ASSESSMENT OF QUALITY IMPAIRMENT OF PRINTED PAPER PACKAGING FROM ALTERNATIVE RAW MATERIALS IN CONTACT WITH SOYBEAN OIL

PROCJENA NARUŠENOSTI KVALITETE TISKANE PAPIRNATE AMBALAŽE OD ALTERNATIVNIH SIROVINA U KONTAKTU SA SOJINIM ULJEM

Ivana Plazonić, Irena Bates, Katja Petric Maretić, Maja Rudolf

University of Zagreb, Faculty of Graphic Arts, Getaldićeva 2, Zagreb, Croatia

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Abstract

Soybean is an important industrial crop grown for oil and protein production. Soybean oil is the second most widely produced edible oil. Except as edible oil, soybean is widely used in human nutrition as flour, milk, cheese and sauces, while soy lecithin is an inevitable additive in many food products. It should be emphasized that soybean has become indispensable in the production of meat and dairy substitute products as the fastest growing trend in the food industry. In addition to human and animal nutrition, soybean is also important for the pharmaceutical, textile and chemical industries and in the production of biodiesel fuel. Many of the listed soybean products also require appropriate packaging that complies with environmental regulations. Due to the global trend of increasing consumption of soybean products, within the scope of this research, the impact of soybean oil on the print quality of paper packaging from alternative raw materials was monitored. The deterioration of the original quality of the print with black UV ink applied by digital, flexographic, gravure, screen and offset printing techniques was evaluated after 24 hours of contact with soybean oil based on measured spectrophotometric values.

***Keywords**: paper packaging, print quality, soybean oil*

Sažetak

Soja je značajna industrijska kultura koja se uzgaja radi dobivanja ulja i bjelančevina. Sojino ulje je drugo jestivo ulje po proizvodnji. Osim kao jestivo ulje, soja se široko koristi u ljudskoj prehrani kao brašno, mlijeko, sir te umaci, dok je sojin lecitin neizbježan dodatak mnogim prehrambenim proizvodima. Treba naglasiti kako je soja postala nezamijenjiva u proizvodnji mesnih i mliječnih zamjenskih prehrambenih proizvoda kao najbrže rastućeg trenda u prehrambenoj industriji. Osim u ljudskoj i životinjskoj ishrani, soja je značajna i u faramceutskoj, tekstilnoj i kemijskoj industriji te u proizvodnji biodizelskog goriva. Brojni navedeni sojini proizvodi zahtijevaju i adekvatnu ambalažu koja je u skladu s ekološkim regulativama. Zbog globalnog trenda sve veće konzumacije sojinih proizvoda, u okviru ovog istraživanja pratio se utjecaj sojinog ulja na kvalitetu otiska papirnate ambalaže iz alternativnih sirovina. Narušenost početne kvalitete otiska crnom UV bojom nanešenom digitalnom, fleksografskom, bakrotiskarskom sitotiskarskom i offsetnom tehnikom tiska evaluirana je nakon 24-satnog kontakta sa sojinim uljem temeljem izmjerenih spektrofotometrijskih vrijednosti.

***Ključne riječi:** papirna ambalaža, kvaliteta otiska, sojino ulje*

Corresponding author: Ivana Plazonić, ivana.plazonic@grf.unizg.hr

1. INTRODUCTION

Demand for packaging materials is constantly increasing. Packaging materials are a means of preserving, protecting, marketing, selling and distributing products. They play a significant role in ensuring that these products reach consumers in a safe and healthy form without compromising quality [1]. Plastic is the youngest in comparison with other packaging materials and is often chosen for packaging applications that require toughness and impact resistance thanks to their enhanced durability, which in turn ensures product safety. The packaging industry is the largest user of plastics, as more than 90% of flexible packaging is made of plastics, compared to only 17% of rigid packaging quality [1]. Unfortunately, the very properties that make plastic so useful also cause plastic waste to become a problem for the environment and many companies are switching to paper packaging rather than plastic packaging to become more sustainable. Paper and cardboard are sheet materials made from an interlaced network of cellulose fibers obtained mainly from wood. Globally, recovered paper is recognized as a cheaper and good enough raw material compared to virgin wood fibres. However, the increasing recycling rate has reduced the quality of the collected recovered paper, produced recycled paper, and replaced virgin pulp [2]. The global usage of recycled fibers in the production of paper and fibre-based packaging has resulted in paper products with reduced strength, which is especially unacceptable for packaging. Adding virgin wood fibers into the pulp of recycled fibres can solve the problem of the product strength [3]. This paper evaluates the possibility of using alternative virgin fibers from cereal straw for the same purpose to reduce the consumption of scarce wood sources.

The posibility of replacing virgin wood fibres in fibre-based packaging was evaluated based on the chemical stability of prints. Prints were gained by five widely used printing techniques on laboratory produced paper made from pulp admixture of recycled fibres and virgin wheat, barley, or triticale fibres and brought into contact with edible soybean oil. Soybean oil was selected from all commercially available edible oils, as one of the vegetable oils with the highest global consumption. From Statista source, in year 2022/23, soybean oil takes second place (Figure 1), after palm oil, with a worldwide comsumption of 60.32 million metric tonnes (60,320,000,000 kg). China is by far the largest producer, followed by the USA, Brazil and Argentina.

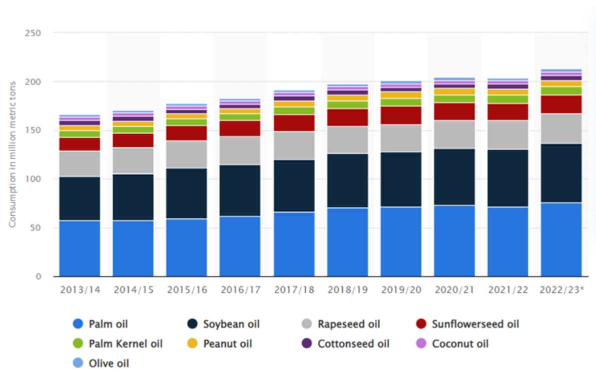
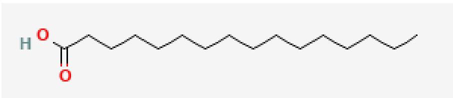
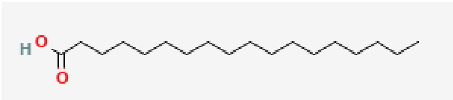
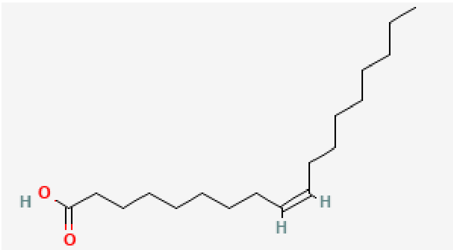
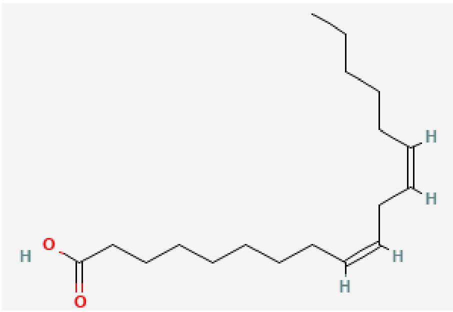
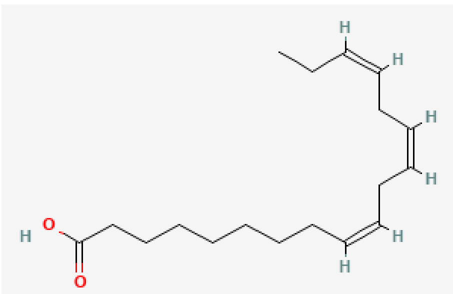


Fig. 1: Consumption of vegetable oils worldwide from 2013/14 to 2022/23, by oil type [4]

Soybean (*Glycine max (L.) Merr.*) is one of the most widely grown and used legumes in the world due to its valuable seed composition. It is a valuable source of protein and oil. Primarily soyebean was used as livestock feed, with some human food applications, while the latter is more broadly incorporated into food, feed, and some industrial applications (as biodiesel). Protein and oil percentages in soybean are influenced by both genotype and environmental factors, average approximately 40% and 20%, respectively [5]. In 2018, about 398 million tonnes of soybeans were produced worldwide, accounting for 61% of the total production of oilseeds [6]. Therefore, it is not surprising that soybean is one of the most valuable, versatile, and nutritionally important legumes globally. The composition of soybean oil in terms of fatty acids content are as follows: lauric acid 0.2%, myristic acid 0.1%, palmitic acid 9.8%, stearic acid 2.4%, arachidic acid 0.9%, oleic acid 28.9%, linoleic acid 50.7%, linolenic acid 6.5% and hexadecenoic acid 0.4% [7]. Commodity soybean oils is composed of five fatty acids in percetange given in Table 1.

Tab. 1: Fatty acid composition of soybean oil

Fatty acid	Structure	Symbol (No. of carbon-carbon double bonds)	% [7]
Palmitic acid		C16:0	10
Stearic acid		C18:0	4
Oleic acid		C18:1	18
Linoleic acid		C18:2	55
Linolenic acid		C18:3	13

Fatty acid composition of soybean oil shows linoleic fatty acid forming a major constituent of fatty acids present. According to its content of linolenic acid this oil is classified as non yellowing oil. Although due to the content of linolenic acid (averaging roughly 10% of the total fatty acids), soybean oil is not expected to be as good in non yellowing as safflower and sunflower oils. From the data presented in Table 1 it is visible that percentage of unsaturated fatty acids (C18:1, C18:2 and C18:3) in soybean oil is 86%, while saturated fatty acids (C16:0 and C18:0) constituted 14%. Unsaturated fatty acids are more susceptible to hydrolysis and oxidation reactions than saturated fatty acids due to weaker carbonbonding in unsaturated carbons. The iodine number of this oil ranges from 124 to 139 [8], according to which, soybean oil is classified as a semi-drying oil. This means that soybean oil cannot be dried at room temperature if its functional groups are not modified. Therefore, the use of soybean oil in both the printing ink and paint industries is significantly limited [9].

Due to its relatively low cost of production, soybean is an exceptional agricultural crop for scientific and technological development. Since the price of the product is always a factor in its success, it is precisely the low price of oil and protein that gives soybean an advantage over similar products made from other oilseeds for industrial markets [10].

1. MATERIALS AND METHODS

1.1. Paper production from pulp of reinforced recycled fibres with virgin straw fibres

According to EN ISO 5269-2:2004 [11], laboratory-made papers with a diameter of 200 mm and a weight of 42.5 ± 2.6 g/m^2 were produced from recycled pulp and unbleached wheat, barley, or triticale straw pulp admixure with a Rapid-Köthen sheet former (FRANK-PTI). Straw collected from the fields of central Croatia after harvesting wheat, barley and triticale crops served as an alternative raw material for obtaining pulp of virgin fibres needed for this research as reinforced fibres. Alkaline pulping process was chosen for obtaining straw pulp. Before cooking, all three types of straw were previously cleaned of impurities and grains and cut by hand to a length of 1 to 3 cm. All cooking batches were performed under the same constant process conditions [12] regarding concentration of sodium hydroxide reagent (16%), cooking temperature (120 °C) and pressure (170 kPa), cooking time (60 min) and a liquid/solid ratio (10:1). Cooked straw was washed to remove residual cooking liquor and fiberized in a Holländer Valley mill at 500 rpm for 40 min, after which the pulp was drained and dryed at room temperature to a moisture content of 10%. Unbleached straw pulp was further used as a reinforcement of recycled fibers in the pulp at a share of 30% for the production of paper for fiber-based packaging.

Laboratory-made papers from pulp of recycled fibres (N) were used as a reference paper for evaluation of three different types of laboratory-made papers from pulp of recycled fibres reinforced with: wheat straw fibres (30NW), barley straw fibres (30NB) and triticale straw fibres (30NTR).

2. 2. Printing of papers with UV curable inks

Five commonly used printing techniques were selected for printing laboratory-produced papers with the addition of straw pulp in order to gain a broader insight into the possibilities of using these papers for fiber-based packaging that requires printing. All produced paper was printed in full tone with black UV curable inks.

In Table 1 are summarized all information regarding printing processes used.

Tab. 1: Description of the printing processes used to obtain prints with black UV curable ink

Printing				Drying	
Techniqe	**Machine**	**Process conditions**	**Ink**	**Machine**	**Power of lamp**
Digital	EFI Rastek H652 UV curable printer	High quality printing mode (8 pass) with a speed of 12.1 m^2/h and a resolution of 600 x 600 dpi.	EFI Rastek	Two dual-intensity UV lamps integrated into the printing machine	Mercury-based UV lamps with the power of 700 W
Flexographic	Laboratory device Esiproof (RK Print Coat Instruments)	Printing speed of 0.5 m/s with a pressure of 300 N and an anilox roller pressure of 200 N, at a temperature of 23 °C and a relative humidity of 50%.	Solarflex Integra (Sun Chemical)	Technigraf Aktiprint L 10-1 dryer	UV-C tube with a light source power of 120 W/cm and intensity of 60%
Gravure	KPP Gravure system with (RK Print Coat Instruments)	Printing speed of 20 m/min with a 65 Shore impression roller and a 100 lines/inch engraving plate, at a temperature of 23 °C and a relative humidity of 50%.	Solarflex Integra (Sun Chemical)	Technigraf Aktiprint L 10-1 dryer	UV-C tube with a light source power of 120 W/cm and intensity of 60%
Screen	Semi-auto Shenzhen Juisun screen printing machine	Squeegee of a mechanical hardness of 75 Shore and a mesh line of 140 l/cm was used, at a temperature of 23 °C and a relative humidity of 50%.	UltraGraph UVAR (Marabu GmbH)	TM-UV750L UV curing machine	Two UV lighting tubes with a light source power of 5.6kW and conveyor speed of 0-25 m/min
Offset	Prüfbau multipurpose printability testing machine	Printing speed of 0.5 m/s with a pressure of 600 N, at a temperature of 23 °C and a relative humidity of 50%.	SunCure Starluxe low migration	Technigraf Aktiprint L 10-1 dryer	UV-C tube with a light source power of 120 W/cm and intensity of 60%

All used UV curable inks are consisted of four main components (Figure 2): monomers/oligomers, colourants (pigments or dyes dispersed or dissolved in a reactive carrier) photoinitiators, and other additives [13].

Reactive monomers are the base of every UV curable ink, and they define the softness/hardness of the ink, the flexibility or stretchability of the ink and help to control the viscosity of the ink. Oligomers in the ink formulation consist of reactive resins and uniquely formulated adhesive components. Dyes and pigments are two main forms of colourant. All printing machines in this study use UV curable inks with inorganic molecules of pigments, except digital ink jet printing machine which uses very small organic molecules of dye. For full development of the colour, the pigment particles in UV curable flexographic, gravure, screen and offset inks must be smaller than 200 nanometers.

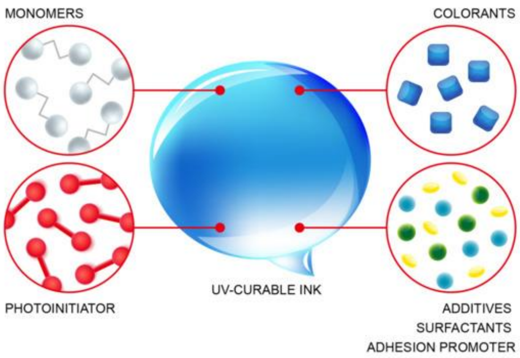


Fig. 2: Compounds in UV curable ink [13]

Exposing the photoinitiators in the ink to UV light source, the oligomers and monomers in ink are cross-linked or polymerized which turns the ink from a liquid into a solid film. So, unlike solvent-based or water-based inks, curing of UV inks does not require heat or air drying.

2. 3. Assessment of resistance of prints to soybean oil

All black prints produced by five different printing techniques on laboratory-made papers with 30% straw pulp (30NW, 30NB and 30NTR) and reference paper without addition of straw pulp (N) were tested for resistance to edible soybean oil in accordance with ISO 2836:2004 standard [14]. This test method can be described as immersion of the four strips of filter paper in edible oil used for the test and then draining them until there is no dripping from the filter papers. Two saturated strips of filter papers were placed on the lower glass plate on which the test specimen of print pre-cut to size 20×50 mm was placed and covered with the remaining two strips of saturated filter papers and another glass plate. On top, a 1 kg mass weight was placed and left for 24 hours. The test specimen was then dried for 30 minutes in an oven preheated to 40 °C.

The oil resistance of prints made by different printing techniques on papers produced from pulp of recycled fibers reinforced with 30% straw pulp and on reference papers (without addition of straw pulp) was evaluated based on the changes in the colorimetric values of the black prints after treatment with soybean oil.

To assess the influence of soybean oil on the UV black prints, the difference between the two black colours within the L*a*b* system was calculated according to Equation 1, using the untreated sample as a reference:

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

Where: $\Delta E_{00}*$ represents the total colour difference, $\Delta L'$ represents the difference in lightness between black prints before and after oil treatment, $\Delta C'$ represents the chroma difference between the black prints before and after oil treatment and $\Delta H'$ represents the hue difference between the black samples before and after oil treatment, R_T represents the rotation function, while k_L, k_C, k_H represent the parametric factors for variation in experimental conditions and S_L, S_C, S_H represent the weighing functions.

3. RESULTS

The change in the black colour of the UV prints made by five different printing techniques (digital, flexographic, gravure, screen, and offset) caused by contact with soybean oil is presented in Figures 2a-d regarding paper type used as a printing substrate. It is noticeable that if reference printing substrate without straw pulp (Figure 2a) is used as a printing substrate to obtain black UV prints regardless of the printing technique used, the colour difference values after contact with soybean oil are within the acceptable range (below ΔE_{00}^* = 2), meaning that the colour difference cannot be perceived by the untrained eye. The stability of the print on this printing substrate from the least to the most stable to soybean oil depending on the printing technique is as follows:

digital < offset < screen < gravure < flexographic.

Although with slightly higher values of ΔE_{00}^*, which indicates a reduced stability to oil, printing substrates with the addition of straw pulp of any cereal by printing with the mentioned printing techniques provide black prints with similar behaviour as one on the reference sample (Figures 2b-d). Generally, on papers with straw pulp the most stable are flexographic prints, while the least stable are digital prints except in the case of 30NB printing substrate where the offset print proved to be the least stable (Figure 2c).

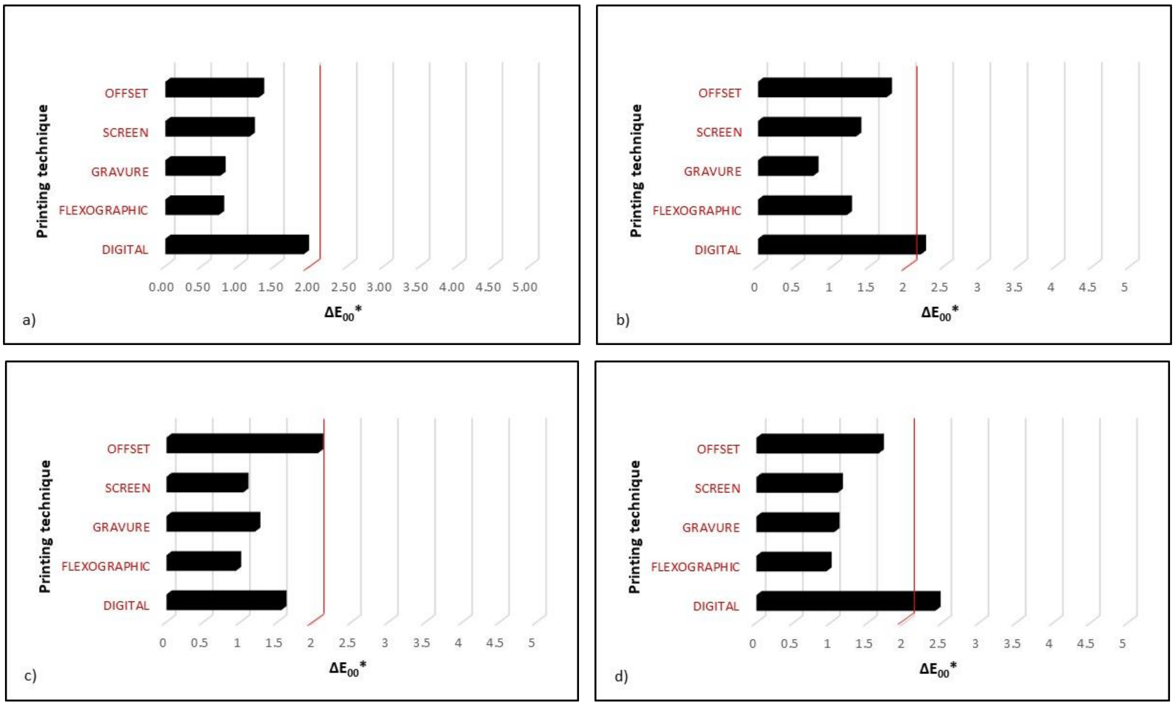


Fig. 2: Change in the black colour of the print caused by contact with soybean oil depending on the type of printing substrate: a) N; b) 30NW; c) 30NB; d) 30NTR

This behaviour of black prints in contact with oil may be related to colourant molecules in the inks and the viscosity of the inks used for printing with different printing techniques. Although UV digital (inkjet) inks are very low in viscosity, not higher than 25 mPa·s [15], the weaker oil resistance observed in digital prints (ΔE_{00}* ranging from 1.55 to 2.41) can be explained by small organic dye molecules that are soluble in water and organic solvents, in contrast to prints obtained by other analysed printing techniques whose black UV curable ink contain organic pigment molecules much larger in size that are insoluble in water and organic solvents. In the case of UV curable inks that contain black pigments as a colourant, the viscosity of the ink is crucial for the stability of the prints in contact with edible soybean oil. The ink viscosity, meaning its stickiness and fluidity, determines its flow properties and suitability for different printing techniques. Reactive monomers in the ink control this property of the ink. Flexographic printing technique requires low viscosity UV curable inks that provide fast and uniform transfer of the ink, i.e., good quality at high printing speeds and are usually in the range of 1000 m Pa·s in viscosity [16], as does gravure printing technique. In screen printing where there is a huge array of process options and applications, the ink viscosity must be tuned to the size of the screen mesh and ink layer thickness. From all printing techniques that use ink with pigments as colourant, offset inks have relatively high viscosity. Lower viscosity of the black ink can be associated with small oil absorption number (OAN) [17], as the oil absorption number is a measure of the ability of a carbon black to absorb liquids. From all of the aforementioned, it can be concluded that flexographic black UV ink with the lowest viscosity is consisted of carbon black pigment with the smallest absorption of soybean oil and therefore the greatest stability on contact with the soybean oil, because the smallest change in black colour occurs. As the viscosity of inks that contain black pigment as a colourant increase, the absorption of soybean oil into the printing substrate also increased, and a larger difference in colour was measured (for offset print on printing substrate 30NB, ΔE_{00}* was 2.04).

4. CONCLUSION

In this reaserch, it was observed that the addition of cereal straw pulp as a reinforcement to the pulp of recycled fibers in the production of the printing substrate did not significantly affect the change in stability of the prints after exposure to edible soybean oil. It has been confirmed that regarding the chemical stability of the prints, the composition of the ink plays the key role, and not the printing substrate. It has been observed that the least stable are digital prints in which the black dye dissolves in contact with oil. In the case of prints with inks that contain pigments, regardless of the type of printing substrate used, the most stable are those with low viscosity - flexographic prints.

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