# Soybean Oil for Enhanced Deinking of Litho Prints

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Keywords: deinking, INGEDE 11p method, soy oils, fatty acids, acid number, saponification number

**Abstract**

Three soy-based oils were characterized by saponification and acid number values. The saponification procedure, in which the soy oils were boiled in diluted 0.1N KOH and titration of non-consumed KOH allowed identifying the amount of free and bound acid groups in tested oils, while acid number allowed determining the amount of free acid groups in soy oils. Free fatty acids were extracted from tested soy-oils and were utilized in flotation deinking of litho-printed paper substrates. The effect of each of the soy-oil byproducts on deinking was observed, quantified and compared with standard INGEDE 11p procedure that employ commercially available oleic acid.

## Introduction

In recycling facilities, the first step of the deinking process focuses on repulping of the printed substrate. Repulping occurrs in an aqueous environment, typically at alkaline pH. Mechanical agitation allows 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 recovered pulp (Renner, 2000). Based on studies performed by multiple researches, the strength of fiber-ink bonding depends on pigment particle size, ink formulation,

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printing process, ink film thickness and ink depth penetration [Carre et al., 2000; Pekarovicova et al., 2003]. Further, ink aging and its raw components will also impact the deinking efforts [Angellier et al., 2004; Haynes, 2000].

The experimental study focused on deinking via INGEDE Method 11p and its modification. The deinking protocol consists of repulping followed by the air flotation and further handsheet preparation (INGEDE Method 11p, 2009). In the proposed deinking study, free fatty acids extracted from 3 types of commercially available soy oils were tested as replacements for oleic acid used in INGEDE Method 11p (INGEDE Method 11p, 2009). The objective of the study was to determine if the fatty acids coming from three types of soybean oil would produce the deinked pulp with worse, similar or better optical properties than the deinked pulp prepared using oleic acid. The effect of each of the soy-oil bi-products on deinking was observed and quantified.

## Experimental

The Michigan Soybean Promotion Committee provided 3 commercially available soybean oils. Their typical use is found in the food industry. The goal during the first step of research was to profile oils and see any differences in their internal structure via saponification and acid number testing (ASTM Standard D94-07, 2012; ASTM Standard D664-11a, 2011). The results of the soybean oil profiling can be found in Table 3. Further, 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 (Method IV.A.4; 1982).

Determination of “saponification number” and “acid number” for three soy-based oils showed slight differences in amounts of bound and free acid groups for soybean oil “B” and soybean oil “C”. Slightly higher values of bound and free acid groups were determined for soy oil “A”.

***Figure 1.*** *Beginning of saponification*

***Figure 2.*** *End of saponification*

The litho-printed substrate was obtained from North American Color, Kalamazoo, MI. The substrate was heavily color-printed from both sides (Figure 3).


***Figure 3.*** *Offset printed paper substrate side 1 and side 2*

Prior to the deinking, printed and unprinted substrates were aged for 72 hours at 60˚C as per INGEDE Method 11p (INGEDE Method 11p, 2009). After aging, printed and unprinted substrate respectively, were torn to 2x2 cm pieces and were conditioned in the paper laboratory for 24 hours, 23±1˚C at 50±2% relative humidity.

Due to unavailability of Holbart type pulper used in INGEDE Method 11p, a MicroMaelstromTM Laboratory Pulper type of slush –maker was used instead. Repulping parameters (RPM and repulping time) versus particle dirt count and diameter size were examined prior to this experimental study. The most suitable conditions were selected and they are listed in the Table 1. 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 TAPPI disintegrator. A total of eight repulping and flotation experiments were conducted. The experiments are listed in the Table 1.

| Experiment # | Paper Substrate | Free Acids used in Experiments |
|---|---|---|
| 1 | Unprinted | Oleic Acid (INGEDE's Standard) |
| 2 | Printed | Oleic Acid (INGEDE's Standard) |
| 3 | Unprinted | Free acid from soy oil "A" |
| 4 | Printed | Free acid from soy oil "A" |
| 5 | Unprinted | Free acid from soy oil "B" |
| 6 | Printed | Free acid from soy oil "B" |
| 7 | Unprinted | Free acid from soy oil "C" |
| 8 | Printed | Free acid from soy oil "C" |

***Table 1.*** *List of free acids that were used in deinking experiments*

The goal of the repulping was to break the ink fiber bonding. 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 minutes. The speed of the MicroMaelstromTM Laboratory Pulper was set to 500 RPM and the temperature was adjusted to 45˚C by using built in thermostat. After defibration, repulped stock was diluted to 4% consistency using dilution water with fixed hardness value of

128mg Ca2+/L. Next, repulped stock was stored for an hour in the water bath at 45˚C. After storage, a TAPPI disintegrator was used to disintegrate fiber bundles for 1 minute. Prior the air flotation, undeinked stock was taken for preparation of 2 filter pads and 10 handsheets. The rest of the undeinked pulp was taken and was subjected to flotation deinking. A small, 2L laboratory cell was used for all deinking trials (Figure 4). Due to the volume of the cell, each of the experiments was repeated.

This way, larger amounts of deinked pulp suitable for handsheets and filter pads formation were obtained. The flotation cell aeration was fixed to a flow rate of 1L/min. The duration of flotation deinking was 12 minutes. A paddle scraper was used for froth removal over the course of flotation. Removed froth was collected in a reject tank. The yield of the flotation was calculated. Final consistency of the deinked stock was calculated and was subjected to preparation of the handsheets, filter pads and membrane filters.

| | | |
|---|---|---|
| **Re-pulping recipe** | Sodium hydroxide | 0.6% |
| | Sodium silicate | 1.8% |
| | Hydrogen peroxide | 0.7% |
| | Oleic acid/Acid from soy oil #1 or #2 or #3 | 0.8% |
| **Re-pulping conditions** | Water hardness adjusted to | 128mg $Ca^{2+}$/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 |
| **2 Filter pads and 10 handsheets were formed from undeinked pulp** | | |
| **Flotation** | Consistency | 0.8% |
| | Duration | 12 min |
| | Temperature | 45˚C |
| | Aeration flow rate | 1L/min |
| **2 Filter pads, 10 handsheets were prepared from deinked pulp, 2 membrane filters were prepared from water obtained after 2 filter pads were formed** | | |

***Table 2.*** *Deinking process parameters*

***Figure 4.*** *Laboratory 2L flotation cell*

## Results and Discussion

Saponification allowed identifying the amounts of free and bound acid groups in tested oils, while acid number allowed determining amount of free acid groups in tested oils. Using both results it was possible to identify the amount of bound acid groups within the tested oil.

| Oil | Acid Number | Saponification Number | Bound and Free Acid Groups |
|---|---|---|---|
| "A" | 0.925 | 196.64 | 197.57 |
| "B" | 1.121 | 189.68 | 190.80 |
| "C" | 0.746 | 189.38 | 190.12 |

***Table 3.*** *Profiling of soy oils*

Some of the basic substrate's physical properties and optical properties are listed in the Tables 4 and 5.

| Physical Properties of Unprinted Base Sheet | |
|---|---|
| Grammage ($g/m^2$) | 115.00 |
| Thickness (µm) | 75.00 |
| Ash content (%) @ 525°C | 45.03 |

***Table 4.*** *Physical properties of unprinted base sheet used for deinking*

| Optical Properties of Unprinted Base Sheet | |
|---|---|
| Brightness | 86.70 |
| Luminosity (Y) | 83.07 |
| L* | 92.87 |
| a* | 1.24 |
| b* | -2.52 |

***Table 5.*** *Optical properties of unprinted base sheet used for deinking*

Deinkability evaluation parameters according to INGEDE Method 11p and their objectives are presented in Table 6.

| OBJECTIVE | EVALUATION PARAMETER | |
|---|---|---|
| High reflection | Luminosity value Y of Deinked Pulp | **Pulp parameter** |
| High optical cleanliness | Dirt particle area A of Deinked Pulp | |
| No discoloration | Chromaticity value a* of Deinked Pulp | |
| Good ink removal | Ink elimination IE | **Process parameter** |
| No discoloration of circuit water | Filtrate darkening ΔY | |

***Table 6.*** *Parameters for deinking evaluation according to INGEDE Method 11p*

Besides INGEDE deinking evaluation deinking evaluation was done using the color difference between unprinted deinked pulp (US) and 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˚ light source at 457nm was used.

$DEM_{Lab}=$

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

(Rao et al., 1998)

Where:

(US) - unprinted deinked pulp
(DS) - deinked pulp
(BS) - printed undeinked pulp

In general, deinkability factor is presented on the scale from 0-100%. A deinking factor closest to 100% will represent the sample that was flawlessly deinked. The color difference of a sample to a reference sample as a vector in the L*a*b* color system (CIELAB) was used to develop above deinkability factor. For three axes interpretation in the color space see Table 7. (CIE Proceedings, 1932; Fleming, 2003).

| | |
|---|---|
| L* = 0 | black |
| L* = 100 | white |
| a* < 0 | green |
| a* > 0 | red |
| b* < 0 | blue |
| b*> 0 | yellow |

***Table 7.*** *Color system (CIELAB)*

During the evaluation, deinkability factor DEMf, developed by Papiertechnische Stiftung (PTS) in Munich, Germany was used. Deinkability factor DEMf considers brightness difference between the deinked pulp and pulp before deinking. It is calculated using averaged brightness's values of unprinted deinked pulp, deinked pulp and printed undeinked pulp (Renner, 2000).

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

Where:

(US) - unprinted deinked pulp
(DS) - deinked pulp
(BS) - printed undeinked pulp

Based on both deinkability factors (DEMLab and DEMf), free acid from soy oil "C" has the highest deinking efficiency, while free acid from soy oil "A" resulted in the least deinked pulp. Free acid from soy oil "B" was somewhat less efficient than free acid from soy oil "C". In presented study the main focus was not necessarily to obtain perfectly deinked pulp but to find out if the free 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, it would have to undergo multi-looped deinking systems, rather than one step deinking flotation in order.

| Acid type used for Deinking | Deinkability $DEM_{Lab}$ [%] | Deinkability $DEM_f$ [%] |
|---|---|---|
| Oleic Acid | 40.13 | 36.83 |
| Free acid from soy oil "A" | 31.62 | 29.13 |
| Free acid from soy oil "B" | 50.16 | 45.90 |
| Free acid from soy oil "C" | 59.20 | 56.36 |

***Table 8.*** *Deinkability efficiency of various free fatty acids based on deinkability factorsDEM $_{Lab}$ and $DEM_f$*

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 1200 dpi. The inspected area was set to 13000mm2. Results are summarized in Table 9.

| | Unprinted deinked pulp (US) | Printed undeinked pulp (BS) | Printed deinked pulp (DS) |
|---|---|---|---|
| **Acid type used for Deinking** | **Dark Objects Count PPM** | | |
| Oleic Acid | 34.0 | 108774.0 | 37188.0 |
| Free acid from soy oil "A" | 15.0 | 101993.0 | 46005.0 |
| Free acid from oil "B" | 60.0 | 94165.0 | 22690.0 |
| Free acid from "C" | 27.0 | 108721.0 | 15362.0 |

***Table 9.*** *Dark Dirt Count*

The lowest dirt count (PPM holey) was measured on the handsheets prepared from deinked pulp using free acid from oil "C". Free acid extracted from oil "B" resulted in deinked pulp with lower dirt count than that processed with standard oleic acid. The least effective was the free acid coming from soy oil "A". Brightness of prepared handsheets was measured at 457nm. Handsheets were prepared from deinked unprinted pulp, printed undeinked pulp and printed deinked pulp. Deinking employed 4 possible acids. It was observed that the brightest handsheets were prepared from the pulp deinked with free acid obtained from soy oil "C", followed by the free acid from soy oil "B". Both free acids resulted in brighter handsheets than those prepared from pulp deinked with standard oleic acid. Deinked pulp with lowest brightness was obtained when free acid from soy oil "A" was employed.

Similarly to handsheets, the brightness of filter pads was measured at 457nm. Filter pads were prepared from the same deinked unprinted pulp, printed undeinked pulp and printed deinked pulp as handsheets. Deinking utilized 4 possible acids. The brightest filter pads were prepared from the pulp deinked with free acid obtained from soy oil "C", followed by the free acid from soy oil "B". Both free acids resulted in brighter handsheets than those prepared from pulp deinked with standard oleic acid. Free acid from soy oil "A" provided deinked pulp with the lowest brightness that was similar to the oleic acid. Luminosity Y of handsheets and filter pads provide similar trend that was observed while measuring brightness. Once again, the free acid that was extracted from soy oil "C" resulted in the deinked pulp with the highest luminosity. The rest of the free acids performed slightly better or similarly to the standard oleic acid. Filtrate darkening represents the variance between the luminosity of the reference membrane filter (tap water) and the test membrane filter (filter pad filtrate). The difference $\Delta Y = YRef - YDP$ represents the filtrate darkening. According to the INGEDE standard, two samples of deinked pulp were submitted to the test. Further, lightness (CIE L*) of handsheets and filter pads was monitored.

For both, filter pads and handsheets, it was found that the free acid obtained from soy oil “C” produces lighter deinked pulp and therefore lighter final product. The rest of the free acids produced similarly light or slightly lighter deinked pulp than oleic acid. The a* value of the unprinted base sheet had value of 1.24 while the deinked pulps produced handsheets that resulted in slightly higher, redder a* values. Deinking with standard oleic acid produced pulp with a* closest to the a* of the unprinted base sheet. The experiment that used free acid from soy oil “A” produced pulp that had largest a* value. Free acid from soybean oil “B” and free acid from soy oil “C” had approximately same effect on the a* value. Evaluation of a* value of filter pads was slightly different. This could be true with the fact that less material is lost during filter pad formation than during handsheet making. The a * value for deinked pulp used for filter pad was smallest when soaps formed from oleic acid facilitated flotation. Further, free acids from soybean oil “B” were found to produce deinked pulp with a* closest to that of unprinted deinked sheet. Lastly, filter pads made from deinked pulps using free acids from “A” and “C” oil had larger a* values.

According to TAPPI standard T-524 om-86 white or near white papers are characterized by values of L* > 84 and (a*2+ b*2)1/2 <10. Further, based on the study done by Shendye (Shendye, 2012) the b* value is more important in how the human eye perceive white or near white papers. In his study, Shendye reveals that lower the b* value the brighter the paper will appear to the observer. Therefore, considering this fact, oleic acid would positively impact the deinking, resulting in pulps with the lowest b* value. Secondly, it would be free acid from soy oil “A”, followed by free acid from soy oil “C”. Lastly, the least negative b* value would be measured on handsheets made from pulps deinked using free acid from the soy oil “B”.

| Free Acid Type | Statistics | Y | ΔY | A | L* | a* | b* | Brightness | Yield % |
|---|---|---|---|---|---|---|---|---|---|
| Oleic Acid | Average | 66.29 | 3.87 | 37188.00 | 85.14 | 1.26 | -2.92 | 69.71 | 86.64 |
| | StDev | 0.82 | - | 1633.00 | 0.42 | 0.09 | 0.18 | 0.73 | 0.14 |
| Free acid from soy oil “A” | Average | 65.02 | 2.64 | 46005.00 | 84.49 | 1.37 | -2.79 | 68.23 | 92.93 |
| | StDev | 1.12 | - | 1581.00 | 0.57 | 0.24 | 0.12 | 1.05 | 0.14 |
| Free acid from soy oil “B” | Average | 70.32 | 1.73 | 22690.00 | 87.15 | 1.34 | -2.30 | 73.15 | 86.56 |
| | StDev | 0.94 | - | 1029.00 | 0.46 | 0.24 | 0.20 | 0.89 | 0.17 |
| Free acid from soy oil “C” | Average | 72.73 | 0.67 | 15362.00 | 88.32 | 1.33 | -2.68 | 76.13 | 84.06 |
| | StDev | 0.88 | - | 1653.00 | 0.42 | 0.18 | 0.32 | 0.95 | 0.07 |

***Table 10.*** *Optical measurements of handsheets from deinked pulp*

The highest deinking yield was obtained with free acid from soy oil “A”. Standard oleic acid and free acid from soy oil “B” resulted in the similar deinking yields while free acid from soy oil “C” gave the lowest yield.

## Conclusion

The deinkability efficiency of three fatty acids obtained by extraction from three types of soybean oil was studied. Their deinkability potential was compared to the deinkability of oleic acid that is used as a 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 substrate in one flotation loop experiment. Overall, it was found that two of the three experimental fatty acids (fatty acid from soy oil "C" and free acid from soy oil "B") will perform better than standardly used oleic acid. Fatty acids from soy oil "A" was found to perform slightly poorer than oleic acid.

## Acknowledgement

Authors are grateful to The Michigan Soybean Association for partially funding this work.

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