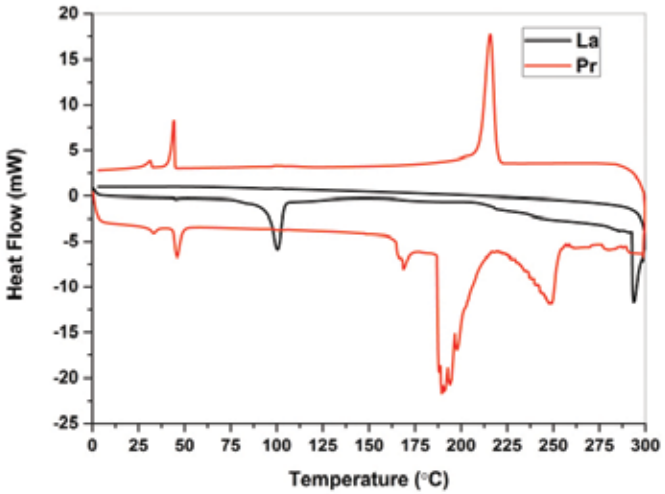

Figure 2. Differential scanning calorimetric investigation of the La/Pr complexes of chromium(III) isothiocyanate.

TABLE II
Color coordinates of the complex before heating to 200°C, at 200°C and after cooling back.

Condition	L*	a*	b*	ΔE	Observed Color
TP2	55	22	-9		
After heating to 200°C	19	-8	-5	47.0	
On cooling to room temperature	65	33	-18	17.4	

employed as replacement to conventional pigment. Compared to **TP1**, **TP2** was easily miscible in the finish formulation and hence employed for further studies.

The color coordinates of the coated leathers prior to heating and immediately after heating are presented in Table III, with corresponding ΔE value calculated as per standard methods being 48.0. A difference figure of 48.0 is indicative of a massive change in color. The corresponding color coordinates on cooling back was more or less same as that of original leather (ΔE value of 13.1), indicating a complete reversibility

of the process. The heating- cooling cycle was repeatable over more than 10 cycles. The produced leather is thus expected to have applications in protective gloves or safety shoes where the color change is an indication of the unsafe environment.

CONCLUSIONS

Chromium isothiocyanate complexes of lanthanum and praseodymium synthesized in this work, found application as a thermochromic pigment ideal for safety shoes and protective gloves. Easily distinguishable change of color from dark pink to near green has been observed at around 200°C, with complete reversibility and repeatability.

TABLE III
Color coordinates of the leather before heating to 200°C, at 200°C and after cooling back

Condition	L*	a*	b*	ΔE (with respect to original)	Observed Color
Finished leather	33	31	-7		
After heating to 200°C	18	-13	5	48.0	
On cooling to room temperature	45	30	-12	13.1	

[1][LaL_8][$Cr(NCS)_6$] complex (**TP2**) as pigment

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