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Evaluation of plant-based oils for production of offset printing ink

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Abstract

The oils and solvents are the main components of the printing ink, and the chemical composition of the ink could be harmful or toxic to human health and the environment. Therefore, there is an increasing demand to develop inks containing green, biobased, sustainable, and renewable raw materials instead of petrochemical substances. In this study, flaxseed oil (FO), pomegranate seed oil, plum kernel oil (PKO), and grape seed oil (GSO) were selected to produce offset printing inks. *Pinus pinaster* (*P. pinaster*) resin was also used in the formulation of inks to examine the effects of natural resin on ink together with vegetable oils. The phenolic content was analyzed for the resin and oils to figure out their potential antioxidant and bioactive characteristics. Optical and rheological tests were applied to evaluate the printability of the inks. $L^*a^*b^*$, ΔE, density, and gloss tests were performed for optical evaluation. The viscosity, tack, and rub resistance tests were applied to perform rheological analysis. The biobased, environmental friendly, and self-drying (cold set) offset printing inks were obtained using natural pine resin and three different plant-based oils FO, PKO, and GSO. The printability analysis of the inks figured out the potential usage of plant-based oils in the offset printing ink formulation.

KEYWORDS
biobased products, offset ink, pine resin, plant-based oils, printing

INTRODUCTION

All printing inks consist of four main components: colorants, binders, solvents, and additives (Hayta & Oktav, 2020). Due to the printing process and the printing substrates contacted with the ink, the specifications of the components are varied. A typical fast-setting sheet offset ink contains pigment, fast-setting varnish (resin phenolic ester, thermosetting oil), desiccant, and wax compounds (Nelson, 2012). The solvents in the offset inks are mineral oils (or petroleum distillates) with a wide range of boiling points and aromatic content. These oils, which generally have weak solvent power, are nonpolar and nondrying fluids composed of paraffinic, naphthenic, and aromatic hydrocarbons (Rousu et al., 2000). To obtain sufficient color power on the printed material, offset inks should be more pigmented than other inks and a homogeneous mixture should be ensured (Ülgen et al., 2019). In general, the most basic features expected from offset printing inks are providing ideal transfer of the ink from the ink reservoir to the plate, from the plate to the printing blanket and from there to the substrate in the printing system, fast drying on smooth substrate surfaces, good color strength and contrast (Hayta, 2021).

Offset printing inks also contain petrochemical binders (phenolic or hydrocarbon resins) and additives. Different types of additives are added at varied rates to obtain the desired properties of the ink. These chemicals used for ink production are volatile organic compounds. In the ink industry, a volatile organic compound (VOC) is any organic material in ink that will “eventually evaporate from the ink, regardless of the time it takes to evaporate” (Erhan & Nelsen, 2001). Almost all VOCs are chemicals that can evaporate at room temperature and have various toxic effects and negative impacts on the environment and human health (Nelson, 2019). For decades, the influence of environmental contamination on humans and the world has been a significant problem that the scientific community

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has tried to overcome (Ural et al., 2018). Due to environmental concerns, the demand for biobased products, especially plant-based products, as sustainable raw materials raised. Research efforts are devoted to identifying the potential of new renewable materials, developing eco-friendly printing inks, reducing dependency on petrochemical resources, and diminishing the environmental impact (Robert, 2015). Examining alternative renewable sources for ink production is significant for reducing the adverse effects of petrochemical components (Hayta et al., 2020). The best alternative sources of biobased and renewable raw materials for offset printing ink are vegetable oils and natural resins. Most vegetable oils contain triacylglycerides that provide them with a desirable quality as a lubricant (Fox & Stachowiak, 2007). Several plant-based oils and vegetable seed oils were identified as suitable for printing ink production such as soya oil, sunflower oil, linseed oil (flaxseed oil), and palm oil (Hayta et al., 2021). However, various oils were not investigated as a potential alternative to minerals oil. Therefore, to evaluate the potential usage of different oils in ink formulation, flaxseed oil (FO), pomegranate seed oil (PSO), plum kernel oil (PKO), and grape seed oil (GSO) were selected in this study.

The grape is the fruit of the vine genus belonging to the *Vitis vinifera* l. family and is especially rich in unsaturated fatty acids because of the content of the oil in its core (Akın & Altındişli, 2010; Uslu & Dardeniz, 2009). Grapes are among the most popular fruits and 58 million tons of production on approximately 7 million hectares, and grape seed is an economically important product and contains about 7%–20% oil. The grape seed oil includes a significant number of unsaturated fatty acids: linoleic acid (18:2), oleic acid (18:1), linolenic acid (18:3), and palmitoleic acid (16:1) and 10% of saturated fatty acids, palmitic (16:0), and stearic (18:0) acid. In the context of recycling waste and converting waste into valuable products, the evaluation of seeds and grape extracts is an economically important parameter (Sevindik & Selli, 2016).

Flax (*Linum usitatissimum* L.) belongs to the *Linaceae* family, which has 13 genera and up to 300 species. Flax seeds are rich in Omega-3 and Omega-6 fatty acids. Flax oil is one of the drying oils, having the highest iodine level of 160–200 (in grams of iodine absorbed by 100 g of sample) (Koçak & Bayraktar, 2011). The drying feature of flax oil is due to its high-linolenic acid (18:3) ratio. It can be widely used, especially in industrial branches such as oil paint, varnish, and lacquer (Örs & Öztürk, 2018).

Pomegranates have more than 500 varieties, different sizes, colors, shapes and, seed firmness. The growth characteristics and other characteristics such as taste, aroma, and fruit quality are also varied. Pomegranates grow on the *Punica granatum* L. tree, a small tree of eastern origin, is one of the most important species belonging to the *Punica genus* of the *Punicaceae* family, *Punica granatum* L. Pomegranate seeds, a valuable waste product, contains an average of 20.80% oil. Pomegranate seed oil is high in vitamin E and antioxidant polyphenols, as well as conjugated fatty acids (Yeniçeri & Küçüköner, 2020).

Plum (*Prunus cerasifera*) is one of the most important fruits grown in Turkey. A high amount of waste arises which cannot be recycled into other products, as peel, stone, seed, and stalk occurred after consuming it freshly or producing jam, juice, molasses, etc. (Uluata & Ozdemir, 2017). The fatty acid content of plum kernel oils is oleic acid (64%–78%) and linoleic acid (17%–21%) (Pićurić-Jovanović & Milovanović, 1993).

The *Pinus* genus has 109 species and spreads widely in the northern hemisphere. Maritime pine (*P. pinaster* Belongs.) is found naturally in Southwest Europe, the Western Mediterranean, and Northwest Africa (Güner et al., 2019). *P. pinaster* is a medium-sized pine that can grow 40 m tall (Ayanz et al., 2016). This maritime pine genus, which is geographically distributed, genetically diverse, and tolerant to ecological conditions, contains a large amount of resin (Çiçekler et al., 2018). Recent research has reported the use of various genus of pine resin in printing ink formulations, demonstrating the suitability of this renewable raw material (Hayta et al., 2020, 2021; Karademir et al., 2020). Throughout history, pine resin (*Pinus* spp.) has been utilized in adhesives, soaps, insecticides, construction materials, artwork, and even embalming fluid. A variety of pine-based food additives and culinary products are also available. Moreover, pine resin is an effective antiseptic and is used to treat skin illnesses, burns and scald wounds, tracheitis, and pulmonary tuberculosis. The VOCs of this resin has different pharmaceutical applications (Tekgüler et al., 2021).

To develop environmental-friendly inks, cyan-colored offset printing inks were produced using natural resources plant-based oils (FO, PO, GSO, and PKO) and *P. pinaster* resin. Test prints of inks were applied on 170 g/m^2 papers, and the $L^*a^*b^*$, ΔE, density, and gloss values of the test prints were analyzed for optical tests. Besides, tack, viscosity, and rub resistance measurements were performed to evaluate the rheological properties of inks.

MATERIALS AND METHODS

Materials

In this study, using the cold-pressing technique flaxseed oil, pomegranate oil, grape seed oil, and plum kernel oil were obtained from products grown in Turkey. The cold-pressing technique can yield pure, safe, nutritionally rich, and sensorially acceptable virgin oils which do not require refining and therefore they can be consumed directly. In this technique, heating is not applied to oilseeds during the pressing. To apply this method

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TABLE 1 The specifications of oils used

	Flaxseed oil	Pomegranate seed oil	Grape seed oil	Plum kernel oil
Physical characteristics				
Odor	Natural-characteristic	Natural-characteristic	Natural-characteristic	Natural-characteristic
Color	Light brown	Yellow	Light green	Yellow
Relative density (20°C)	0.9250–0.9350 g/ml	0.930–0.950	0.922–0.927 g/ml	0.905–0.925 g/ml
Chemical characteristics				
Iodine value (Wijs)	Min. 182 g I_2/100 g	Min. 130.4 g I_2/100 g	Min. 141 g I_2/100 g	90–108 g I_2/100 g
Saponification value	187–195 mg KOH/g	185–200 mg KOH/g	186–194 mg KOH/g	188–200 mg KOH/g
Fatty acid profiles (%)				
16:0 palmitic	4.88	4.6	8.30	6.01
18:0 stearic	3.79	2.8	4.38	1.38
18:1 oleic	19.80	7.8	13.87	75.19
18:2 linoleic	15.72	5.8	73.42	15.93
18:3 linolenic	55.80			
18:3 punicic		78.3		
17:0 heptadecanoic				1.07

TABLE 2 Main resin acids and turpentine distribution in the resin depending on the type of resin

Resin acids %					
Abietic	**Neoabietic**	**Palustric**	**Dehydroabietic**	**Pimaric**	**Iso pimaric**
22	20	25	6	5	17
Turpentine compound %					
α-Pinene	**Β-pinene**	**Camphene**	**Other terpenes**		
60–65	25–35	-	5–8		

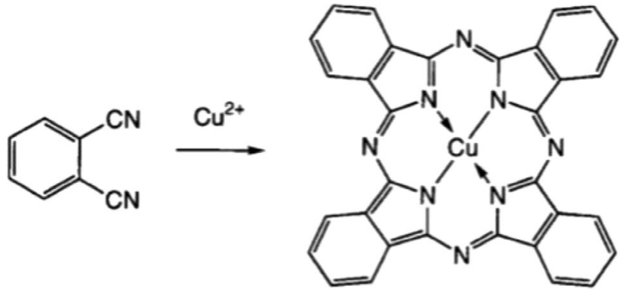

FIGURE 1 Cyan pigment molecular structure

TABLE 3 Technical properties of the papers

Properties	Standard	Paper
Grammage (g/m^2)	ISO 536:2019	170
Thickness (μm)	TAPPI T 411:2105	147
Gloss (75°)	TAPPI T 480:2015	64.2
*L**	TAPPI T 524	95.56
*a**	TAPPI T 524	1,07
*b**	TAPPI T 524	−3.40

oilseeds must be very clean, uniform, and have an appropriate moisture level to be processed by cold pressing (Aydeniz et al., 2014). The technical properties of the oils are presented in Table 1.

P. pinaster resin that was acid-paste method was obtained from Kerpe Research Forest Area. In the *Pinus* type, there are normal resin channels, and they are formed because of injury. By dividing in parallel around the canal, the thin-walled parenchyma cells surrounding the channels replicate and divide into epithelial cells where resin biosynthesis is performed. With the acid-paste method, the resin is leaked from the channels by applying acid to the wound opened on the tree (Acar et al., 1996). The colophon and turpentine technical information of resin are given in Table 2.

The cyan color pigment blue 15:3 pigment (commercial) was used in ink formulation. The pigment was provided by a company that operated in the pigment market. The molecular structure of pigment blue 15:3 is shown in Figure 1.

Test prints were made on 170 g/m^2 coated paper with the IGT C1 (IGT Testing Systems, Almera, the Netherlands) offset printability tester to evaluate the generated inks. The technical specifications of the papers are given in Table 3.

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TABLE 4 Ingredient of the varnishes

Ingredient	Varnish 1	Varnish 2	Varnish 3	Varnish 4	Quantity
Oil	Flaxseed oil	Pomegranate seed oil	Grape seed oil	Plum kernel oil	40 g
Resin	*Pinus pinaster*	*Pinus pinaster*	*Pinus pinaster*	*Pinus pinaster*	70 g
°C/Time	180°C/30 min				

TABLE 5 Formulations of the offset printing inks produced

Ingredient	Aim	Quantity
Cyan pigment	Colorant	15%
Varnish	Binding	80%–85%
Oil	Solvent	1%–5%
	Total	100%

TABLE 6 Types of the environmental friendly offset printing inks produced

Inks	Quantity
Ink 1	Varnish 1 (82.5%) + cyan pigment (15%) + flaxseed oil (2.5%)
Ink 2	Varnish 2 (80%) + cyan pigment (15%) + pomegranate seed oil (5%)
Ink 3	Varnish 3 (80.5%) + cyan pigment (15%) + grape seed oil (4.5%)
Ink 4	Varnish 4 (82.5%) + cyan pigment (15%) + plum kernel oil (2.5%)

METHODS

Offset printing inks varnishes production

Varnishes were prepared according to our previous studies as described below (Hayta et al., 2020, 2021).

P. pinaster resin that was obtained by the acid-paste method was pretreated to clean the large impurities. The physical pretreatment methods such as collecting, sieving, and shredding were applied. For each varnish sample, 70 g of resin and 40 g of oil sample were prepared. The components of the varnishes given in Table 4. Forty grams of oil (FO, PO, GSO, and PKO) was placed separately in 150 ml Erlenmeyer flasks. Flasks were placed in the heaters set at 150°C in the fume hood and the oils were heated to 150°C. Seventy grams of *P. pinaster* resin was added to the oils that reached the desired temperature by mixing slowly. Mixing was continued until the resin completely dissolved in the oil. The oil was filtered using a cotton cloth filter to eliminate the impurities after a homogenous solution was obtained. After filtering, the mixture was reheated to 180°C and cooked for 30 min. The varnish obtained with the desired viscosity was kept at room temperature and cooled. The cooled varnishes were taken into the sample container to be used in the ink formulation.

Offset printing inks production

Inks were produced by combining the previously prepared varnish, pigment blue 15:3 and the oil used in the production of varnish, in the appropriate proportions used in commercial inks. The formulation of inks is given in Table 5. The pigment, oil, and varnish amounts for ink composition are also presented in Table 6.

Test prints of inks

Test prints were achieved with an IGT C1 (IGT Testing Systems, Almera, the Netherlands) test printing device working with a pressure of 300 N and 0.010 g ink was transferred to the paper. Test printing samples ground tone intensity values were carried out under 20° observer angle and D50 light source. Before test prints, papers were conditioned in the printing room at 23 ± 1°C and 50% ± 3% relative humidity for 24 h. Test prints were performed based on ISO 12647-2:2013 standards.

Optical measurements were performed within 400–700 nm range with a D50 light source, 2° observers, and an open polarization filter at 0°/45° geometry with X-Rite eXact Spectrophotometer (X-Rite, Germany). Color measurements were performed with CIE $L^*a^*b^*$ method according to ISO 12647-2:2013 standard. Color differences in test prints were calculated with the below-given Formula (1) according to CIE ΔE^* 2000 ISO 13655 standard. Gloss measurements of the prints were performed using a micro-TRI-gloss (60° geometry) gloss meter (BYK Gardner, Germany) by ISO 2813.

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

L^* indicates lightness from black (0) to white (100); a^* is greenness (−) to redness (+) and b^* indicates blueness (−) to yellowness (+). The terms of the formula can be described as follows: A hue rotation term (R_T), to deal with the problematic blue region (hue angles about 275°), compensation for neutral colors (the primed values in the L^*C^*h differences), compensation for lightness (S_L), compensation for chroma (S_C), compensation for hue (S_H), k_L is the lightness parametric factor, k_C is the chroma parametric factor,

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k_H is the hue parametric factor (Mokrzycki & Tatol, 2012; Sharma et al., 2005).

Rub resistance of inks on test prints was measured with The Sutherland 2000 Ink Rub Tester (Danilee Co., LLC, USA) with 920 g load and 30 oscillations. The rub resistance was ranked due to reference as 1 = excellent, 2 = good, 3 = bad, 4 = very bad.

The viscosity of the inks was measured with a rheometer Anton Paar MCR 101 (Anton Paar, Germany). The measurement conditions were 23°C, 25 s^{-1}, Pa s. The tack values of the inks were measured with a Thwing-Albert Inkometer 1100 (Thwing-Albert Instrument Company, USA) device with measurement conditions of 32°C, 400 rpm.

Total phenol analysis

The phenolic content of resin and oils was investigated. The total amount of phenol was determined by the Folin–Ciocalteu method. According to this method, a 0.2 ml sample (diluted if necessary) was mixed with a 1.5 ml Folin–Ciocalteu reagent (0.2 M). After waiting 5 min, 1.2 ml was added from the sodium carbonate solution (75 g/L) and the mixture was kept at room temperature and in the dark for 60 min. Absorption was measured at 765 nm and the results were expressed in gallic acid equivalence [(mg GAE)/g or kg].

RESULTS AND DISCUSSION

Optical measurements and printability

The optical properties and printability of the ink were analyzed by measuring $L^*a^*b^*$, density, ΔE, and gloss on the test prints of the inks. The measurement results are presented in Table 7, and the surface and interface images of the test prints are given in Figure 2. As seen from Figure 2, the cyan inks printed on coated paper showed a desired characteristics on the paper surface compatible with previous studies (Hayta et al., 2021). The inks maintained their stability on the coated paper surface. When the surface images were examined, the density differences between the inks could be observed.

TABLE 7 Measurement results of the inks, $L^*a^*b^*$, ΔE, density, and gloss

Inks	L^*	a^*	b^*	ΔE	Density	Gloss (GU)
Ink 1	57.87	−34.01	−49.23	4.35	1.43	46.9
Ink 2	NA (it could not be printed because of its high tackiness)					
Ink 3	56.65	−34.56	−49.54	5.85	1.42	42.4
Ink 4	59,78	−34.59	−49.60	5.97	1.44	17.9
Commercial offset ink (cold set)	54	−36	−49	5	1.45	35–70 GU[a]

[a] This value may vary depending on the substrate material and the characteristics of the work to be printed in commercial inks. In general, 35–70 GU of brightness is expected.

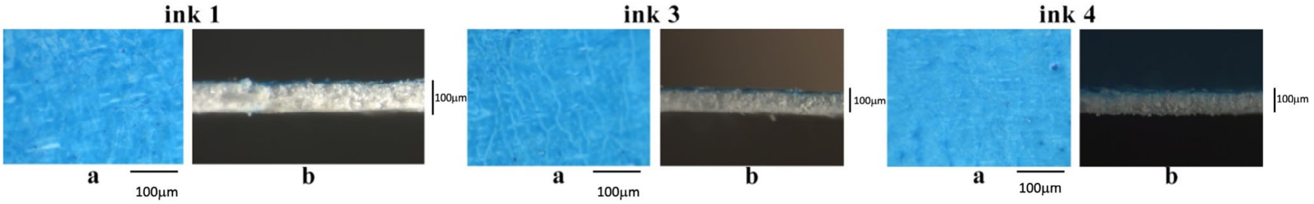

FIGURE 2 Surface and interfaces of inks. (a) Test print surface image; (b) test print interface view

TABLE 8 Rheological behaviors of the inks, viscosity, tack, rub resistance, and setting

Inks	Viscosity (23°C, 25 s^{-1}, Pa s)	Tack (32°C, 400 rpm)	Rub resistance[a]	Setting[a]
Ink 1	12.5 Pa s	9.2 (g m)[c]	1	4
Ink 2	23.6 Pa s	42 (g m)[c]	-	-
Ink 3	14.1 Pa s	9.3 (g m)[c]	1	4
Ink 4	22.3 Pa s	9.3 (g m)[c]	3	4
Commercial offset ink (cold set)	20–50 Pa s	9–10 (g m)[c]	1–2	1–2

[a] Rub test and setting are evaluated as follows: 1 = excellent, 2 = good, 3 = bad, 4 = very bad.

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The reference value is defined according to ISO 12647-2:2013 and the values for cyan color are *L** 54, *a** −36, *b** −49, and Δ*E* deviation tolerance value is defined as 5. The density values of the inks were evaluated according to the ISO 13655:2017 standard regarding the value of 1.45. The *L***a***b**, density, and Δ*E* measurement results of the inks demonstrated close values compared to the cyan color values defined in the ISO offset printing standards. Test printing could not be applied since ink 2 had a high-adhesion value. In terms of *L***a***b** and Δ*E* values, ink 1 demonstrated the most compatible result for the standards. The density value of ink 1 was *m* 1.43 that was close to the standard value. The ink 1 gloss value was obtained as an ideal value of 46.9. The gloss values showed that FO and *P. pinaster* resin were compatible. Ink 1 printability results show that FO is suitable for printability. The Δ*E* tolerance value of ink 3 and ink 4 was at the limit where their densities were close to the standard value. To improve the ink 3 and ink 4 properties, different rates of oil and resins may be used for future studies.

According to the universal standards, brightness values measured at 60° and in the range of 0–100 GU (gloss units). 10–25 GU, 20–35 GU, 35–70 GU, and 70–85 GU are accepted as eggshell-like, satin-like, semi-gloss, and gloss, respectively (MPI, 2021). The gloss values of ink 1 (FO) and ink 3 (GSO) inks were determined as semi-gloss. Ink 4 (PKO) brightness value was obtained as eggshell-like (Table 7). While the results for gloss value demonstrated the ideal behavior for printing in ink 1 and ink 3, it gave a lower value for ink 4. The gloss value depends on the colorant's existence (pigment), particle size, form, surface feature, and quantity of resin (Aydemir & Özakhun, 2014). In this case, by adjusting the resin ratio in the ink 4 formulation, the influence of PKO on brightness could be improved. In addition, the surface properties of the substrate and the ink film thickness and roughness that will form on the substrate are effective in gloss. Print gloss is affected by both the topography and refractive index of the printed surface (Preston et al., 2003). Changes in gloss value can also be observed with test prints being made on different types of paper with Ink 4.

RHEOLOGICAL MEASUREMENTS

Viscosity

The rheological properties of the inks are significant parameters related to the strong adhesion of the ink on the substrate and resistance to physical and chemical effects after printing. A well-balanced set of rheological properties is related to a proper printing process, good printing image, clearer and sharper pictures (Hayta et al., 2021). The ink should have a viscosity that allows it to flow on the container, rollers, and printing plate surface. Low-ink viscosity can cause the ink to be more fluid during printing in the passage between the cylinders and weaker in adherence to the surface of the mold. Also, more ink on the paper surface may be absorbed. The ink should disperse uniformly in the rollers and adhere to them as a thin film. Besides, it should be transferred to substrates at the same thinness level and should dry in a short time (Aydemir et al., 2017).

The viscosity measurements demonstrated that ink 1 showed the lowest viscosity value of 12.5 Pa s while ink 2 showed the highest viscosity value of 23.6 Pa s (Table 8). Viscosity values of other inks were ideal for inks. Although the viscosity value ranges of the inks were different, the viscosity did not cause any problem during the test prints. By adjusting the oil ratio in the solution, the viscosity value will be set to desired values.

Tack

Tack involves mainly the viscous behavior of the ink fluid phase. In respect of ink formulation, it is thus the resin, vegetable oil/alkyd, and distillate choice that contributes most to tack (Rousu et al., 2000). The tack value of ink 2 is specified as very high value 42 (g m)^c in the tack measurement results due to its adhesive characteristic caused by PO. Ink 2 has a high-tack value that cannot be printed. Considering the compatibility of resin with other inks, PO is not a suitable oil for ink formulation. Tack results were 9.2, 9.3, and 9.3 (g m)^c for ink 1, ink 3, and ink 4, respectively. These tack results showed that FO, GSO, PKO give the ideal tack result and are compatible with *P. pinaster* resin. The tack results demonstrated the effect of vegetable oils on rheology since all the inks are composed of the same amount of pine resin.

Rub resistance

Ink rub resistance refers to the degree of ink film being scratched off and stripped under rubbing action. The main factors influencing the rub resistance of the ink are the basic properties of paper (smoothness, absorption ability, etc.), the composition of the ink, and printing conditions. The rub will also influence print gloss (Wenhua et al., 2012). The degree of rub resistance is a factor of the ink used, the type of resin contained in the ink, and the additives (Sappi, 2004).

The amount of resin and oil in the ink composition is one of the important factors affecting the rub resistance. The drying of the ink and the degree of bonding of the pigment are proportional to the abrasion resistance. The oil in the structure of the ink acts both as a binder and as a varnish with the resin and provides a

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TABLE 9 Total phenolic content of pinus resin and vegetable oils

Ingredient	Total phenolic content (mg GAE/kg)
Pinus resin	8218.2
Flaxseed oil	287.9
Pomegranate seed oil	335.6
Grape seed oil	503
Plum kernel oil	212.1

protective effect against scratching the ink on the substrate. The amount of resin and oil in the formulation is effective in low- or high-friction resistance (Aydemir & Özakhun, 2014). The results of the rub resistance show that FO, GSO, and *P. pinaster* resin are suitable components that will be used for offset printing inks.

Rub test are evaluated as follows: 1 = excellent, 2 = good, 3 = bad, 4 = very bad. When the rub resistance results of the inks were examined, while ink 1 and ink 3 were evaluated as excellent (1), ink 4 was evaluated as bad (3). The evaluation of bad shows that the ink film can be easily scratched on the substrate. This shows that the ink is more susceptible to external factors after printing than other inks. The friction resistance could also be effective in print brightness. The lowest brightness ink4 presented the lowest rub resistance value. For future studies, ink 4 will be formulated with different oil and resin ratios to improve the rub resistance. Due to the high adhesiveness of ink 2, the rub resistance could not be measured. The results of the rub resistance show that FO, GSO, and *P. pinaster* resin are suitable components that will be used for offset printing inks.

Setting

Ink placement occurs mainly through a reaction with oxygen before evaporation of drying oils or polymerization of ink connectors (Chen, 2012). Settling is the final step in the printing process and determines the final quality of the printed product. The main processes for settling ink are "absorption," "polymerization," and "solvent evaporation" (Desjumaux, 1996). In this study, the settling processes of inks prepared with vegetable oils were performed by oxidation-polymerization, and some absorption was obtained by the paper surface. The best placement values of inks are poor according to the setting results. However, this situation is not sufficient to affect the quality of printing. Because friction resistance tests of inks showed high friction-scratching tendencies (Figure 2). The setting values could not be measured because the test prints of pomegranate core oil could not be made. The setting of other inks was scored as 4 = very bad.

The thixotropic nature of offset printing inks accelerates settling, but ink manufacturers add quick-setting varnish to increase settness by allowing the second printed ink to be accepted by the first printed ink. Therefore, the printing process for the inks obtained in this study should be improved by further studies.

Total phenolic content

The procedure of determining the quantity of phenolic content in samples is known as total phenolic content (TPC) activity. The redox characteristics of phenolic chemicals found in plants allow them to act as antioxidants (Johari & Khong, 2019). In biological systems, phenolic compounds display free radical inhibition, peroxide breakdown, metal inactivation, or oxygen scavenging, according to many reports in the literature, and reduce the burden of oxidative illness (Aryal et al., 2019).

The results showed that *P. pinaster* resin exhibited a high TPC as 8218.2 mg GAE/kg (Table 9). The TPC of GSO (503 mg GAE/kg) was measured higher than other oils while TPC of FO, PO, and PKO showing TPC activity of 287.9, 335.6, and 212.1 mg GAE/kg, respectively. The findings demonstrated the expected potential for antioxidant and antibacterial activities.

CONCLUSION

Ink production using natural and renewable raw materials has become very important for sustainability and environmental contamination. The printing inks form volatile reaction products that lead to indoor air pollution during the drying processes. Therefore, using nontoxic, human, and environmentally compatible raw materials is emerging as an essential fact for printing ink production.

Environmentally friendly and self-drying (cold set) inks were developed within the scope of this study using natural pine resin and natural vegetable oils. Printability evaluation of these newly developed inks as bio-based products were favorable. The printability parameters of ink 1 and ink 2, which applied to the uncoated paper surface, persisted within standard quality ink values. The optical analysis demonstrated the suitability of the ink 1 prepared with flaxseed oil and *P. pinaster* resin and ink 2 prepared with grape seed oil and *P. pinaster* resin since the color, gloss, and density of the ink film on the substrate surface were as an ideal based on the standards. The rheological analysis expressed the ideal structure and behavior of ink during printing and, its resistance to external factors after printing. The compatibility of these oils with *P. pinaster* resin supported the potential production of commercial inks with natural ingredients.

On the other hand, the printability analysis of the ink 4 prepared with plum kernel oil and *P. pinaster* resin

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was resulted in unsuccessful due to the low gloss and viscosity values. In addition, the rub resistance result showed that the ink film was prone to scratching after printing. For future studies, it is possible to try plum kernel oil with different resins for developing offset printing inks. The printability analysis of ink (ink 2) prepared with pomegranate oil and *P. pinaster* resin could not be performed. Due to its adhesiveness, pomegranate oil is not suitable for offset printing or cold-set ink production.

AUTHOR CONTRIBUTIONS

Pelin Hayta carried out the research, analyzed the data, and wrote the first draft of the manuscript. Mehmet Oktav conceived and designed the study, performed some experiments, and analyzed the data. Özlem Ateş Duru conceived, designed, and supervised the study, performed some experiments, and analyzed the data. All authors contributed to reviewing and editing the manuscript and approved the final draft of the manuscript.

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ETHICS STATEMENT

The present study is the authors' own original work, which has not been previously published elsewhere. The paper reflects the authors' own research and analysis in a truthful and complete manner.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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