https://doi.org/10.24867/GRID-2022-p14 Original scientific paper

PRODUCTION OF INK CONTAINING THERMOCHROMIC DYESTUFF

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Abstract: *Security inks are functional inks containing a binder and a special colorant used in money, checks and valuable documents. In security inks, thermochromic dyes, UV emitted, infrared emitted dyes can be used. Thermochromic dyestuffs provide different colors at different temperatures and ensure the requirements in the field of security. Thermochromic inks are generally used in smart packaging applications, high temperature alarms and security inks. Thermochromic dyes are generally metal-containing chemical materials.*
In this study, ink will be produced for metal surfaces by using commercial thermochromic dyestuff and it will be provided to act as a temperature warning plate. For this purpose, UV spectra of the thermochromic dyestuff was determinate with different temperature.
Solvent-based ink with polyurethane binder containing 1; 3; 5% commercial thermochromic substance was produced. Screen prints were made on the metal surface with the produced ink. The color and gloss properties of the prints were measured with a spectrophotometer and glossmeter, respectively, at different temperatures. Print quality and surface properties were determined with an optical microscope. In addition, alkali, nitro, acid resistance tests were carried out. The reusability (color change) number was determined depending on how many temperature changes the print has. As a result, inks that change color at 38 °C with commercial thermochromic material were produced and successfully printed.

Key words: security ink, screen printing, UV –Viz. Spectroscopy, printability

1. INTRODUCTION

The reversible coloration that occurs as a result of temperature change is called thermochromism. The color change of thermochromic substances occurs rapidly and at a certain temperature, called the thermochromic transition temperature. Taking advantage of these properties, thermochromic paints are generally used in the textile industry, thermometers, metal surfaces, cosmetics or food packaging application areas (Civan et al., 2021; Arman et al., 2021)
Thermochromic dyes; It is suitable for use on various base materials such as metals, polypropylene, polyethylene, PVC and polystyrene. In this way, color-changing plastics are obtained. Polymers are light, inexpensive, easily shaped and non-corrosive materials. Today, the mechanical and thermal durability of polymers, increasing their resistance to solvents and insulating properties, as well as their conductive properties, have become important. As a result, it has been focused on the conductivity properties of polymers (Arman et al., 2021).
In this study, a polymeric coating was obtained for metal surfaces by using commercial thermochromic dyestuff. The prepared polymeric material was coated on the metal surface and its usability as a warning sign was determined.

2. EXPERIMENTAL

2.1 Materials and Instrumentation

2-hydroxy-2-methylproplophenone NaOH and HNO_3 were purchased from Merck. Aliphatic urethane acrylate resin was obtained MCT chem. Thermochromic dye (TS Orange) 31 was used.
Shimadzu UV-Vis spectrophotometer was used for spectrophotometric measurements.IR spectrums was obtained by Perkin Elmer Spectrum100 ATR-FTIR in the wavelength range 4000-400 cm^{-1}

2.2 Method

2.2.1 Synthesis of UV curable coatings

Thermochromic dye (1,3,5 wt.%), aliphatic urethane acrylate resin (100 wt.%), were added to a round-bottom flask. Manual mixing was done for 3 minutes. Afterwards, an ultrasonic bath was used to ensure homogeneous distribution. Then, the photoinitiators (2-hydroxy-2-methylproplophenone (IRGACURE

2022) were added. The prepared matrix was then poured into a Teflon® mold (10 mm radius circle). After 180 s irradiation under UV light, photocured polymeric coatings were obtained (Aydın Urucu et al. 2020). F1, F3, F5 contain 1, 3, 5 thermochromic dye respectively. Figure 1 shows the production of the polymer coating.

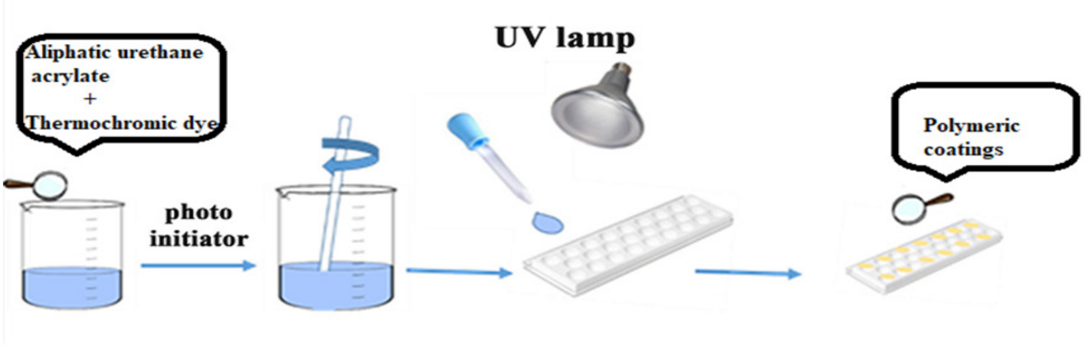


Figure 1: The production of the polymer coating

3. RESULTS AND DISCUSSION

In the IR spectra of the UV curable coatings, the band at around 3348 cm^{-1} is due to the -NH groups of the urethane bond. Urethane carbonyl groups were observed at around 1713 cm^{-1} while the peaks at around 1637 cm^{-1} were attributed to the characteristic methacrylate double bonds. Addition to these, the absence of the -C=C- double bond peak around 1640 cm-1 in the IR spectrum proves that the UV curable coatings were prepared (Figure 2)

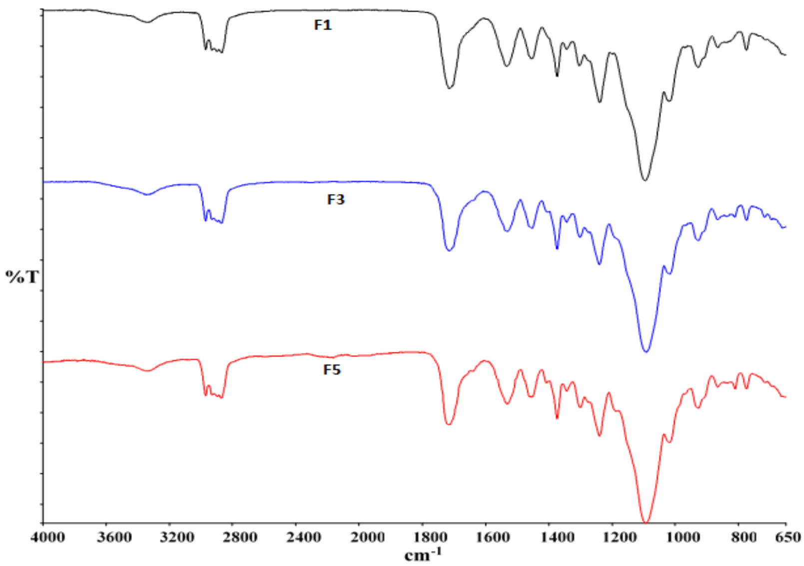


Figure 2: ATR-FTIR spectra of UV curable coatings

The discoloration of the thermochromic polyurethane coating by increasing with temperature was investigated by UV spectroscopy. Figure 3 shows the UV spectrum of the thermochromic polyurethane film at 25 °C and 40 °C. At a temperature of 25 °C, the absorption band due to the orange color of the UV curable coating (F5) gives maximum absorbance at about 520 nm (Figure 3). However, when heated to 40 °C; the color suddenly became transparent and the peak disappeared at 520 nm.

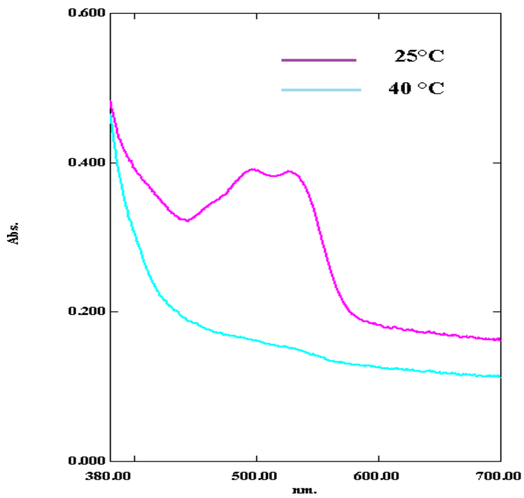


Figure 3: UV absorption spectra of UV curable coating (F5)

Figure 4 shows the colors of UV curable containing at two different temperatures (25℃ and 40 ℃). While the orange color is obvious at 25 ℃, it is observed that the color disappears with increasing temperature. (Contains thermochromic dye in the ratio F1:1%; F2:3%; F3:5%)

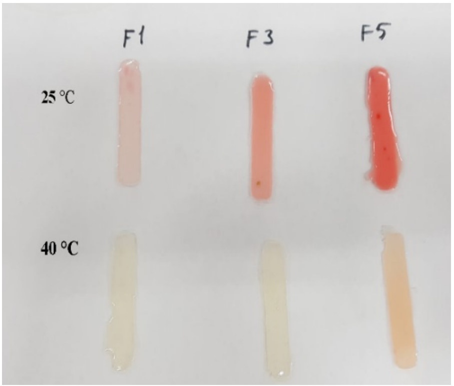
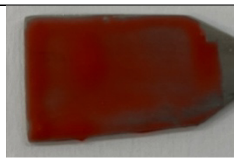


Figure 4: UV curable coating at two different temperatures

For the alkali, acid and alcohol resistance tests of the polymer coating, 1% NaOH, 1% HNO_3 and isopropyl alcohol were used, respectively. It has been observed that the coating is resistant to acid, base and alcohol.

The metal surface was coated with a polymer coating prepared with thermochromic dyestuff and the color values were compared at different temperatures. The results are summarized in Table 1.

Table 1: Color characteristics and glosses of thermochromic prints at different temperature

	L	a	b	Delta E	Gloss	Image
Thermochromic print at 25 °C	21	40	34		14.8	
Thermochromic print at 40 °C	36	5	14	33.74	12.7	

4. CONCULUSION

In this study, a UV curable coating, which can be used as a warning sign, was successfully obtained. According to the color results, it is seen that the color is orange at 45℃, colorless at 25℃, and the color difference was 33.74. While this color change can be clearly observed with the spectrophotometer, it can also be determined very easily with the eye. Thus, an easily recognizable and inexpensive metal warning sign material was produced. The gloss values of the obtained coating are quite high. When the amount of thermochromic dye used in the preparation of the coating material is increased by more than 5%, there are difficulties in its synthesis. Therefore, dyes were used in amounts below the percentage.

5. REFERENCES

Arman Kandirmaz, E. (2021) Fabrication of rosemary essential oil microcapsules and using in active packaging. *Nordic Pulp & Paper Research Journal*. 36, 323 - 330. Available from: doi:10.1515/npprj-2021-0014

Arman Kandırmaz, E., Ozcan A. & Er Ulusoy, D. (2020) Production of thermochromic microcapsulated inks for smart packaging and examination of printability properties. *Pigment & Resin Technology*. 49, 273 – 281.

Aydin Urucu, O., Beyler Cigil, A., Birtane, H., Kok Yetimoglu, E. & Kahraman, M.V. (2020) Selective molecularly imprinted polymer for the analysis of chlorpyrifos in water samples. *Journal of Industrial and Engineering Chemistry*. 87, 145 - 151. Available from: doi: 10.1016/j.jiec.2020.03.025

Civan, L., Kurama, S. & Ayas, E. (2021) Temperature Effect in Thermochromic Pigment Containing Coatings. *International Journal of Engineering Research and Development*. 13 (2), 462 - 477. Available from: doi:10.1016/j.porgcoat.2020.105978