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DETERMINATION OF CHEMICAL MIGRATIONS OF PHOTOINITIATORS, WHICH ARE FREQUENTLY ENCOUNTERED IN UV-CURABLE INKS IN THE PRINTING INDUSTRY

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Abstract: *Some photoinitiators used in inks, lacquers and print films are minor chemicals and have high chemical mobility. Since these substances are also harmful to human health, their use has been limited by some regulations by the European Union. In the printing industry, ITX, benzophenone, and Irgacure are among the most commonly used. Within the scope of this study, equal amounts of different photoinitiators (ITX, benzophenone, and Irgacure) were added to the formulation of UV-cured ink with the same chemical content, and their chemical migrations were determined by the LC-Ms method with the help of Tanex LC–MS conditions for calibration experiments: Flow rate 0.4 mL pre-column, 50 wt.% ACN–50 wt.% water. First of all, the calibration curve of each photoinitiator was prepared and then the amount of photoinitiator passing through the square meter was calculated with the help of the calibration curve. As a result, it was determined that Irgacure had the lowest migration and ITX had the highest migration.*

Keywords: *migration, ink, pPrinting, Lc-MS*

INTRODUCTION

The emergence of ITX in infant milk products in Italy in 2005 had an intriguing and alarming effect. As a result of the researches, it was found that the source of this chemical found in infant milk is the photoinitiator, which undergoes chemical migration from the printing of the packaging package. In the light of these developments, the European Food Safety Agency (EFSA) has published a declaration on the subject and has given an opinion on the use of all of Europe by determining the maximum amount of migration of some chemicals that can pass from the material to be printed, ink, lacquer, varnish or adhesive to food products. For this reason, the concept of low migration ink and varnish has come to our agenda.

Polymerization using UV light is a fast, easy and effective polymerization technique that has been used since the 1970s. It is frequently encountered in lacquers and varnishes, high speed printing, metal packaging, lamination and bonding, 3D printing processes in the printing industry [1-3]. Curing with UV has some advantages over other drying systems. These; It is fast, polymerization takes place at a high level and monomer residues are low, the liquid binder part takes a solid structure for a minimum time, it does not need an extra heating process, and there are almost no solvent residues with high mobility [4-7].

Photoinitiator is the substance that forms active particles and initiates photopolymerization when exposed to light in the UV curing process [8]. Photopolymerization is examined in 4 steps, these are initiation, growth, chain transfer and termination steps. UV polymerization steps can be seen in Figure 1.

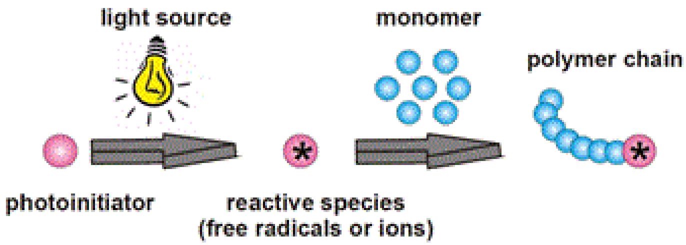

Figure 1: The scheme of UV polymerization

For UV-cured inks, the photoinitiator selection should be chosen by considering the structure of the ink film to be formed, the drying rate, and its value in terms of human health, depending on whether the by-product is harmful or not. The most commonly used photoinitiators in the printing industry are free radical photoinitiators and cationic photoinitiators. Free radical photoinitiators are the most widely used and common photoinitiators whose radical formation and curing stages are well known. Radical generation is of two main types; one-component (Type 1) and two-component (Type 2) foroinitiators that need a co-initiator. Cationic photoinitiators are a polymerization technique that has gained industrial importance in the last quarter century. The advantages of this technique include better adhesion, low oxygen termination, stable polymer dimensions, and homogeneous polymerization process [9-14].

In recent years, greener, cheaper, more effective photoinitiator research continues for the printing industry. In this context, longer-lasting light sources are used, photopolymerization time is shortened, inks curing even with natural light have been produced, and moreover, biodegredable monomers have begun to be researched.

The concept of low migration ink has emerged in order to meet regulatory compliance requirements. Photoinitiators are known to be smaller than 500 D when examining normal UV-curable inks, and their degradation products are even smaller. Small molecules are more prone to chemical migration because of their greater mobility. This poses a risk to human health. The easiest way to reduce migration is to enlarge the photoinitiator. The use of ‘multicomponent photoinitiating systems’ is another novel alternative Another solution to the problem is self-starting systems where the photoinitiator is not used. This is a property of the resin. however, it is not an effective method that can be processed industrially. Electron beam curing, a process that provides some advantages over UV curing such as: instantaneous complete curing, no requirement of photoinitiators, and the possibility of curing thick and pigmented coatings. Chemical migration occurs in two ways, from ink, varnish, lacquer, printing material or adhesive to food. These are direct migration or indirect migration. In direct migration, photoinitiators or other chemically migrated substances diffuse from the printed material to the food. In indirect migration, the migrant substance (photoinitiator or other migrants) is transmitted to the food by steam. Determining chemical migration is a very difficult task. because inks with very complex material content undergoing chemical migration also form by-products. This makes it difficult to determine the amount of migrant. The type in which all chemicals transferred from a print to the food are determined is called the total migration, and the migration in which the presence and amount of only a single material is determined is called specific migration. While it is quite difficult to determine the total migration, the specific migration is comparatively easier. Analytical methods are used to indicate migration. the most common of these are HPLC, LC-MS, GC and GC-MS.

In this study, UV-curable inks were prepared with 3 photoinitiators (ITX, Irgacure and benzopenone), which are known to be widely used in inks, and the migration amounts of the prepared inks were determined. In addition, printed materials were compared in terms of color and their printability was compared.

EXPERIMENTAL

Material

Photoinitiators isopropyl-9H-thioxanthen-9-one, benzophenone, 1-hydroxycyclohexyl-phenylketone (IRGACURE 184) were obtained from Sigma–Aldrich. Methyl alcohol, n-hexane, and ethyl acetate acetontryl solvents were supplied by Fluka. Laromer, the binder used in the ink preparation, was purchased from BASF. Deionized water was supplied from the Milli-Q SP Reagent Water System.

Methods

In the study, screen printing ink was prepared by using 3 photoinitiators (ITX, benzophenone, and Irgacure), which are frequently used in the printing industry. The formulation of the prepared ink is given in Table 1.

Table 1: The Formulation of prepared inks

	Acrylate Prepolymer (%)	Triethyl amine (%)	Photoinitiator (%)	Colorant (%)
ITX-based ink	96.8	0.2	3	20
Benzophenone-based ink	96.8	0.2	3	20
Irgacure-based ink	96.8	0.2	3	20

Viscosities of the inks were adjusted to 25 seconds with water. With the obtained inks with different photoinitiators, solid prints with a weaving density of 77 tpc, 75° scraping angle and 75° shore hardness by using an Arus semi-automatic screen printing were made on 80g/m2 uncoated paper. The prints obtained were dried with a laboratory type UV drying lamp. Color measurements were made with X-Rite exact spectrophotometer (Spectral Range 400 -700 nm, with D50 light, 2° observer angle, with polarized filter, 0/45-degree) spectrophotometer for three different inks. Color differences were calculated according to the CIELab (2000) technique.

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \quad (1)$$

Gloss values were measured by BYK Gardner gloss meter at 60° according to TAPPI T480 OM-15. In chemical migration studies; calibration curves of all substances to be quantitatively analyzed were created. Eight concentrations from 0.5 ppb to 3 ppm were used to create the calibration curve. It was started to calculate the specific migration amounts of three different photoinitiators for which calibration curves were created. Solid prints made with an ink amount of 3 g/m^2 were left in room conditions for 24 hours by putting Tanex inside after leaving the UV curing lamp. Tanex obtained overnight was treated with dichloromethane. and the photoinitiators passing into the Tanex were taken to the organic phase. After evaporation of some of the dichloromethane in the organic phases, the samples were prepared by diluting the products with acetonitrile. LC-Ms analyzes were performed with water containing 50% (0.2% formic acid contained) water- 50% Acetonitrile mobile phase, flow rate 0.4 mL/min, pressure 80 bar, Kromasil 3 µm particle size 100 mm×4.6 mm C8 column conditions.

RESULTS

Calibration curves of three different photoinitiators were successfully prepared and analyzed by LC-MS for use in calculating the amount of migration. When the calibration curves are examined, it is seen that even a very small amount of photoinitiator can be determined. In addition, all calibration curves gave sensitive, fast and effective results. Regression value of each curve was calculated as 0.99. In other words, it was determined that the standard deviations in the calibration curve were very low.

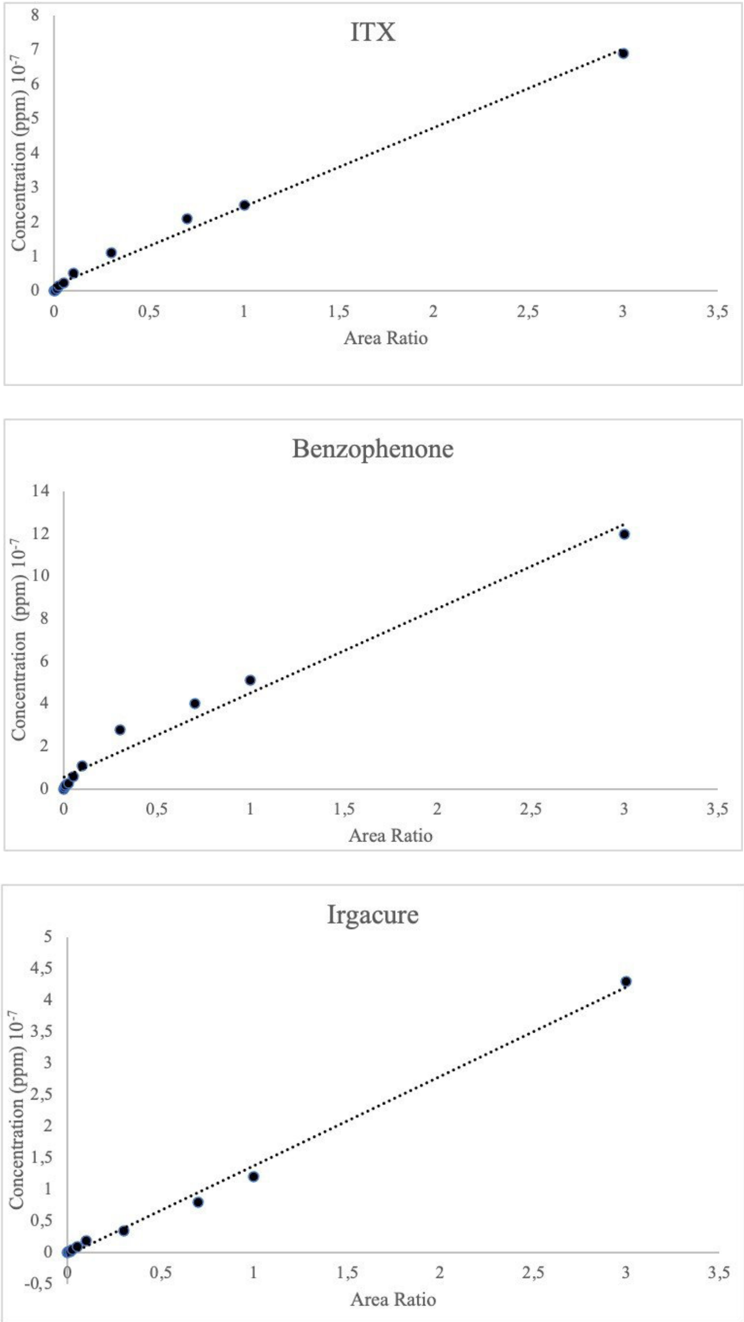

Figure 2: Calibration curves of ITX, Benzophenone and Irgacure.

The chemical migrations of three different photoinitiators used in the printing industry were determined by the LC-MS method, and the absorption values were replaced in the calibration curve and the migration amounts were found. Chemical migration amount of ITX was 0.1 mg/kg, chemical migration amount of benzophenone was 0.039 mg/kg, chemical migration amount of Irgacure was 0.016 mg/kg. When the results were examined, it was concluded that the photoinitiator with the lowest migration rate among the compared three photoinitiators, Irgacure had the lowest migration amount and ITX was the highest.

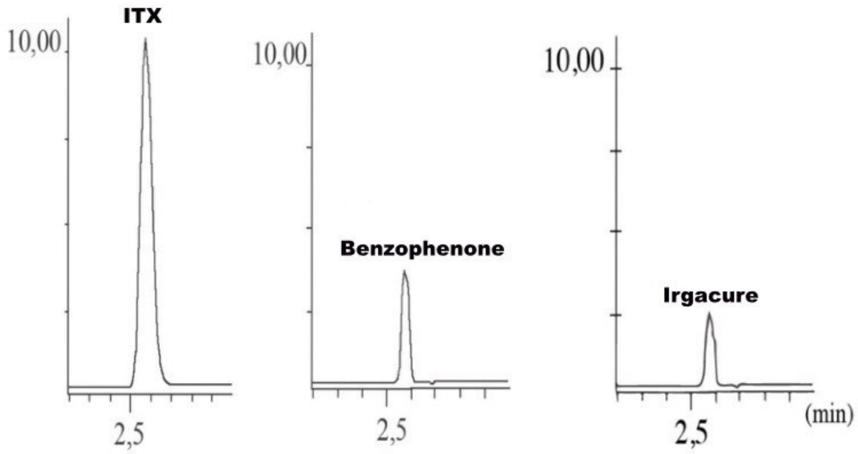

Figure 3: Migration amounts of ITX, Benzophenone and Irgacure based inks

When the color values of the prints were examined, it was determined that the deviation in the colors where the differences between the colors were very small, when the print made with ITX-containing ink was taken as reference, occurred at the L value the most. It was concluded that the inks changed in direct proportion to the drying time. The resulting color differences are within the ISO standard reference range, and the difference has a color difference that is difficult to detect by the human eye. When the gloss values were examined, it was determined that the gloss value of the ink containing Irgacure, where the glossier print was obtained with inks containing ITX and Benzophenone, was lower than these two inks. Drying times of ITX and benzophenone are shorter than Irgacure. In fact, non-drying problems were encountered during the drying process of inks containing Irgacure. For this reason, the acrylic resin, which is in contact with the air before it dries, has undergone oxidation and a less glossy surface is formed. However, this difference is around 10%.

Table 2: The color and gloss values of prepared ink's prints

	L	a	b	ΔE_{00}	Gloss
ITX-based ink	72.5	82.9	-2.9	Ref	30.5
Benzophenone-based ink	72.4	81.6	-2.3	0.59	30.4
Irgacure-based ink	70.9	82.6	-2.6	1.2	27.3

CONCLUSIONS

Screen printing inks have been successfully prepared with three different photoinitiators, which are frequently used in the printing industry. Screen prints were made on the paper surface with the obtained inks. A fast, selective method has been developed for the photoinitiators used and calibration curves have been prepared. Photoinitiator migrations in prints using inks were calculated by means of calibration curves. When the three photoinitiator inks were compared, it was determined that the ink with the highest migration was the ink containing ITX, and the ink with the least migration was the ink containing Irgacure. In terms of color and printability, it has been determined that all colors comply with the ISO standard and the difference between the colors is too small to be distinguished by the eye. In terms of gloss, it was determined that inks containing Irgacure were more matte due to longer drying time. As a result, it was concluded that among these three photoinitiators used in the printing industry, Irgacure is more suitable for health, but the drying time should be extended.

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