DEINKABILITY OF SOY INKJET INK PRINT BY MODIFIED INGEDE METHOD USING SOY OLEIC ACID

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A soy protein-based cyan inkjet ink was formulated. The obtained inkjet ink was printed using an Epson WF-2540 inkjet printer on office paper. Deinking of the soy protein-based water-based inkjet ink prints was performed using a modified version of the INGEDE method with soy-based fatty acid. Fatty acid extracted from food grade soybean oil was employed in one-loop flotation deinking of soy-based inkjet printed paper. The extracted fatty acid had varied acid and saponification numbers. The effect of the soy oil fatty acid on inkjet ink printed paper deinking was studied. Deinking results are compared to INGEDE 11p procedure, using oleic acid. It was discovered that the laboratory formulated soy ink is deinkable using both standard and modified INGEDE method with similar results.

Keywords: soy-based inkjet, ink, soy oleic acid, deinking, INGEDE method

INTRODUCTION

Non-impact inkjet digital printing has been gaining popularity in recent years, due to its fast turn-around, on-demand printing capabilities, and sufficient print quality.[1] Several reviews dealing with new applications of inkjet printing technology and inks are now available.[2] The development of digital printing technologies also brings an increased amount of digital prints into the waste paper stream. Thus, recycling of digital print is becoming very important for the paper industry, as well as for the environment. Digital inks have been around for a few decades, but the study of their deinkability is still at its beginnings.[3] Recycling of office waste paper (photocopy, inkjet, and laser prints) is a major problem due to the difficulty in removing certain non-impact inks.[4] Because of the huge variety of digital prints, caused by print process variations, as well as the variety of pigments and dyes, resins and additives used for making these inks and toners, digitally printed papers do not fit into high grade-paper recycling systems. Thus, it is crucial to look for efficient methods for remove inkjet inks from paper fibers. Early studies of the deinking process started successfully on lithographic prints printed with oil-based hydrophobic ink. The large particle size of the pigment in the litho ink, reaching around 800 nm, and the water repelling properties of litho resins aided ink separation from the pulp in the flotation system, where air bubbles attract ink particles. The bubbles with ink are floated to the top of a flotation chamber for skimming.[5] The hydrophobicity of ink particles is another factor, affecting flotation deinking process.[6] Hydrophobic particles are easy to remove, as can be seen by the example of efficient litho inks deinking.

In inkjet systems, a proper print is achieved if the diameter of the print head nozzle orifice is about 100 times larger than the diameter of the pigment particle.[7] Thus, inkjet inks contain either dyes or very small particle size pigments.[8] Inkjet ink pigment particle size is often around 100 nm, which is too small to create efficient agglomerates in the deinking process. This is especially true for water-based inkjet inks, which are hard to remove *via* the flotation deinking method,[9] because the fine pigments or dyes cannot be efficiently agglomerated. Water-based inks are made with acrylic resins, which do not agglomerate efficiently in the alkaline environment regularly used for deinking. Therefore, only dark-shaded recycled paper may be produced.[10,11] Often, the ink industry competes for acrylic polymers for making water-based inks, which inspired our work on formulating alternative inks based on renewable soy-based raw material.[12] This study is the continuation of the work on the formulation of soy-based inkjet inks, but the aim was to find out if besides successful drop formation, lines formation, and other printability features, as previously proven,[12] this ink would allow its removal from paper during deinking. Deinking of soy-based inkjet ink is also the continuation of another project of ours, which was looking into the modification of the INGEDE method.[13] In that project, three types of food-grade soybean oils were tested to determine if their by-products could be utilized in the paper recycling industry. Free fatty acids were extracted from these commercially available soybean oils, "A", "B" and "C". Experimental fatty 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, in acid number and saponification number. During the work, it was found that two of the three experimental fatty acids (fatty acid from oil "C" and free acid from soy oil "B") performed better than the standard, using oleic acid.[13] It was also found that the lower was the acid number of free fatty acid, the better was the deinking performance.[13] The aim of the current work was to use the best performing experimental soy fatty acids in the modified INGEDE method to deink printed office paper using soy-based inkjet ink formulated in our laboratory. It was decided that only cyan ink would be tested to narrow down the experimental work.

EXPERIMENTAL

Formulation of soy inkjet ink

Resin Pro-Cote 4610E soy polymer, with glass transition temperature of Tg > 160 °C (DuPont), was used to formulate soy-based inks. NH_4OH was used to solubilize the soy polymer and keep an alkaline pH of the solubilized resin. Ink was made in two stages, first solubilizing the soy resin, followed by incorporating the solubilized resin into the ink. Solubilization of Pro-Cote resin was done as follows:[12]

1. Soy protein was mixed with 60 °C deionized water for two minutes in order to wet out the soy powder;
2. NH_4OH was added under stirring and mixed for 20 minutes in order to neutralize the carboxylic acid groups and solubilize the protein;
3. Finally, biocide was added to prevent of growth of bacteria. The pH of the final solution was 9.25, which was in the required range. Table 1 shows the composition of the soy resin solution.

The second step was to formulate the soy ink. For the ink formulation, the best ink formula from the design of experiment done previously[12] was used. The soy polymer solution (Table 1) was mixed with commercial cyan pigment dispersion (Hostajet PT, Clariant), and surfactant Carbowet 300 (Air Products) was added. Ethylene glycol was applied as a humectant. The final formula of the inkjet ink is shown in Table 2.

Table 1
Soy protein solution

Ingredient	Amount (g)
Soy powder	7.4
DI water (60 °C)	91.7
NH_4OH (100% theory)	0.4
Biocide	0.5
TOTAL	100

Table 2
Final formula of an inkjet ink

Ingredient	Amount (g)
Soy polymer solution	12
Pigment dispersion	15
Surfactant	0.1
Humectant (ethylene glycol)	10
DI water	62.9
TOTAL	100

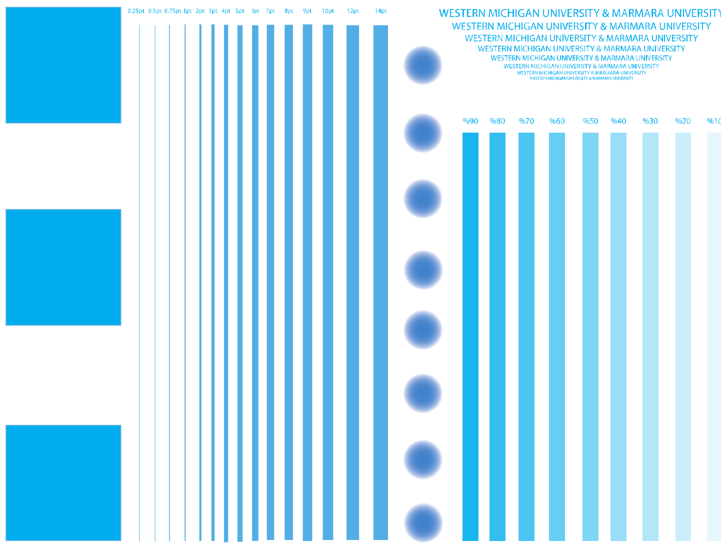

Figure 1: Test image printed using Epson WF-2540 with soy ink
(Epson WF-2540 uses refillable cartridges, thus it could be filled with our custom-made soy inkjet ink)

Table 3
Acid number of free fatty acids

Free fatty acid	Acid number
From oil “A”	202.6
From oil “B”	196.2
From oil "C"	194.8
Standard oleic acid	200.3

The formulated inkjet ink (Table 2) was used to print with an Epson WF-2540 inkjet printer on uncoated office paper with basis weight of 75 g/m^2. The print image is illustrated in Figure 1.

Deinking of soy inkjet ink printed office paper

Office paper printed with the formulated soy protein ink was deinked according to INGEDE method 11p.[14] Printed samples were torn into 2 x 2 cm^2 pieces, and oven dried for 72 hours at 60 °C to simulate accelerated aging. Aged paper was loaded into Micro-Maelstrom pulper to create the pulp slurry at 250 RPM for 20 min at 45 °C and a consistency of 15%. During pulp storage at 45 °C, its consistency was 5%. The pulp was disintegrated for 1 minute at 3000 RPM. After disintegration, the consistency dropped to 0.8%. Some pulp was stored to form undeinked handsheets as a control.

In the first part of the experiments, standard deinking chemicals recommend by INGEDE method 11p were used. The second step of the experiments involved using fatty acids, isolated from soy oil instead of the prescribed oleic acid.

Handsheets (1.2 g OD) and pads (4 g OD) were prepared using a handsheet mold according to TAPPI T272 standard. A total of five sheets and two pads were prepared for each pulping trial, including both deinked (DP) and undeinked (UP) pulp. Unprinted paper (UNPR) of the second batch was also prepared the same way with standard INGEDE method 11p deinking chemicals and flotation deinking procedure.

The brightness of these samples was measured using a Technidyne BrightiMeter Micro S-5 (T458, C/2° light source, 457 nm). Luminosity (Y, 557 nm), CIE a* and b* values were also taken with this instrument based on T524 geometry (45/0). X-Rite Eye One spectrophotometer was used to measure Y, and CIE a*, b* values at D65/2° conditions.

Two types of oleic acid were used for deinking. One of them was standard oleic acid, which was recommended by INGEDE, and the second one was extracted from food-grade soybean oil. The extracted fatty acid from different oils had varied acid and saponification numbers (Table 3). In previous work on deinking of hydrophobic litho-inks,[13] it was confirmed that the lower the bound and the free fatty acids in the oil, the better the deinking performance. Thus, soy oil with the lowest acid number (Oil C) was selected for the deinking trials. Deinking results were compared to INGEDE method 11p procedure, using standard oleic acid.

RESULTS AND DISCUSSION

Soy protein-based and acrylic inkjet inks were formulated in our laboratory. The rheology, surface tension and density of these inks were measured. These data were used to calculate Z numbers, combining the influence of density, surface tension and viscosity on inkjettability.[15-17] Applying Weber, and Ohnesorge calculations, Fromm used the reciprocal value of Oh number and came to the conclusion that the Z number should be in the range 2≦Z≦14, for ink formulations to be suitable for inkjetting.[17-19]

According to preliminary formulations with an appropriate Z number (data not shown), a design of experiments was employed to optimize the formulation of soy- and acrylic-based inks.[12] Inks were printed on a Dimatix Material Printer DMP-2800. The print design is illustrated in Figure 2. The previous study showed that soy protein formulated inks perform very similar to commercial inkjet ink, concerning line sharpness, solids uniformity, and dot formation.[12] The soy ink with the best print performance was chosen and used for the deinking study presented here. A new print design was selected with the aim to cover a larger area (Fig. 1), and soy inkjet ink was printed with an Epson WF-2540 inkjet printer. The printed sheets were used in the deinking study presented here.

In this study, INGEDE method 11p was modified using a soy-based fatty acid fraction instead of pure oleic acid, because it was found that the composition of fatty acids, especially the acid number may affect the deinking results.[13] Handsheets and filter pads were prepared using both chemicals, and the obtained results were compared.

Optical properties

A comparison of the brightness values of repulped non-printed paper with those of undeinked and deinked paper with oleic acid and a fraction of soy fatty acids according to INGEDE method 11p is shown in Figure 3.

The brightness value of the unprinted handsheet is of 91.36%. The soy-ink soy-oleic acid deinked handsheet displays the nearest handsheet brightness with 89.76%. When the filter pads are compared, the unprinted paper has a brightness value of 92.09%, and the soy-ink soy-oleic acid deinked fılter pad shows an almost similar brightness value of 89.76%. When the handsheet brightness values are compared, the value of the soy-ink std.-oleic acid sample is slightly higher than those achieved using soy-oleic acid, and is closer than the soy-oleic acid to the value of unprinted paper. It can be concluded that for deinking of soy polymer inks, fatty acids with higher acid number are preferable. The result is different from what was previously found for deinking with these acids, but in that case, litho hydrophobic inks were deinked.[13]

A comparison of luminosity (Y) of soy ink printed sheets deinked by standard oleic acid and by fatty acids from soy oil under C/2° and D65/2° light sources is shown in Figure 4.

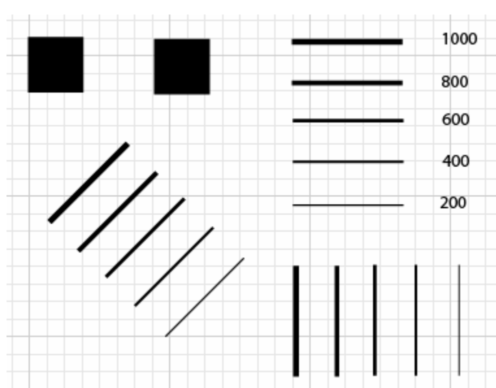

Figure 2: Design for printing acrylic and soy inks on a Dimatix printer[12]

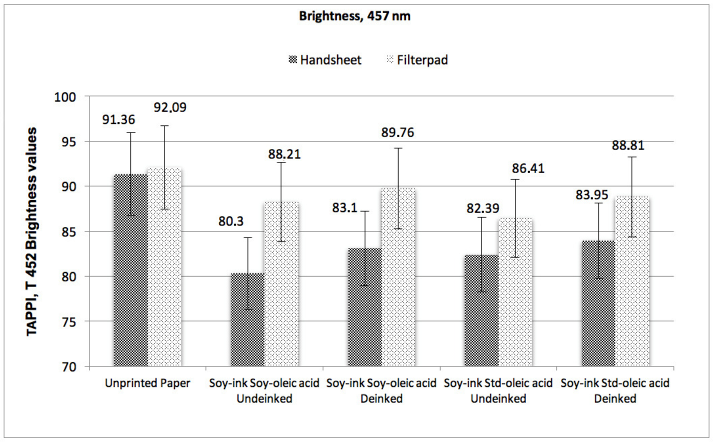

Figure 3: TAPPI brightness of deinked and undeinked handsheets

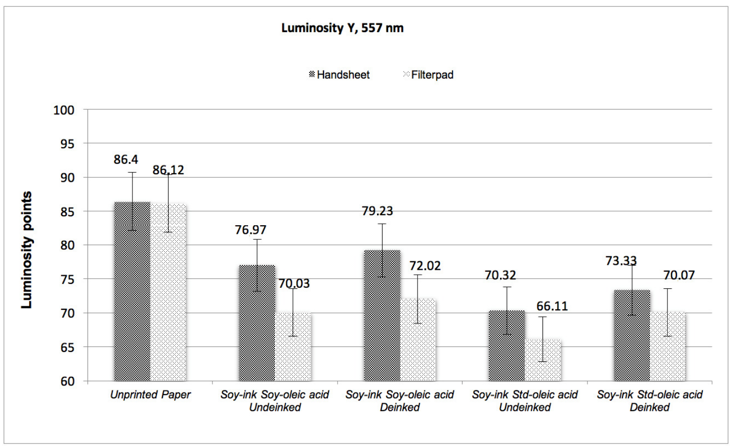

Figure 4: Luminosity Y values of all handsheets and filter pads

According to Figure 4, the luminosity Y value of the unprinted handsheet is of 86.4. The soy-ink soy-oleic acid deinked handsheet displays a luminosity Y value of 79.23. When the filter pads are compared, the unprinted paper has a luminosity Y value of 86.12, but the soy-ink soy-oleic acid deinked filter pad shows a luminosity Y value of 72.02. When the handsheet luminosity values are compared, the values of the soy-ink soy-oleic acid sample are higher than those achieved using soy oleic acid, and are closer to the value of unprinted paper. These results agree with those found for brightness (Fig. 3).

A comparison of CIE a* values is shown in Figure 5. According to Figure 5, the CIE a* value of the unprinted paper handsheet is 1.8, which is neutral grey towards red. The soy-ink soy-oleic acid deinked handsheet displays a CIE a* value of -1.93, *i.e.* neutral grey towards green. When the filter pads are compared, a* values changed from neutral grey in the red quadrant towards green. The unprinted filter pad has a value of 1.8, the soy-ink std.-oleic acid deinked filter pad shows a CIE a* value of -4.84, and all other conditions had very similar values. When the handsheets are compared as regards the CIE a* value, the CIE a* value for soy-ink soy oleic acid is higher than that achieved using soy oleic acid, all of them being neutral grey in the green quadrant, which is most likely connected with the deinking of cyan ink. A comparison of CIE b* values is shown in Figure 6.

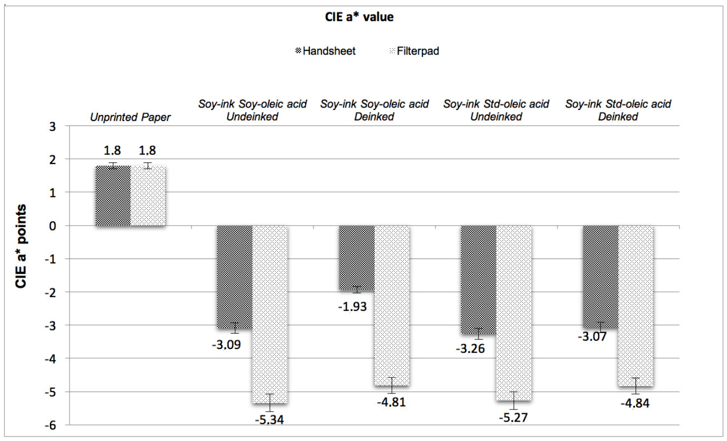

Figure 5: CIE a* values of variously deinked papers

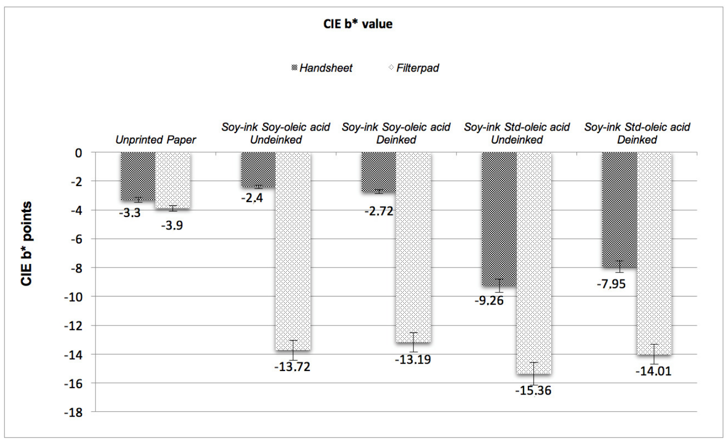

Figure 6: CIE b* values of deinked papers

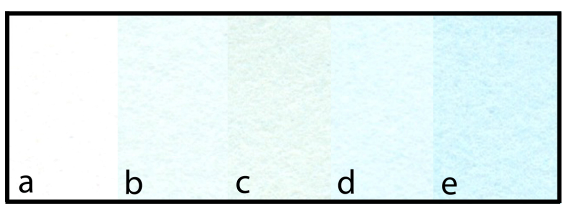

Figure 7: Comparison of 1200 dpi scanned surface images, a) unprinted, b) soy oleic acid deinked, c) soy oleic acid not deinked, d) std. oleic acid deinked, e) std. oleic acid not deinked

According to Figure 6, the CIE b* value of the unprinted paper handsheet is of -3.3, *i.e*. neutral grey in the blue quadrant. The soy-ink soy-oleic acid deinked handsheet displays a CIE b* value of -2.72. When the filter pads are compared, the unprinted sample has a value of -3.9, but the soy-ink soy-oleic acid deinked fılter pad shows a CIE b* value of -13.19. When the handsheet values are compared for CIE b*, the soy-ink soy oleic acid values are lower than that achieved using soy oleic acid. A visual evaluation of the paper surface allows concluding that the surface of the soy-ink soy-oleic acid deinked handsheets was in better condition than that of the other handsheets.

Visible dirt area count

Verity IA Light and Dark Dirt v3.4 software was applied for the measurement. All handsheets were scanned at 1200 ppi and then the count of dark objects was performed. The measured area was 13000 mm^2 on the handsheets.

Table 4
Visible dirt area count

Sample	Count of dark objects	Count of dark objects/mm^2	Measured area (mm^2)
Soy-ink soy-oleic acid undeinked	422	0.032	13000
Soy-ink soy-oleic acid deinked	184	0.014	13000
Soy-ink std.-oleic acid undeinked	468	0.036	13000
Soy-ink std.-oleic acid deinked	202	0.015	13000

When looking at the obtained results, the visible dirt area value for the soy-ink soy-oleic acid deinked sample is 0.019. This is the best result, since it has the least dark objects.

In this experiment, the DEM Lab factor was calculated according to the following formula:

$$\text{DEM Lab} \left(1-\frac{\sqrt{(L*_{US}-L*_{DS})^2+(a*_{US}-a*_{DS})^2+(b*_{US}-b*_{DS})^2}}{\sqrt{(L*_{US}-L*_{BS})^2+(a*_{US}-a*_{BS})^2+(b*_{US}-b*_{BS})^2}}\right)100[\%] \quad (1)$$

where US – unprinted deinked pulp, DS – deinked pulp, BS – printed undeinked pulp.

Thus, the DEMLab factor was calculated for the soy-ink soy-oleic acid samples as follows:

$$\text{DEMLab} = \left(1-\frac{\sqrt{(94.49-90.72)^2+(1.8-(-1.93))^2+(-3.9-(-2.72))^2}}{\sqrt{(94.49-90.19)^2+(1.8-(-3.09))^2+(-3.9-(-2.4))^2}}\right)100\ [\%]$$

$$\text{DEMLab} = \left(1-\frac{\sqrt{(3.77)^2+(3.73)^2+(-1.18)^2}}{\sqrt{(4.3)^2+(4.89)^2+(-1.5)^2}}\right)100\ [\%]$$

$$\text{DEMLab} = \left(1-\frac{\sqrt{29.5182}}{\sqrt{44.6521}}\right)100\ [\%]$$

$$\text{DEMLab} = 18.69\%$$

Similarly, the DEMLab factor was calculated for the soy-ink std.-oleic acid as follows:

$$\text{DEMLab} = \left(1-\frac{\sqrt{(94.49-88.41)^2+(1.8-(-3.07))^2+((-1.64)-(-7.95))^2}}{\sqrt{(94.49-87.38)^2+(1.8-(-3.26))^2+((-1.64)-(-9.26))^2}}\right)100\ [\%]$$

$$\text{DEMLab} = \left(1-\frac{\sqrt{(6.08)^2+(4.87)^2+(6.31)^2}}{\sqrt{(7.11)^2+(5.06)^2+(7.62)^2}}\right)100\ [\%]$$

$$\text{DEMLab} = \left(1-\frac{\sqrt{100.4994}}{\sqrt{134.2201}}\right)100\ [\%]$$

$$\text{DEMLab} = 13.46\%$$

The deinkability factor DEM *f* for the soy-ink soy-oleic acid sample was estimated using the following relation:

$$DEMf = \frac{Brightness\ (DS) - Brightness\ (BS)}{Brightness\ (US) - Brightness\ (BS)}\ 100\ [\%] \quad (2)$$

where: US – unprinted deinked pulp, DS – deinked pulp, BS – printed undeinked pulp.

$$DEMf = \frac{83.1 - 80.3}{91.36 - 80.3}\ 100\ [\%]$$

$$DEMf = \frac{2.8}{11.06}\ 100\ [\%]$$

$$DEMf = 25.31[\%]$$

Similarly, DEM *f* was calculated for the soy-ink std.-oleic acid sample:

$$DEMf = \frac{83.95 - 82.39}{91.36 - 82.39}\ 100\ [\%]$$

$$DEMf = \frac{1.56}{8.97}\ 100\ [\%]$$

$$DEMf = 17.39\ [\%]$$

CONCLUSION

We formulated soy-based inkjet inks, which exhibited excellent printability on two inkjet ink printers. Current work was focused on testing their deinkability. Only cyan inkjet ink was tested due to ease of color analysis of deinked sheets. These prints were deinked via INGEDE Method 11p, and also with a modified method, which used soy-based fatty acids. Both methods confirmed that soy-based inkjet ink is deinkable using both standard and modified INGEDE method. Looking at the results of the deinked handsheets, which were obtained with soy fatty acid, the handsheet brightness was slightly higher at deinking with standard oleic acid, while luminosity results are quite similar for both standard and soy oleic acid. CIE b* values are slightly better for soy oleic acid (modified INGEDE method) than standard oleic acid. There were not found any dramatic differences between deinking performance of standard and soy oleic acid.

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