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Soybean oil based inks for enhanced deinkability of litho prints

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Abstract

Three types of food grade soybean oils were tested to determine if their byproducts could be utilized in the paper recycling industry. Free fatty acids were extracted from these commercially available soybean-oils. These acids were utilized in one loop air flotation deinking of litho-printed paper substrates. It was found that the three experimental fatty acids used in deinking differ in their chemical composition, namely Acid number and Saponification number. The effect of each of the soy-oil free fatty acid on deinking was studied, quantified and compared to the standard INGEDE 11p procedure. The INGEDE method employs commercially available oleic acid and experimental fatty acids were tested as its replacement. INGEDE method 11p was slightly modified due to unavailability of a Hobart type pulper. Therefore, a MicroMaelstrom™ Laboratory Pulper was used instead. The substrate used for deinkability study was heavily printed from both sides by sheetfed offset lithography. Due to heavy ink mileage, none of the four fatty acids had the power to deink such substrates in a one loop flotation recycling experiment. Besides INGEDE deinking evaluations, further deinking assessments were performed. Deinkability factors DEM_{Lab} and DEM_{f} were used to express the success of ink removal from the pulp, since ERIC instrument measuring equivalent residual ink concentration, considered in INGEDE scoring, was not available. Dirt count analysis of deinked handsheets was performed by scanning them using an Epson Perfection V500 Photo scanner followed by processing of scanned images by Verity IA Color Image Analysis software. Overall, it was found that two of the three experimental fatty acids (free fatty acid from everyday pure soy oil and the one from high oleic soy oil) performed better than the standard, using oleic acid. It was also found that these free fatty acids had lower acid number than the standard oleic acid, which could improve the deinking performance.

Keywords: deinking, offset litho printing, recycling, acid number, deinkability factor

1. Introduction

In the recycling facilities, the first step of the deinking process focuses on repulping of the printed substrate. Repulping occurs in an aqueous environment, typically in a basic pH range.

Mechanical agitation allows the breaking of the fiber network. Breaking of the bonding between the fibers and the ink particles is fundamental for the ink detachment from the fibers. Addition of deinking chemicals in the repulping stage facilitates the ink detachment. In general, repulped stock will be dark with visible contaminants floating on the surface. Such pulp will produce a dark, speckled paper substrate that will be unacceptable for the customer. Therefore, the major goal of the recycling is to eliminate the ink particles and improve the optical properties of the recovered pulp (Renner, 2000). Based on studies performed by multiple researches, the strength of the fiber-ink bonding depends on pigment particle size, ink formulation, printing process, ink film thickness and ink depth penetration (Carré et al., 2000; Pekarovicova, Pekarovic and Frimova, 2003). Further, ink aging and its raw components will also impact the deinking efforts (Angellier, Bousfield and Dimotakis, 2004; Haynes, 2000).

This experimental study was focused on deinking via INGEDE Method 11p (2009) and its modification. The deinking protocol consisted of offset printed stock repulping followed by the air flotation and further handsheet preparation. Free fatty acids extracted from three types of commercially available soy oils were tested as a replacement of oleic acid used in INGEDE Method 11p (2009). The objective of the study was to determine if three fatty acids coming from three types of soybean oil would produce the deinked pulp with comparable optical properties to the deinked pulp prepared using oleic acid. The effect of each of the soy-oil byproducts on deinking was observed and quantified. The main focus was to investigate whether the free acid extracted from food grade soybean oil can replace commercially available oleic acid. This work is applicable in the field of utilization of byproducts from soybean processing and also in improving deinking process as designed by the INGEDE method.

2. Materials and methods

2.1 Analysis of soy oils

The Michigan Soybean Promotion Committee provided three commercially available soybean oils. Their typical use is found in the food industry. The differences in their internal structure were analyzed via saponification and acid number testing (ASTM D94-07, 2012; ASTM D664-11a, 2011). Sodium soaps were prepared from each of the three soy-oils. In order to replace oleic acid used in INGEDE protocol, it was necessary to extract free fatty acids from the soy oils. The extraction of fatty acids was performed by use of Method IV from Standard methods for the analysis of oils, fats and derivatives (Hautfenne, 1982).

2.2 Offset sheetfed printed substrate

The offset sheetfed litho printed substrate was obtained from North American Color, Kalamazoo, MI. The substrate was heavily color-printed in multicolor offset lithography from both sides, with dual picture on one side, see Figure 1. Physical and optical properties of the unprinted sheet are illustrated in Table 1.

Table 1: Properties of unprinted base sheet used for deinking

Physical properties of Unprinted Base Sheet	
Grammage (g/m^2)	115
Thickness (µm)	75.0
Ash content (%) @ 525 °C	45.0
Optical properties of Unprinted Base Sheet	
Brightness	86.7
Luminance (*Y–value*)	83.1
L^*	92.9
a^*	1.24
b^*	−2.52

2.3 Deinking

Prior to the deinking, printed and unprinted substrates were aged for 72 hours at 60 °C as per INGEDE Method 11p (2009). After aging, printed and unprinted substrates, respectively, were torn to 2 cm × 2 cm pieces and were conditioned in the paper laboratory for 24 hours, 23 ± 1 °C at 50 ± 2 % relative humidity.

Due to the unavailability of a Hobart type pulper used in INGEDE Method 11p, a MicroMaelstrom™ Laboratory Pulper type of slush–maker was used instead. Repulping parameters (rpm – revolutions per minute and repulping time) versus particle dirt count and diameter size were examined prior this experimental study. The most suitable conditions were selected and they are listed in Table 2. Dilution water hardness was adjusted as per INGEDE requirement. INGEDE protocol lists the homogenization process as optional. During our experimental study, all of the pulps were homogenized using a TAPPI disintegrator. A total of eight repulping and flotation experiments were conducted using the four fatty acids.

The goal of the repulping is to break the bonds between ink and fibers. It was achieved first by applying shear forces, secondly by addition of deinking chemicals. Pulping time was constant for all experiments and its length was 10 min. The speed of the MicroMaelstrom™ Laboratory Pulper was set to 500 rpm and the temperature was adjusted to 45 °C by using the built in thermostat. After defibration, repulped stock was diluted to 6 % consistency using dilution water with fixed hardness value of 128 mg Ca^{2+}/L. Next, repulped stock was stored for an hour in the water bath at 45 °C. After storage, TAPPI disintegrator was used to disintegrate fiber bundles for 1 minute. Prior to the air flotation, undeinked stock was taken for preparation of 2 filter

Figure 1: Sheetfed offset litho printed paper side 1 and side 2

papers and 10 handsheets. The rest of the undeinked pulp was taken and was subjected to flotation deinking. A small 2 L laboratory flotation cell was used for all deinking trials. Due to the volume of the cell, each of the experiments was repeated twice. This way, larger amounts of deinked pulp suitable for handsheets and filter pads formation were obtained. "Filter pad" was filtration paper Whatman 1, through which pulp slurry was filtered to obtain filtrate as well as the fibers from slurry without washing needed for further study. Variable amount of fibers was trapped on filter paper. The flotation cell aeration was fixed to flow rate of 1 L/min. The duration of flotation deinking was 12 minutes. A paddle scraper was used for froth removal over the course of flotation. The removed froth was collected in a reject tank. The yield of the flotation was calculated once the reject was dried and deducted from the original floated slurry weight. The final consistency of the deinked stock was calculated and the deinked stock was subjected to preparation of the handsheets, filter pads and membrane filters. 2 filter pads and 10 handsheets were formed from undeinked pulp, as well as from deinked pulp. 2 membrane filters were prepared from water obtained after 2 filter pads were formed.

Table 2: Repulping, storage and disintegration process parameters

Re-pulping recipe	Sodium hydroxide	0.6 %
	Sodium silicate	1.8 %
	Hydrogen peroxide	0.7 %
	Oleic acid/Acid from soy oil A or B or C	0.8 %
Re-pulping conditions	Water hardness	128 mg Ca^{2+}/L
	Temperature	45 °C
	pH	9.5 ± 0.5
	Consistency	6 %
	Mixing speed	500 rpm
	Re-pulping time	10 min
Storage	Consistency	5 %
	Duration	60 min
	Temperature	45 °C
Disintegration	Consistency	4 %
	Duration	1 min
	Temperature	45 °C
Flotation	Consistency	0.8 %
	Duration	12 min
	Temperature	45 °C
	Aeration flow rate	1 L/min

3. Results and discussion

In order to better understand the differences between three soy-based oils, determination of Saponification number of oils and Acid number of free fatty acids was performed. Saponification number allowed identifying the amounts of free and bound acid groups per gram of tested oils, while the Acid number determines amount of free acid groups per gram of tested oil or fatty acid. The slight differences in amounts of Saponification numbers were found for soybean oil B (199.40) and soybean oil C (197.71). Slightly higher saponification values were determined for soy oil A (201.19). Further processing of oils A, B and C resulted in their free fatty acids, further designated as FFA-A, FFA-B and FFA-C, respectively. Their Acid numbers were determined and are represented in Table 3 with that of oleic acid.

Table 3: Acid numbers of free fatty acids

Free fatty acid	Acid number
FFA-A	202.6
FFA-B	196.2
FFA-C	194.8
Oleic acid	200.3

Deinkability evaluation parameters according to INGEDE Method 11p focus on pulp and process parameters. The objective of pulp parameters are high reflection of deinked pulp represented by luminance value *Y*, high cleanliness of deinked pulp characterized by low dirt particle area *A* and no discoloration of deinked pulp depicted by *a** coordinate of CIELAB space, where three axes, *L**, *a** and *b**, evaluate the color in three dimensional color space (CIE Proceedings, 1932; Fleming, 2003). The goal of process parameters is to assure good ink removal represented by ink elimination and lastly the cleanliness of circuit water characterized by filtrate darkening ΔY. Due to unavailability of the instrument capable of measuring the effective residual ink concentration (ERIC), deinking evaluation assessment by DEM_{Lab} factor (Rao and Stenius, 1998) was done. The DEM_{Lab} factor uses the color difference between unprinted deinked pulp (US) and printed deinked pulp (DS) in relation to the color difference between unprinted deinked pulp (US) and printed undeinked pulp (BS). Technidyne Brightness Meter S-5 with C/2° geometry of light source was used. The DEM_{Lab} factor was calculated according to following Equation [1]:

$$DEM_{\mathrm{Lab}} = \left(1 - \frac{\sqrt{\left(L^*_{\mathrm{US}} - L^*_{\mathrm{DS}}\right)^2 + \left(a^*_{\mathrm{US}} - a^*_{\mathrm{DS}}\right)^2 + \left(b^*_{\mathrm{US}} - b^*_{\mathrm{DS}}\right)^2}}{\sqrt{\left(L^*_{\mathrm{US}} - L^*_{\mathrm{BS}}\right)^2 + \left(a^*_{\mathrm{US}} - a^*_{\mathrm{BS}}\right)^2 + \left(b^*_{\mathrm{US}} - b^*_{\mathrm{BS}}\right)^2}} \right) \quad [1]$$

where US represents unprinted deinked pulp, DS represents printed deinked pulp, and BS represents printed undeinked pulp.

In general, the deinkability factor is presented on a scale from 0 to 100 %. A deinkability factor closest to the 100 % will represent the sample that was flawlessly deinked. The color difference of a sample to a reference sample as a vector in the CIELAB color system was used to develop DEM_{Lab} deinkability factor.

During the evaluation, deinkability factor DEM_{f} developed by Papiertechnische Stiftung (PTS) in Munich, Germany was used. Deinkability factor DEM_{f} considers brightness difference between the deinked pulp and pulp before deinking. It is calculated (Equation [2]) using averaged brightness values of unprinted deinked pulp, printed deinked pulp and printed undeinked pulp (Renner, 2000).

$$DEM_{\mathrm{f}} = \frac{Brightness(\mathrm{DS}) - Brightness(\mathrm{BS})}{Brightness(\mathrm{US}) - Brightness(\mathrm{BS})} 100 \left[\%\right] \quad [2]$$

Based on both deinkability factors (DEM_{Lab} and DEM_{f}), FFA-C has the highest deinking efficiency, while FFA-A resulted in the least deinked pulp (Table 4). FFA-B was somewhat less efficient than FFA-C, but still provided better results than oleic acid.

In the present study, the main focus was not necessarily to obtain perfectly deinked pulp, but to determine if the free fatty acid extracted from food grade soybean oil can replace commercially available oleic acid.

In addition, the paper substrate was heavily printed. In order to achieve more progressive deinkability results, deinked pulp would have to undergo multi-looped deinking systems, rather than one step deinking flotation.

Table 4: Deinkability efficiency of various free fatty acids

Acid type used for deinking	**Deinkability DEM_{Lab} [%]**	**Deinkability DEM_{f} [%]**
Oleic acid	40.1	36.8
FFA-A	31.6	29.1
FFA-B	50.2	45.9
FFA-C	59.2	56.4

Additionally, the deinking evaluation focused on the dirt count. Handsheets were scanned using Epson Perfection V500 Photo scanner. Evaluation of the scanned handsheets was done with the help of Verity IA Color Image Analysis software (VERITY IA Light and Dark Dirt, 3.4.0). Scanning resolution was set to 1 200 ppi. The inspected area was set to 13 000 mm^2. Dirt count is illustrated in Table 5.

Optical properties of handsheets from deinked pulps, including the deinking yield, are summarized in Table 6. The highest deinking yield was obtained with FFA-A from low linoleic soy oil. Standard oleic acid and FFA-B from high oleic acid resulted in the similar deinking yields, while FFA-C from everyday pure soy oil gave the lowest yield.

Table 5: Handsheets Dark Objects Count (in ppm) of different pulps

Acid type used for deinking	**Unprinted deinked (US)**	**Printed undeinked (BS)**	**Printed deinked (DS)**
Oleic acid	34	108 774	37 188
FFA-A	15	101 993	46 005
FFA-B	60	94 165	22 690
FFA-C	27	108 721	15 362

Table 6: Optical properties of handsheets from deinked pulp (average and standard deviation σ)

Free acid type	Statistics	Y	ΔY	A	L^*	a^*	b^*	Brightness	Yield [%]
Oleic acid	Average	66.3	3.87	37 188	85.1	1.26	−2.92	69.7	86.6
	σ	0.8	–	1633	0.4	0.09	0.18	0.7	0.1
FFA-A	Average	65.0	2.64	46 005	84.5	1.37	−2.79	68.2	92.9
	σ	1.1	–	1581	0.6	0.24	0.12	1.1	0.1
FFA-B	Average	70.3	1.73	22 690	87.2	1.34	−2.30	73.2	86.6
	σ	0.9	–	1029	0.5	0.24	0.20	0.89	0.2
FFA-C	Average	72.7	0.67	15 362	88.3	1.33	−2.68	76.1	84.1
	σ	0.9	–	1 653	0.4	0.18	0.32	1.0	0.1

4. Conclusion

The deinkability efficiency of three experimental fatty acids obtained by extraction from three types of soybean oil A, B and C was studied. The deinkability potential of experimental fatty acids was compared to the deinkability power of oleic acid that is used as a standard fatty acid in INGEDE 11p method. The substrate used for deinkability study was heavily printed from both sides and therefore none of the four fatty acids had power to deink such a substrate in one flotation loop experiment. Overall, it was found that two of the three experimental fatty acids from soybean oils (FFA-C and FFA-B) performed better than in standard used oleic acid. One of the fatty acids was found to perform poorer than oleic acid. Based on acid number analysis characterizations performed on the fraction of fatty acids from soy, it was assumed that the lower Acid number of fatty acid is more beneficial in ink removal. However, further study will be required to statistically confirm this assumption.

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