Anadolu Orman Araştırmaları Dergisi
Anatolian Journal of Forest Research

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Preparation of Ecofriendly Offset Printing Ink Varnish with Safflower Oil and *Pinus pinaster* Resin and Printability

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Original Article

ARTICLE INFO

Recieved: September 28th, 2020
Accepted : December, 18th, 2020

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ABSTRACT

Offset printing inks are composed of four main components including colorants, binders, solvents and additives. When these components are examined, it is seen that they contain petrochemical substances. During and after the printing process, some of these components are separated from the ink as waste material and are mixed with air, water or soil, thus damaging nature and human beings. Considering this problem, safflower oil and natural (*Pinus pinaster*) resin were used in this study to produce bio based offset printing ink varnish, one of the main components of the ink. Safflower oil and (*Pinus pinaster*) resin were mixed in different proportions to form varnish with suitable viscosity to the printing ink composition. The usability of these varnishes as an alternative for varnishes produced with mineral oil in standard offset printing ink was investigated. Magenta color standard offset printing ink was prepared with these varnishes and sample prints were printed on coated paper, uncoated paper, Bristol board with IGT C1 offset printability tester. Test prints were examined in terms of specialties such as drying, L*a*b and density with a spectrophotometer. As a result of the measurements and determinations, it was determined that the varnish produced with safflower oil and (*Pinus pinaster*) resin can be used instead of offset printing ink varnishes produced with mineral oil.

Key Words: Ink gloss, varnish, resin, safflower oil, printability, vegetable oil ink.

Aspir Yağı ve Sahil Çamı Reçinesi ile Çevre Dostu Ofset Baskı Mürekkebi Hazırlanması ve Basılabilirliği

ÖZ

Ofset baskı mürekkepleri; renklendirici, bağlayıcı, çözücü ve katkı maddeleri olmak üzere dört ana bileşenden oluşmaktadır. Bu bileşenler incelendiğinde petrokimyasal maddeler içerdiği görülmektedir. Baskı sürecinde ve sonrasında bu bileşenlerin bazıları mürekkepten atık madde olarak ayrılarak havaya, suya veya toprağa karışmakta bu nedenle de doğaya ve insana zarar verebilmektedir. Bu problem göz önüne alındığında, mürekkebin ana bileşenlerinden biri olan biyo bazlı ofset baskı mürekkep verniği üretmek için aspir yağı ve doğal *Pinus pinaster* reçinesi kullanılmıştır. Aspir yağı ve sahil çamı reçinesi farklı oranlarda karıştırılarak baskı mürekkebi bileşimine uygun viskoziteye sahip vernik oluşturulmuştur. Elde edilen bu verniğin standart ofset baskı mürekkebinde mineral yağla üretilen vernikler yerine kullanılabilirliği incelenmiştir. Hazırlanan vernikle magenta renginde standart ofset baskı mürekkebi hazırlanarak IGT C1 ofset basılabilirlik test cihazı ile mat kuşe, 1. hamur kağıtlar ve Bristol karton üzerine numune baskılar yapılmıştır. Test baskıları üzerinde spektrofotometre ile inceleme ve ölçümler yapılarak verniğin; kuruma, densite ve L*a*b değeri gibi temel özelliklerine bakılmıştır. Ölçüm ve tespitlerin sonucunda aspir yağı ve sahil çamı reçinesi ile üretilen verniğin mineral yağla üretilen ofset baskı mürekkebi vernikleri yerine kullanılabileceği tespit edilmiştir.

Anahtar Kelimeler: Mürekkep parlaklığı, vernik, reçine, aspir yağı, basılabilirlik, bitkisel yağ mürekkebi.

Citing this article:
Hayta, P., Oktav, M., Ateş Duru, Ö., Özomay, Z.., 2020. Preparation of Ecofriendly Offset Printing Ink Varnish with Safflower Oil and *Pinus pinaster* Resin and Printability. Anatolian Journal of Forest Research 6(2): 62-67.

1. Introduction

Inks typically dissolve or disperse in a coloring agent (binder + solvent + additive) (Aydemir and Özakhun, 2014). A typical quick-drying sheet-fed offset ink contains pigment, varnish, drying agent, wax compounds, and solvent (Ülgen et al., 2012). Binders and solvents are used to obtain varnish contained in ink (Özomay, 2009). The binders used in oil-based inks are phenolic resins or hydrocarbon resins (Aydemir and Özakhun, 2014). These resins are synthetic resins. Resins used as binders contribute to the properties of hardness, gloss, adhesion, and flexibility in an ink (Leach et al., 1988). Solvents contained in offset printing ink contain oil. Solvents dissolve the binders and adjust the viscosity of the ink (Robert, 2014). Mineral oils with different boiling points are mainly used in ink production. Synthetic resin and petroleum-derived mineral oils are used in varnish production; thus these petrochemicals are contained in the ink. Petrochemicals in the varnish and other ingredients of an offset printing ink separate from the ink after printing, thus becoming potentially harmful. Especially, almost all VOCs (volatile organic compounds) being chemicals that can easily evaporate at room temperature have some toxic effects (Ülgen et al., 2019). Studies were also conducted on ink production to eliminate the damages caused by petrochemicals and to produce alternative solutions to the oil crisis that occurred in the 1970s. In the 1970s, the Newspaper Association of America sought alternative ways to produce ink and reduce dependence on standard petroleum-based ink (Ural et al., 2018; Morkbak et al., 1999). In the 1980s, soy-based inks were first used in offset web presses for printing newspapers for environmental purposes to improve worker safety and reduce environmental emissions (Simpson et al., 1994). Following the attempts to produce soy oil-based inks, researches have been performed to use different herbal products in ink production. In 1994, S.Z. Erhan and M.O. Bagby investigated the polymerization of vegetable oils and their uses in printing inks by using safflower, soybean, sunflower, cottonseed and canola oils in ink formulations, respectively (Erhan and Bagby, 1994). With developing technology, researches have been accelerated in many sectors to use bio-based raw materials in production processes involving the use of petrochemical raw materials. The results of these researches showed that there are applications for commercial products. Accordingly, there has been an increasing demand for using vegetable and renewable sources in the production of inks as an important part of the printing industry. When recent studies since the 1970s were examined, it was seen that vegetable oils such as soybean oil, palm oil, flaxseed oil have been used in ink ingredients. Y.B. Ha et al. synthesized natural resins to produce environmentally friendly ink and analyzed their uses in offset printing ink formulations and the properties of the ink such as gloss, discoloration (Ha et al., 2012). When the studies on ecological balance and sustainable life instead of petrochemicals that adversely affect the environment and human health were examined, it was seen that renewable sources have been rarely used in ink production. Investigating alternative renewable sources for inks being one of the important raw materials in the printing industry is important for the elimination of adverse effects of petrochemicals. The economic and environmental effects of converting vegetable wastes, which may be generated during the use of local sources and the production of various oils and resins, to high-value-added products such as printing inks have also gained importance. In this study conducted for this purpose, a standard offset printing ink was prepared by the combination of magenta pigment and varnish which has been produced using the oil of safflower plant growing in our country and *Pinus pinaster* resin from Kefken region. Sample prints were printed on coated paper, uncoated paper, bristol board with IGT C1 offset printability tester using the offset ink that was prepared to test the varnish. The visual quality of the print result largely depends on the optimum level of the coalescence process of the underprint material and ink (Özomay, 2016). Thus, sample prints were printed on different types of paper and cardboards. Test prints were evaluated by comparing their L*a*b and densitometry measurement results with the standard values and the mineral oil-based offset printing ink.

2. Materials and Methods

The varnish was made of cold-pressed safflower oil and natural *Pinus pinaster* resin that was obtained from the Kefken Region using the acid-paste method. The properties of the safflower oil used in the varnish production are given in Table 1.

Table1. The free fatty acid and fatty acid profile of safflower oil used in this study (Katkade et al., 2018).

Properties	Content (%)
Free Fatty Acid	0.16
Fatty acid profile	%
Palmitic	6.36
Stearic	2.39
Oleic	17.34
Linoleic	73.89

In the study, the *Pinus pinaster* resin was cleaned from large-sized particle impurities and weighed 70 g in a weighing bottle. Safflower oil (40 g) was placed into flasks, which then were placed on the heaters set at 150 °C in the fume hood. The oil was heated up to 150°C. The resin was slowly added into the heated safflower oil and mixed to obtain a homogeneous mixture with the resin completely dissolved in the oil. After the homogeneous mixture was obtained, the oil was filtered using an appropriate filter to remove resin-based impurities. After the temperature of the mixture reached 180 °C, it was fired for 30 min. The temperature of the resin-oil mixture was also checked using a thermometer at regular intervals. After the firing process, varnish sample, which was obtained from the mixture of (*Pinus pinaster*) resin and safflower oil, was taken from the heater and kept at room temperature until its temperature reaches down to 100-120 °C, and then transferred to a sample jar while its fluidity is high, i.e. before its viscosity is increased.

The varnish prepared to produce offset printing ink was mixed with magenta pigment. The prepared ink contained 20% pigment and 80% varnish. To determine the printability of the ink, coated paper, uncoated paper and bristol board, being used in the printing industry, were selected, and 3 samples were taken from each. Stiffness length, stiffness width, ash content, tensile strength width, tensile strength length, contact angle, and surface energy measurement results of the samples were taken into account. The physical and optical properties of the sample papers and cardboards used for test printing are given in Table 2 and Table 3, respectively. To determine the surface properties, the surface flatness properties of these samples were measured per ISO 8791-4 and TAPPI T 555 standard. It was performed based on the average of the values given in the standards; ISO 2470 for whiteness, ISO 2493 for stiffness, ISO 536 for grammage, ISO 534 for thickness.

Table 2. Physical properties of uncoated, coated and bristol boards used in this study (ISO 8791-4:2007, TAPPI T 555, ISO 2470-1:2016, ISO 2493, ISO 536:2019, ISO 534:2011)

Physical Properties	Measurement Results		
	Coated Paper (250 g/m$^{2)}$	Uncoated Paper (80 g/m^2)	Bristol Board (250 g/m^2)
Grammage / m^2	250 g/m^2	80 g/m^2	242 g/m^2
Contact Angle .WGS	64.50	82.90	68.80
Surface Energy ASTM D5946	41.70	35.10	40.20
Stiffness Length 5° L&W mNm	5.2	0.6	11.8
Stiffness Width 5° L&W mNm	4.2	0.2	7.5
Ash % 525 °C	47.69	24.43	23.8
Tensile Strength Width Nm/g	20.77	64.91	21.46
Tensile Strength Length Nm/g	30.12	94.13	31.12
Thickness	207	104	269
Gloss µm	1.27	5.11	3.72
IGT m/s	0.86	-	2.46
Surface Coating Formation	2.1	-	1.8

Table 3. Optical properties of uncoated, coated and bristol boards used in this study

Optical Properties	Measurement Results		
	Coated Paper (250 g/m$^{2)}$	Uncoated Paper (80 g/m^2)	Bristol Board (250 g/m^2)
Whiteness	86.72	83.32	79.84
Yellowness	-0.59	-4.17	5.56
L (lightness)	94.16	91.68	92.75
a (-a green / +a red value)	-0.55	0.03	-0.68
b (-b blue / +b yellow value)	-0.09	-2.08	3.45
Brightness	43.3	-	53.5

The sample prints (Figure 1) were made using IGT C1 offset printability tester, and the solid tone density of the printing samples prepared in this study was measured at 2° observer angle and under D50 light source. Before the sample printing, the papers and cardboards were conditioned at 23 ± 1 °C and 50% ± 3% relative humidity for 24 h in the printing room. The densitometric measurements were performed using Gretag Macbeth SpectroEye with reflection measurement capability (measurement conditions: D50 light source, 2º observer angle, 0/45 or 45/0 geometry, black background). The L*a*b measurements were performed using X-Rite eXact Color Spectrophotometer.

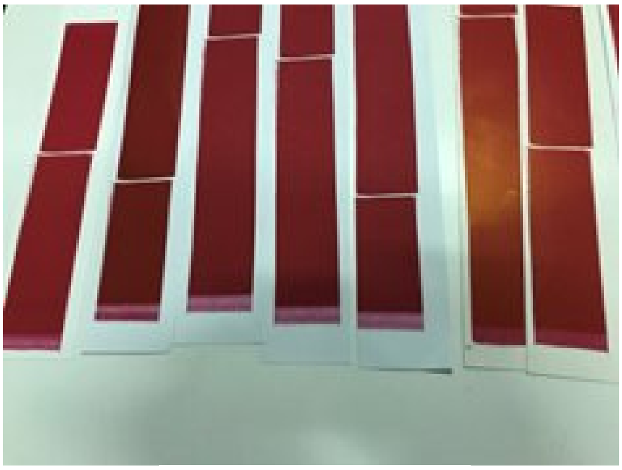

Figure 1. Sample print image

3. Results

In this study, for printability analysis of the ink that was made of varnish prepared with safflower oil and *Pinus pinaster* resin, sample prints were printed on a part of the sample papers and cardboards using this ink. For control sample printing, prints were printed on the same kind of sample papers and cardboards using mineral oil-based offset printing ink. Thus, the mineral oil-based offset printing ink and the plant-based offset printing inks prepare in this study could be compared. The sample prints were measured using the ΔE tolerance difference formula according to the uniform color space CIE L*a*b * (formula 1).

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

Formula 1: ΔE tolerance difference formula

The spectrophotometric measurement results during the printing process of the sample prints for the ink produced using the varnish prepared with safflower oil and *Pinus pinaster* resin and for the control ink contained mineral oil are given in Table 4. The spectrophotometric measurement results of the sample prints after the drying process are given in Table 5.

Table 4. Measurement results of the samples during the printing process

	Offset printing ink containing safflower oil and (*Pinus pinaster*) resin				Mineral oil-based offset printing ink				
Samples	L	a	b	Density	L	a	b	Density	Delta E (ΔE)
Uncoated Paper	44.26	56.84	21.25	1.16	44.35	58.21	26.32	1.21	5.25
Coated Paper	45.96	66.21	26.47	1.28	44.07	63.41	35.18	1.33	9.32
Bristol Board	44.92	64.82	31.70	1.31	42.40	61.26	37.12	1.37	6.94

When the measurement results of the sample papers and cardboards obtained during printing as given in Table 4 are examined, it is seen that the offset printing ink containing safflower and (*Pinus pinaster*) resin has exceeded the tolerance values for coated paper, according to ISO 12647-2 offset printing standard. The measurement results for uncoated papers and bristol boards are close to each other.

Table 5. Print results of the samples after drying.

	Offset printing ink containing safflower oil and (*Pinus pinaster*) resin				Mineral oil-based offset printing ink				
Samples	L	a	b	Density	L	a	b	Density	Delta E (ΔE)
Uncoated Paper	45.03	59.88	22.63	1.17	44.82	57.70	27.33	1.19	5.18
Coated Paper	46.02	66.62	26.57	1.31	43.93	64.00	35.23	1.34	9.28
Bristol	44.49	65.68	31.99	1.33	42.80	61.71	36.17	1.40	6.00

When the print measurement results of the samples obtained after drying as given in Table 5 are examined, it is seen that the offset printing ink containing safflower and *Pinus pinaster* resin has exceeded the tolerance values for coated paper, according to ISO 12647-2 offset printing standard. The measurement results for uncoated papers and bristol boards are close to each other.

3. Discussion

In this study, printability tests were carried out considering the ISO 120647-2 offset printing standard. The reference values in the ISO 12647-2 offset printing standard are shown in Table 6, and the color universe is shown in Figure 2. When the measurement results during the printing process on uncoated paper is examined; it is seen that the L value of the ink obtained with safflower oil and (*Pinus pinaster*) resin is below the standard value, a value is close to the standard value and the b value is above the standard value. The density value is above the standard value. When the measurement results of the same paper after drying were examined, it was concluded that the L value was low, a value was close and the b value was high compared to the standard values. The results of during the printing process and after drying results of uncoated paper with standard ink containing mineral oil were found to be lower, a value is close and b value is higher than the ink obtained with renewable resources.

Table 6. ISO 12647-2 Standards of offset printing magenta color for density, L*a*b and Delta E (ΔE)

Paper type	L	a	b	Density	Delta E (ΔE)
Uncoated Paper	54	58	-2	0.95	5
Coated Paper	46	72	-5	1.45	5
Bristol Board	46	72	-5	1.45	5

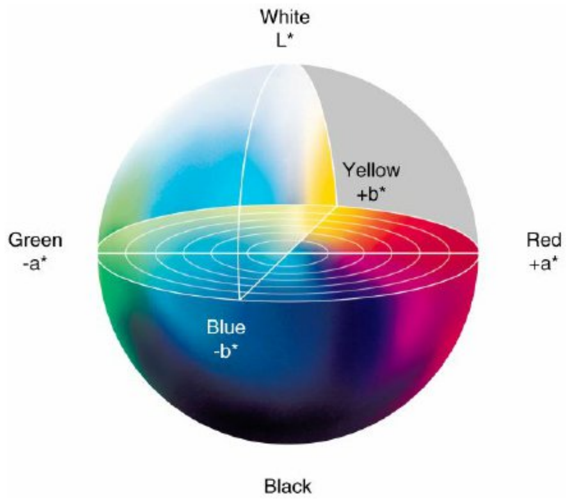

Figure 2. CIE L * a * b * color space

When the coated paper during the printing process and after drying results were examined, it was seen that the closest result of the L value of the ink produced with renewable resources in both cases was that a value was lower than the desired value and the b value was far from the desired value. The density value was measured close to the standard value. In the sample printing made using coated paper, during the printing process of the mineral oil standard offset printing ink and the measurement results after drying, especially the b value is far from the desired value, and the L and a values are below the desired value. Density results are close to the standard value. Coated paper measurement results gave more positive results in ink obtained with renewable resources as in the matte coated paper.

When comparing during the printing process and after drying values in the Bristol board, Delta E value is closer to the ISO 12647-2 standard after drying. Although a and b values differ from the standard value in both ink formation, the desired value as the L value occurs within the standards. When viewed as densitometric, while it has low values within the standards in coated paper and Bristol board; it has been found to have a high value within standards in the uncoated paper.

4. Conclusion

Petrochemicals contained in inks potentially cause environmental and health problems. Using bio-based and renewable sources instead of chemicals in the production of ink, which is the basic raw material for the printing industry, is important for the health of workers and end-users in the printing industry, the prevention of environmental pollution, and the promotion of a sustainable life. This study showed that when safflower oil instead of mineral oil, and natural resins instead of synthetic resins are used in offset printing ink composition, the obtained results were close to the values in the ISO standards for uncoated and bristol boards. In future studies, to obtain results in compliance with the standards for different paper types, the composition of varnish may be changed or different vegetable oils and resin types may be tried to enhance the print quality. The obtained results showed that renewable sources instead of petrochemicals can be used in printing ink production, which has importance for studies in this field. The results obtained in this study will also help in conducting effective studies for the utilization of sources in our country. Moreover, the health and environmental effects associated with the printing industry would be reduced with environmentally friendly inks.

Conflict of Interest

The authors declare that they have no conflict of interest.

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