PRODUCTION AND PRINTING OF SOLVENT-BASED FLUORESCENT INK FOR USING IN ANTI-COUNTERFEITING DOCUMENTS

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Abstract: *Security inks are used in areas such as money, expensive products, identity cards, passports. Generally, they are more expensive than conventional inks. A good security ink is expected to be fairly inexpensive and non-replicable. Pigments used in security ink are usually produced from rare earth elements. It is very difficult to produce ink from rare earth elements and high performance ink carrier systems are needed. There is no need for special carrier systems to produce ink from organic fluorescent pigments, and they allow cheaper ink production while reducing reproducibility. In this study, it is aimed to produce ink using organic-based fluorescent pigment. For this purpose, solvent-based ink formulations containing commercial solvent based organic fluorescent blue pigment in different ratios were prepared with polyurethane resin. The prepared inks were printed on the paper surface with the inkjet printing system. The colour properties of the prints obtained were determined under daylight and UV light. In addition, the gloss, adhesion, abrasion resistance, light fastness and drying times of the prints were determined. As a result, it has been determined that the ink produced is transparent in daylight, has a blue glow in UV light and can be used as a security ink in valuable documents.*

Keywords: security ink, fluorescent, anti-counterfeiting, printability.

1. INTRODUCTION

Due to the fact that counterfeiting creates economic problems in our age, security inks appear in many areas, both in government institutions and in the private sector (Kumar et al., 2014). Security inks are used in tamperable counterfeit products such as money, checks, stocks, passports, special drugs. Security inks are an additional security parameter used to prevent the duplication of valuable documents, packaging, labels or end products and to protect them against counterfeiting (Muthamma et al., 2021). Many security inks can be produced depending on the printing technique, the product to be used, the security level and the purpose of use. Due to the reasons such as the pandemic in recent years, increasing internet and technology use, the security printing market, which is growing day by day, is becoming more diverse every day to meet the needs (Schell, 1988).
When security printers are considered, two basic raw materials emerge. These; substrates and inks (Chambers et al., 2015). When examined in terms of printing materials, the most widely used products are papers, polymeric materials and cardboard (Warner & Adams, 2016). New and different features can be added to some substrates as safety parameters. Most countries moneys are made of heavy paper from cotton fibres, in some cases flax or specially coloured or forensic fibres are added to the paper to give it individuality and protect against counterfeiting. In some countries, extra security parameter is gained by adding money polymeric small frames (Spiridonov et al., 2018).

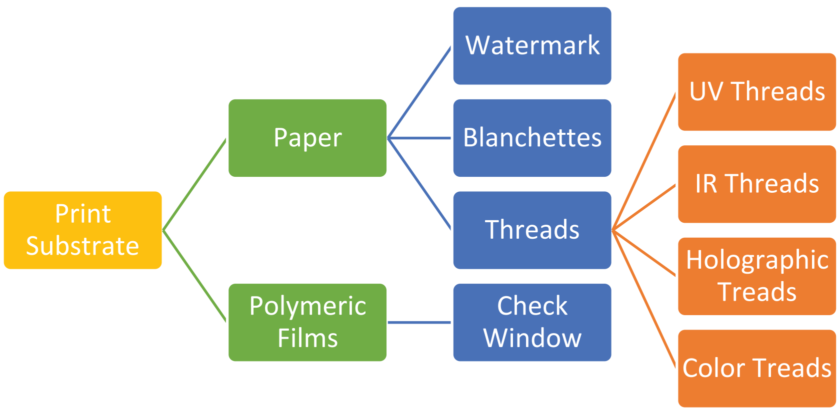


Figure 1: Substrates used in security printing

Another material used in security printing is inks and top-varnishes. Security inks are used in many areas where it is desired to prevent counterfeiting, from labels to money, from the pharmaceutical industry to packaging. In addition to security inks, it directs the studies in this field in top-coat varnishes. Many different types of security inks are produced to meet market needs. Although inks that do not make visible radiation to the visible region but become visible in the UV region are most commonly used, there are many security inks such as hologramic, thermochromic, photochromic, magnetic, etc. that glow in the IR region (Reardon, 2008).

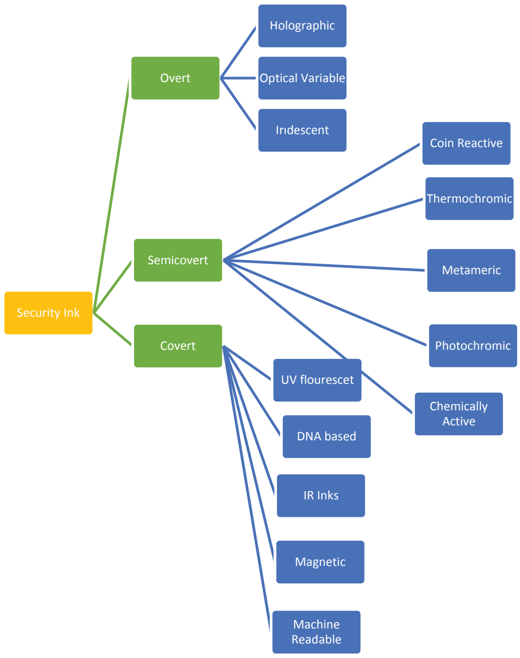


Figure 2: Inks used in security printing

Microtext, Guilloches patterns, Void pantographs, Prismatic colour, Digital watermarks, Fake watermarks are used during the design to try to prevent counterfeiting (Bozhkova et al., 2017). There is a wide variety of technologies used to ensure the security of printing materials. The main industrial printing processes are offset lithographic printing, flexography, intaglio printing and screen printing.
Traditional anti-counterfeiting Technologies and materials are expensive, complex and can be easily copied. Hence, it is a significant challenge to develop a kind of anticounterfeiting label that is cost-effective and hard to duplicate (Feng et al., 2022). Stimulus-reactive fluorescent materials from security materials are frequently used in counterfeiting due to their unique backscattering properties. Organic materials with fluorescent properties absorb light of lower wavelengths and backscatter at higher wavelengths. These can be used alone in inks or mixed with various pigments to produce inks (Ramanna et al., 2017).
In this study, it is planned to prepare and print inkjet ink using solvent based fluorescent blue pigment. Thus, we aimed to determine the quality parameters in order to produce anti-counterfeiting security ink and to use it in different areas.

2. METHODS

2.1 Materials

The colorant used in the study, which emits blue in the UV region, was obtained from Tüver Pigment (Istanbul-Turkey). Solvent-based polyurethane resin suitable for ink was obtained from İldeş Kimya AŞ (Gebze-Turkey). With the produced inks, prints were made on 80 g/m^2 white office paper. The technical specifications of the paper are given in Table 1.

Table 1: Technical specifications of 80 g/m² white office paper

	Standard	Paper
Grammage (g/m²)	ISO 536	80
Thickness (µm)	TAPPI T411	189
Whiteness (D65/10) (%)	ASTM E313	97
Gloss (75°)	ISO 8254-1	5.7
Yellowness	ASTM E313	0.08

2.2 Ink production

Polyurethane binder and isopropyl alcohol solvent inkjet printing inks were produced in the formulations shown in Table 2. Before the ink is produced, the polyurethane-isopropyl alcohol-dispersant mixture is prepared as the ink dispersant phase. Different amounts of commercial UV-radiating colorant were added to the mixture obtained. It was mixed with a butterfly type high-speed mixer at 750 rpm for 10 min, and isopropyl alcohol was added slowly until the viscosity was adjusted for 20 sec. As soon as the created inks were prepared, they were directly printed (Ozcan & Kandirmaz, 2020).

Table 2: Inkjet ink formulation

Ingredients	Purpose of usage	Quantity %
UV irradiating colorant	Effect substance	F1: 0.5 F2: 1 F3: 2.5
Polyurethane resin	Forming the dispersant phase for the colorant and giving it physicochemical properties	15
Dispersant	Stabilizing the colorant in the resin	2.5
Isopropyl alcohol	Adjusting the viscosity	Balance to 100
	Total	100

2.3 Printing of obtained ink

The obtained inks were printed on the 80 g/m² office paper surface as a background with the BENTSAI BTHH 6105 handheld thermal inkjet printing machine. The colours of the prints obtained were measured by X-Rite eXact portable spectrophotometer, gloss measurements were measured with BYK Gardner gloss measuring device at an angle of 60° according to ISO 8254-1. Colour differences were calculated according to the CIELab (1994) technique. The prints were subjected to the light fastness test to determine how the colour would change over time in the ground prints. In the light fastness test, all prints made with a blue wool scale were kept in a UV light cabinet for 192 hours, the initial and final CIELab values were measured and how much the colour changed according to BS4321.

3. RESULTS

Inkjet printing security inks were successfully produced with using different ratio radiant in the UV region dyestuff, polyurethane binder and isopropyl alcohol. The produced three inks were printed on the paper surface as a solid tone with inkjet printing. The colours of the prints were measured by X-Rite eXact portable spectrophotometer. Table 3 shows the CIELab values, gloss and visual samples of the prints under daylight.

Table 3: Colour characteristics and glosses of security prints under daylight

	L	a	b	ΔE	Gloss	Image
Base paper	95.46	2.41	-9.32		5.8	
F1 Ink's Print	97.28	2.67	-9.45	1.31	12.6	
F2 Ink's Print	96.83	2.84	-9.43	0.98	12.3	
F3 Ink's Print	96.27	2.96	-9.40	0.88	12.1	

When the colour measurements made under daylight are examined, it has been observed that the L value has increased slightly in inks containing UV-radiating dyestuff, which is the safety parameter in the ink formulations prepared when the base paper without dyestuff is taken as reference. This is due to the ink resin. However, as the amount of active substance in the content increases, there is a slight decrease in the L value, which is due to the fact that the solid UV-radiating substance in the ink creates a slight roughness on the surface. Similar results are supported by brightness measurements. In addition, when ΔE colour differences are examined in Table 3, it is seen that the colour differences of all inks are below the visible limit. In addition, the slight blue shift caused by the ink binder was tolerated by the increased UV active substance, thus decreasing the ΔE. The colour and gloss characteristics of the prints obtained were measured under UV light and the results are given in Table 4.

Table 4: Colour characteristics and glosses of security prints under UV light

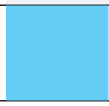
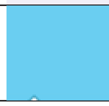
	L	a	b	Gloss	Image
Base paper	95.46	2.41	-9.32	5.8	
F1 Ink's Print	87.59	-21.02	-22.39	15.49	
F2 Ink's Print	83.21	-25.10	-27.85	15.20	
F3 Ink's Print	78.09	-33.39	-34.17	14.86	

When the prints were placed under UV light and the colour properties were examined, it was seen that the colour changed completely and took on a blue colour. All of the L, a, and b values have changed in the negative direction. When the colour was examined, the colour became darker as the amount of UV active substance increased. Gloss, on the other hand, increased according to its values under daylight. This is due to the optical banishing effect. As in the measurements under daylight, there was a small decrease in the gloss as the UV active substance increased.

Prints made with ink with the highest concentration of dyestuff were selected from the obtained inks, and the adhesion, abrasion resistance, light fastness and drying times of the prints were determined.

Lightfastness test was applied to print according to BS4321 and colour differences were calculated. ΔE values are given in Table 5.

Table 5: Color changes of UV reflective prints with lightfastness test

	ΔE	Blue wool scale color change	Image before light fastness test	Image after light fastness test
F3 Ink's print under daylight	3.04	7		
F3 Ink's print under UV light	1.2	8		

When the light fastness results are examined, it is seen that the colour changes slightly under daylight, and the change is towards yellow. This can be explained by the formation of yellowing due to the breakage of the double bonds in the ink by daylight. When examined under UV light, it is seen that the color difference decreases. It has been determined that the UV active pigment already has open double bonds, so the color changes less. It has been concluded that the ink is suitable for the application and has high color stability according to BS4321 under both lights.

Table 6: Quality control tests of inks

	F3 Ink's Print
Abrasion resistance	1
Adhesion	5
Drying times	5 sec

Abrasion resistance test (weight: 920 g load, 30 cycle) 1 = excellent, 2 = good, 3 = bad, 4 = very bad.*

To test for the effect of adhesion, ink was prepared and print onto paper substrates and allowed to dry thoroughly overnight. The tape adhesion test was then carried out, the results of which can be seen in Table 6. A visual assessment of the adhesion was made. Zero indicates that all ink has left the surface (poor adhesion) and 5 indicates no separation (excellent adhesion). When examined in ultraviolet and daylight on the band, it was determined that there was no ink residue, so the adhesion result was given as 5. that is, the ink adheres to the surface quite well. When drying times were examined, it was determined that drying took less than 5 seconds. this is an expected result. The absorbent paper helped the ink dry quickly, while the solvent of the ink was quickly removed. Thermal inkjet inks dry in approximately 2-10 sec, so the ink easily meets this quality parameter. The evaluation made using the abrasion resistance test 30 oscillations and a weight of 920 grams was evaluated visually. The tests of the prints were examined under both daylight and UV light. It was evaluated as 1 because there was no deformation even after 30 oscillations. In other words, ink with high friction resistance has been produced. This is due to the strength of the resin of the ink.

4. CONCLUSIONS

As a result, the ink, which cannot be seen under daylight, has been successfully prepared by using polyurethane resin and radiating in the UV region. Thermal inkjet prints can be made easily with the prepared inks. Properties such as colour and brightness of the prints were determined. It was determined that the ink, which is transparent at room conditions, radiates blue in the UV region and a stable print is created. It has been determined that the prints made with the obtained ink have high light fastness, high adhesion and abrasion resistance and dry for a short time. It can be suggested that the obtained ink can be used in areas such as packaging, valuable documents, money, as a security parameter.

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