Effect of pigment concentration on fastness and color values of thermal and UV curable pigment printing

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Abstract. In the current study, it is aimed to determine the effect of pigment concentration on fastness and colour values of thermal and ultraviolet (UV) curable pigment printing on synthetic leather. For this purpose, thermal curable solvent-based and UV curable water-based formulations were prepared with different pigment concentrations (3, 5 and 7%) separately and applied by screen printing technique using a screen printing machine. Samples printed with solvent-based formulations were thermally cured and samples printed with water-based formulations were cured using a UV curing machine equipped with gallium and mercury (Ga/Hg) lamps at room temperature. The crock fastness values of samples printed with solvent-based formulations showed that increase in pigment concentration was not effective on both dry and wet crock fastness values. On the other hand, in samples printed with UV curable water-based formulations, dry crock fastness was improved and evaluated as very good for all pigment concentrations. However, increasing the pigment concentration affected the wet crock fastness values adversely and lower values were observed. As the energy level increased for each irradiation source, the fastness values were improved. In comparison with samples printed with solvent-based formulations, samples printed with UV curable water-based formulations yielded higher K/S values at all pigment concentrations. The results suggested that, higher K/S values can be obtained in samples printed with UV curable water-based formulations at a lower pigment concentration compared to samples printed with solvent-based formulations.

1. Introduction
Pigment printing has been widely used in textile printing industry. This is due to the fact that it is applicable to all fiber and fiber blends with easy application and fixation methods [1, 2]. During fixation processes, in order to bind the pigments onto the textile surfaces via binders, dry air at high temperature is used in conventional thermal curing technique, in that, there is no need for complicated equipment and after wash treatment [3-6]. Despite its high energy consumption and cost, conventional thermal curing technique has still been used in textile finishing processes such as coating and pigment printing. Although the pigment printing has been commonly applied in textile industry, the UV curing technique has been rarely used or investigated. Due to its low energy consumption, space saving, short start-up period, fast and reliable curing, UV-curing technology has been utilized in many other industrial applications [2, 7]. Classical thermally curable solvent-based, water-based or powder
coatings consume high energy and particularly, solvent-based systems contain a high amount of organic solvent. On the other hand, UV curable formulations contain very low amount of volatile organic compounds (VOCs) than those of thermal curable. In addition, UV curable formulations contain almost no harmful substances causing air pollution and therefore are accepted as environmentally-friendly. Along with mentioned advantages, UV cured films offer improved abrasion and solvent resistance, and good bonding. In UV curing, the photo initiators release radicals when they are induced by irradiation. This initiates the polymerization of the binder which leads to a crosslinked network of polymers. Irradiation sources can be mercury (Hg) and gallium (Ga) lamps. Particularly, medium pressure Hg lamps provide high power and emission which is absorbed by most of the photoinitiators, whereas Ga lamp is usually used for deep curing. The pigments in UV curable coatings affect the curing behavior of the film, since they scatter or absorb the UV light [10].

Screen printing is a versatile printing technique since it is applied onto various types of substrates such as paper, plastics, textiles, etc. with different size and thickness [11]. In this study, for the first time, pigment printing on a polyurethane based synthetic leather using a water based UV curable polyurethane acrylate binder will be applied by screen printing technique. The study will focus on the effect of different pigment concentrations on fastness and color values of thermally and UV cured printed samples. The results will show the potential use of water based UV curable formulations as an alternative to traditionally applied solvent-based thermal curable formulations in printing on polyurethane based synthetic leather.

2. Experimental

2.1. Materials
Polyurethane (PU) based synthetic leather samples (Flokser Tekstil, Turkey) with a mass of 545 g/m², were used as they are supplied. PU (Dincerler Tekstil, Turkey), dimethylformamide (DMF) (Kimetsan, Turkey) and toluene (Tekkim, Turkey) were used for the preparation of the solvent-based thermal curable pastes. In the preparation of UV curable water based printing pastes, a flexible, water based, aliphatic PU acrylate resin (Laromer® UA 9059) was used as the binder and bisacyl phosphine (Irgacure® 819 DW) and α-hydroxyketone (Irgacure® 500) were used as the photoinitiators. In addition to binder and photoinitiators, wetting agent (Exosel 54, Acar Kimya, Turkey), defoamer (Foamaster® 8034, BASF), thickener (Orgal P 460, Organik Kimya, Turkey) deionized water and ammonia solution (NH₄OH) were used in the formulation. In order to compare the color values, a red pigment (Irgazin® Red K 3840, BASF) compatible with both solvent-based and water-based systems was used in both thermal curable solvent and UV curable water based formulations.

2.2. Method

2.2.1. Preparing of solvent-based and water based printing pastes. Thermal curable solvent-based and UV curable water-based formulations were prepared with different pigment concentrations (3%, 5% and 7%) separately and applied by screen printing technique using a flat screen printing machine (Rapid Tag, ASPE) and a screen having mesh number of 62. Solvent-based pastes were prepared according to a commercial formulation as given in Table 1. The viscosity and pH of the solvent-based paste was measured as 6.8 and 1600 cP (at 30 rpm with spindle 3) respectively. The samples were cured at 150 °C for 120 s.
Table 1. Solvent-based printing formulation.

| Materials                           | Ratio (%) |
|-------------------------------------|-----------|
| Solvent-based PU binder             | 50        |
| DMF                                 | 25        |
| Toluene                             | 25        |
| Pigment (Irgazin® Red K 3840)       | 3%, 5% and 7% |

In the preparation of water-based printing pastes, aliphatic PU acrylate resin (Laromer® UA 9059) was used as the binder. Bisacyl phosphine (Irgacure® 819 DW) and α-hydroxyketone (Irgacure® 500) were used as the photoinitiators, which are responsible for initiating the polymerization through formation of free radicals during UV curing, were used. In addition to binder and photoinitiators, pigment, wetting agent, defoamer, deionized water and ammonia solution (NH₄OH) were used in the formulation. The pH and the viscosity of the printing paste were adjusted to 8.0 - 9.0 and 20,000 - 25,000 cP (at 20 rpm, with spindle 6), respectively. The formulation of UV curable water based printing pastes were prepared as given in Table 2. Samples printed with UV curable water based pastes were cured at room temperature using a UV curing machine (Raycon®), equipped with Ga and Hg lamps and a conveyor belt with an adjustable speed. UV curing of printed samples was conducted at 3 energy levels (60, 90 and 120 W/cm) at a belt speed of 10 m/min under different UV lamp combinations (Hg, Ga, GaHg, GaGaHg). Total applied energy amount was determined with a UV-Integrator Type D radiometer. The applied energy and the UV lamp combinations are given in Table 3.

Table 2. Water-based printing formulation.

| Materials                           | Quantity (%) |
|-------------------------------------|--------------|
| Deionized water                     | 26           |
| Binder (Laromer® UA 9059)           | 66           |
| Photoinitiator (Irgacure® 500)      | 1.8          |
| Photoinitiator (Irgacure® 819 DW)   | 1.8          |
| Pigment (Irgazin® Red K 3840)       | 3, 5 and 7   |
| Thickener (Orgal® P 460)            | 2.63         |
| Wetting agent                       | 0.49         |
| Defoamer                            | 0.1          |
| Ammonia                             | 0.33         |
Table 3. UV lamp combinations and amount of total applied energy.

| Lamp source | Hg  | Ga  | GaHg | GaGaHg |
|-------------|-----|-----|------|--------|
| Energy level (W/cm) | 60  | 90  | 120  | 60     |
| Applied energy (mj/cm²) | 90  | 60  | 120  | 90     |
| Applied energy (mj/cm²) | 120 | 60  | 120  | 90     |
| Applied energy (mj/cm²) | 60  | 90  | 120  | 120    |

The crock fastness tests were performed according to ISO 105-X12 Textiles-Tests for Colour Fastness standard in a James H. Heal crockmeter. The color parameters of the printed samples were evaluated with X-Rite Color i5 spectrophotometer. The crock fastness and colour values of water-based UV cured and solvent-based thermal cured printed samples were compared.

3. Results and Discussion

3.1. Crock fastness and color values of printed samples with solvent-based thermal cured formulations

The synthetic leather samples printed with solvent-based thermal cured (at 150 °C for 120 s) formulations are shown in Figure 1. Their dry and wet crock fastness results are shown in Table 4.

![Figure 1. Photographic images of printed synthetic leather samples (SB: solvent-based paste, P: pigment).](image)

Table 4. Crock fastness results (SB: solvent-based, P: pigment)

| Sample | SB (P3%) | SB (P5%) | SB (P7%) |
|--------|----------|----------|----------|
| Dry    | 3        | 3        | 3        |
| Wet    | 3/4      | 3/4      | 3/4      |

The crock fastness values of samples were evaluated as 3 and 3/4. The results suggested that the increase in pigment concentration was not effective on both the dry and wet crock fastness values. The color measurement test results of the printed samples are shown in Table 5.
According to the color measurement results, with the increase in pigment concentration, L* (lightness-darkness) value decreased while a* (redness-greenness) value increased and b* (yellowness-blueness) value decreased. Moreover, K/S (color strength) value increased with increased pigment concentration. The maximum K/S value of 10.61 was obtained for 7% pigment concentration.

Table 5. Color values of printed samples at 500 nm (SB: solvent-based, P: pigment)

| Sample     | L*    | a*    | b*    | K/S |
|------------|-------|-------|-------|-----|
| SB (P3%)   | 44.56 | 53.58 | 33.35 | 10.33 |
| SB (P5%)   | 44.48 | 53.88 | 33.03 | 10.58 |
| SB (P7%)   | 43.76 | 54.84 | 32.65 | 10.61 |

3.2. Crock fastness and color values of printed samples with water-based UV curable formulations

Photographic images of the UV cured printed synthetic leather samples with pigment concentration of 3% are shown in Figure 2. The wet crock fastness results are given in Table 6. Dry crock fastness was evaluated as 4/5 for all pigment concentrations.

Increasing the pigment concentration affected the wet crock fastness values adversely and lowered the values to 1/2. However, as the energy level increased for each irradiation source, the fastness values improved. These results can be explained by the fact that at higher concentrations, pigment in the formulation absorb more UV-light, competing and consequently hindering the formation of the free radicals which are responsible for polymerization reaction of the binder [2, 12]. Thus the curing level of the binder decreases which leads to poor fixation of the pigments on the synthetic leather surface. The highest wet fastness values (3, 3/4) were obtained at a pigment concentration of 3%.

Figure 2. Photographic images of synthetic leather samples printed with UV curable water-based formulation having a pigment concentration of 3%.
Table 6. The wet crock fastness test results (WB: water-based, P: pigment).

| Lamp source | Hg  | Ga  | GaHg | GaGaHg |
|--------------|-----|-----|------|--------|
| Energy level (W/cm) | 60  | 90  | 120  | 60  | 90  | 120  | 60  | 90  | 120  |
| Applied energy (mj/cm²) | 186 | 287 | 497  | 288 | 439 | 731  | 444 | 679 | 1166 | 630 | 966 | 1663 |
| WB (P3%) | 2   | 2/3 | 3/4  | 2/3 | 3   | 3/4  | 2/3 | 3   | 2/3  | 3   | 3/4 | 3/4 |
| WB (P5%) | 1/2 | 2/3 | 3    | 2/3 | 3   | 3/4  | 2/3 | 3   | 2/3  | 3   | 3   | 3   |
| WB (P7%) | 1/2 | 2   | 2/3  | 2   | 2   | 3/4  | 2/3 | 2   | 2/3  | 3   | 3   | 3   |

Table 7. Color values of printed samples at 500 nm (WB: water-based, P: pigment)

| Lamp source | Hg  | Ga  | GaHg | GaGaHg |
|--------------|-----|-----|------|--------|
| Energy level (W/cm) | 60  | 90  | 120  | 60  | 90  | 120  | 60  | 90  | 120  |
| Applied energy (mj/cm²) | 186 | 287 | 497  | 288 | 439 | 731  | 444 | 679 | 1166 | 630 | 966 | 1663 |
| L* | WB (P3%) | 44.62 | 44.72 | 44.79 | 44.67 | 45.05 | 44.81 | 44.89 | 45.02 | 45.24 | 44.8 | 44.76 | 45.1 |
|   | WB (P5%) | 43.62 | 44.06 | 43.87 | 43.78 | 43.66 | 44.22 | 44.4  | 44.12 | 44.08 | 44.11 | 44.08 | 44.06 |
|   | WB (P7%) | 43.64 | 43.54 | 43.69 | 43.48 | 43.96 | 43.81 | 43.38 | 43.54 | 43.75 | 43.28 | 43.38 | 43.37 |
| a* | WB (P3%) | 53.25 | 53.21 | 53.52 | 53.41 | 53.61 | 53.75 | 53.79 | 53.82 | 53.88 | 52.88 | 53.21 | 53.56 |
|   | WB (P5%) | 53.92 | 53.94 | 54.13 | 54.02 | 53.77 | 53.58 | 53.7  | 53.45 | 53.56 | 53.69 | 53.77 | 53.64 |
|   | WB (P7%) | 54.95 | 54.76 | 54.7  | 54.96 | 55.03 | 55.03 | 54.99 | 54.94 | 54.98 | 54.9  | 54.78 | 55.19 |
| b* | WB (P3%) | 34.79 | 34.53 | 34.47 | 34.69 | 33.66 | 34.84 | 34.93 | 34.86 | 34.23 | 34.65 | 34.55 | 34.88 |
|   | WB (P5%) | 33.68 | 34.15 | 34.25 | 33.66 | 33.79 | 33.91 | 33.72 | 33.64 | 33.86 | 33.85 | 32.88 | 33.27 |
|   | WB (P7%) | 32.55 | 32.61 | 33.24 | 32.75 | 33.08 | 33.13 | 33.51 | 33.3  | 33.87 | 32.1  | 32.4  | 32.8  |
| K/S | WB (P3%) | 10.62 | 10.72 | 10.84 | 10.67 | 10.69 | 10.86 | 10.59 | 10.64 | 10.66 | 10.21 | 10.36 | 10.59 |
|    | WB (P5%) | 10.77 | 10.8  | 10.91 | 10.84 | 10.88 | 10.92 | 10.8  | 10.83 | 10.96 | 10.64 | 10.66 | 10.99 |
|    | WB (P7%) | 11.06 | 11.21 | 11.35 | 11.02 | 11.23 | 11.88 | 11.3  | 11.66 | 11.71 | 11.82 | 11.83 | 11.94 |
Color values of printed samples for different pigments concentrations (3, 5, 7\%) are shown in Table 7. Similar to the results obtained with thermal cured solvent-based samples, with the increase in pigment concentration the value of L* decreased, while the value of a* increased and the value of b* decreased. Moreover, K/S values increased with the increase in pigment concentration. In case of single or combined use of Ga and Hg lamps, K/S values increased as the total amount of applied energy increased during curing. This trend was not observed for L*a*b* values.

4. Conclusion
In comparison with solvent-based thermal cured samples, the water-based UV cured samples yielded higher K/S values at all pigment concentrations. In samples printed with thermal cured solvent-based formulations, maximum K/S value of 10.61 was obtained in 7\% pigment concentration, whereas maximum K/S value at the same pigment concentration was measured as 11.94 for samples printed with water-based UV curable formulations at high energy levels under UV lamp combinations. In addition, the maximum K/S value obtained at 7\% pigment concentration in solvent-based formulation could be achieved with only 3\% pigment concentration with water-based formulation. The increase in pigment concentration led to a decrease in L* values in both water and solvent-based formulations.

Crock fastness results showed that, for all pigment concentrations, dry crock fastness value of 3 was obtained with solvent-based thermal cured formulations. On the other hand, for water-based UV curable formulations dry crock fastness values of 4/5 were obtained. Dry crock fastness values were not affected by the lamp combinations or increase in applied total energy. These results showed that samples printed with water-based UV curable formulations had better dry crock fastness than samples printed with solvent-based thermal cured formulations.

Wet crock fastness value of 3/4 was obtained with solvent-based thermal cured formulations for all pigment concentrations. Wet crock fastness results of water-based formulations indicated that, increase in pigment concentration led to a decrease in fastness values. However, as the energy level increased, an improvement in fastness values was observed for each combination of lamps. The highest wet crock fastness value of 3/4 was observed at high energy levels. In order to improve the wet crock fastness values, curing should be applied at higher energy levels for UV curable formulations. According to the results, since GaGaHg combination yielded the same fastness values with GaHg combination, at 3\% pigment concentration, the use of GaHg combination is suggested for curing of water-based formulations for energy efficiency.

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