Deinking difficulties related to ink formulation, printing process, and type of paper

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ABSTRACT

This paper investigates the deinking ability of several types of paper printed with different processes and inks. Conventional alkaline deinking can produce good results, but too often the result is poor deinkability, producing pulps with low brightness, high speck contamination, or residual color. This paper focuses on deinking problems caused by vegetable-oil-based newsprint offset inks, offset heat-set inks, and red rotogravure inks. Deinking difficulties are clearly identified and solutions are proposed. Cooperative research efforts with ink manufacturers have led to the reformulation of new vegetable-oil-based inks that deink as well as mineral-oil-based inks. Additional work explains why red rotogravure ink gives a red shade to the deinked pulp, although the problem has not yet been solved. The effects of printing and paper characteristics on the deinking of offset heat-set printed papers were also studied. For all these trials, deinking ability is expressed in terms of pulp brightness, effective residual ink concentration (ERIC), attached and detached ink, and speck contamination. Color coordinates were used to characterize the effects of residual dye.

INTRODUCTION

The deinking plant must deal with a wide variety of paper types, ink types, and printing techniques. Some papers are easy to deink, while others create problems. From this mixture of recovered papers, the deinking plant is expected to produce a pulp of consistently high quality. Unfortunately, this ambitious goal is sometimes difficult to reach. Most problems can be traced to one or more of the following sources:

- Insufficient ink detachment
- Resistant ink particles that form specks
- Extensive ink fragmentation
- Release of a soluble color from dyes
- Poor hydrophobic character of the ink

Each of these problems, in turn, can usually be linked with specific inks and printing techniques. This paper evaluates deinkability in terms of ink type, printing technique, and the type of paper surface. Experimental results focus on specific problems involving deinkability of vegetable-oil-based offset ink for newsprint, red rotogravure ink, and offset heat-set paper.

DEINKABILITY VS. PRINTING PROCESS, INK TYPE, AND PAPER

SURFACE: REVIEW OF THE DIFFERENT BEHAVIORS

Deinkability behavior depends mainly on four factors:

- Ink type
- Printing technique and printing conditions
- Aging of the print
- Paper surface

These four factors can be grouped into two main categories:

- Ink properties
- Paper surface

Ink properties are the most important, since they strongly influence deinkability. Ink detachment from the sheet depends on the ink formulation, printing conditions, and aging, while removal of detached ink particles from the pulp depends on ink formulation (ink particle size, ink particle surface properties, ink or soluble dye).

Paper surface properties are also important, since they affect the ease of ink detachment. Inks printed on a coated paper surface detach more easily than inks printed directly on the fibers of an uncoated sheet.

DEINKABILITY VS. INK FORMULATION, PRINTING PROCESS, AND DRYING MECHANISMS

Ink detachment from the sheet is a direct function of the sheet surface properties, the ink formulation, the printing process, and ink-drying mechanisms.

Borchardt made an extensive review of the different printing processes and drying mechanisms *(1)*. **Table I** summarizes the influence of the printing processes and drying mechanisms on deinkability.

Printing process	Drying mechanisms	Deinkability
Offset newspaper Letterpress Offset sheet-fed Offset heat-set	Absorption (and oxidation) Absorption and oxidation Absorption, evaporation, and oxidation	Good if not aged After aging, bad ink detachment, smeared pulp, specks
Rotogravure	Evaporation	Good, possibility of colored pulp (dye)
Flexo	Evaporation	For water-based Bad at alkaline pH
Laser and copiers UV and IR	Radiation curing	Bad toner detachment, strong speck contamination

Table I: Influence of printing processes and drying mechanisms on deinkability

As described in Table I, offset printing on uncoated papers leads to ink detachment problems and smeared pulp with aging. Deinkability of newspaper is generally good after two to three months, but oxidation of some ink components can occur with aging, depending on the ink formulation, leading to a strong attachment of the ink onto fibers. This can be the case with vegetable-based inks *(2)*, especially some unsaturated vegetable oils, which can lead to ink detachment problems and specks. Some resins added into the ink can also lead to strong attachment of the ink onto fibers, even with some mineral-based inks.

Ink attachment is still more pronounced with sheet-fed offset ink, because the ink formulation contains oxidizable components that are necessary for the printing process. Drying has to be very quick. This oxidation continues with aging and once more leads to ink detachment problems and sometimes to specks. Appropriate choice of ink components can retard the oxidation mechanism.

The worst case with offset printing is heat-set offset. In addition to the evaporation of some oil components in the heat-set oven, there is also rapid oxidation of some ink components. Depending on the oven temperature (180–300°C, which gives sheet temperatures of 100–130°C) and the ink formulation, ink attachment can be very strong at the outlet of the oven; otherwise, it develops after some days or weeks. Heat-set drying is thus an artificial aging of the ink. Heat-set offset inks can cause severe problems, and ink detachment during pulping is generally not sufficient. Additional kneading stages are then necessary both to break down residual specks and to detach residual attached ink.

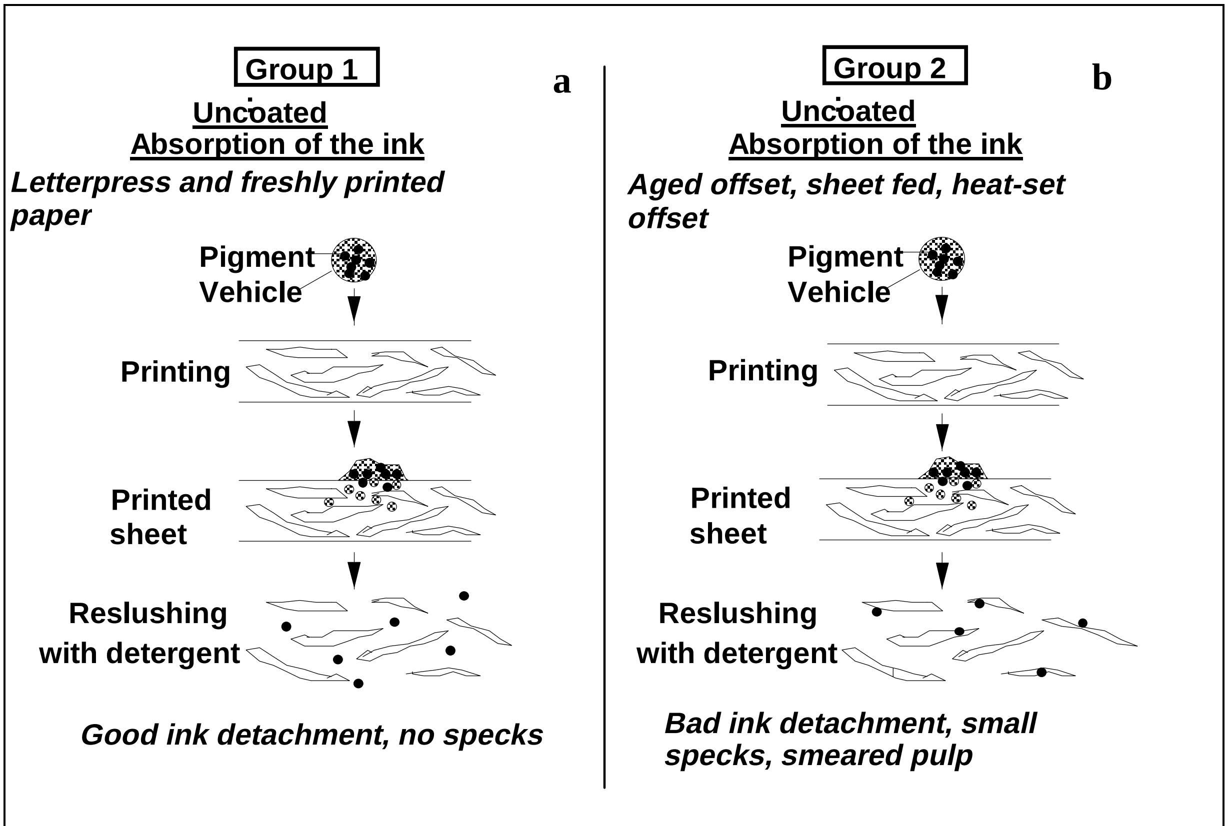
Rotogravure printing no longer induces any deinkability problems except for the presence of some residual colors due to dyes in the ink formulation. This is especially true for red inks, which include dyes that impart a reddish color to the deinked pulp. In the near future, however, this printing technique (mainly employed for printing high circulation magazines) may be slightly modified, with the toluene solvent being substituted by water. If that occurs, the deinkability of these prints will not be possible using conventional deinking processes *(2)*. This threat must then be taken into account by deinkers.

Concerning flexo printed papers, the solvent can also be water, and in this case, similar problems to water-based rotogravure are observed, i.e., it is not possible to deink these papers with a conventional deinking process. Flexo is employed mainly in North America and for some newspapers in England and Italy. However, the development of this printing process for newspaper in the future seems to decrease strongly because of a lower quality and now a slightly higher cost. The deinkability of these papers is addressed in a work by Galland *(3)*.

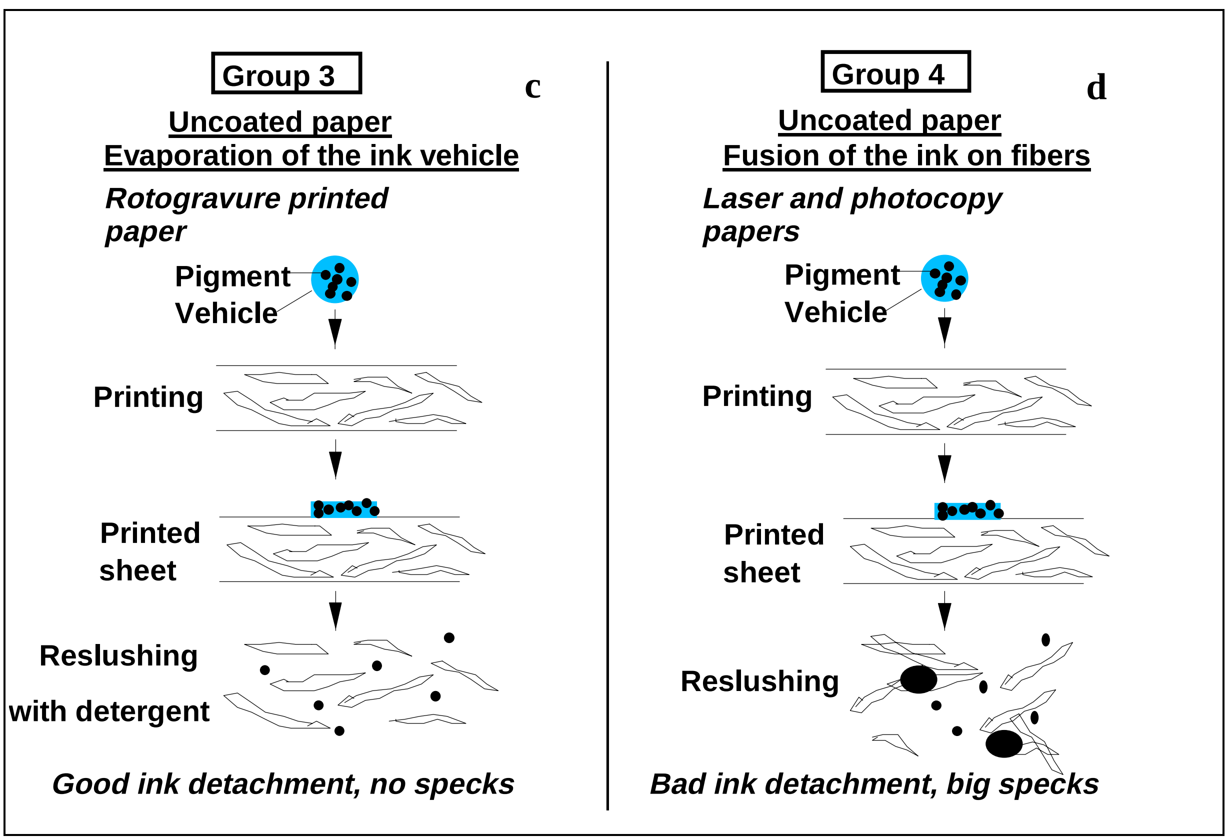
Finally, concerning radiation-cured inks, considerable toner detachment problems are observed for laser and copier prints. This is the subject of another paper *(4)*. Inks cured by UV or IR radiation generally lead to resistant specks that have to be fragmented. This is achieved mainly by dispersing or kneading treatments.

DEINKABILITY VS. PAPER SURFACE

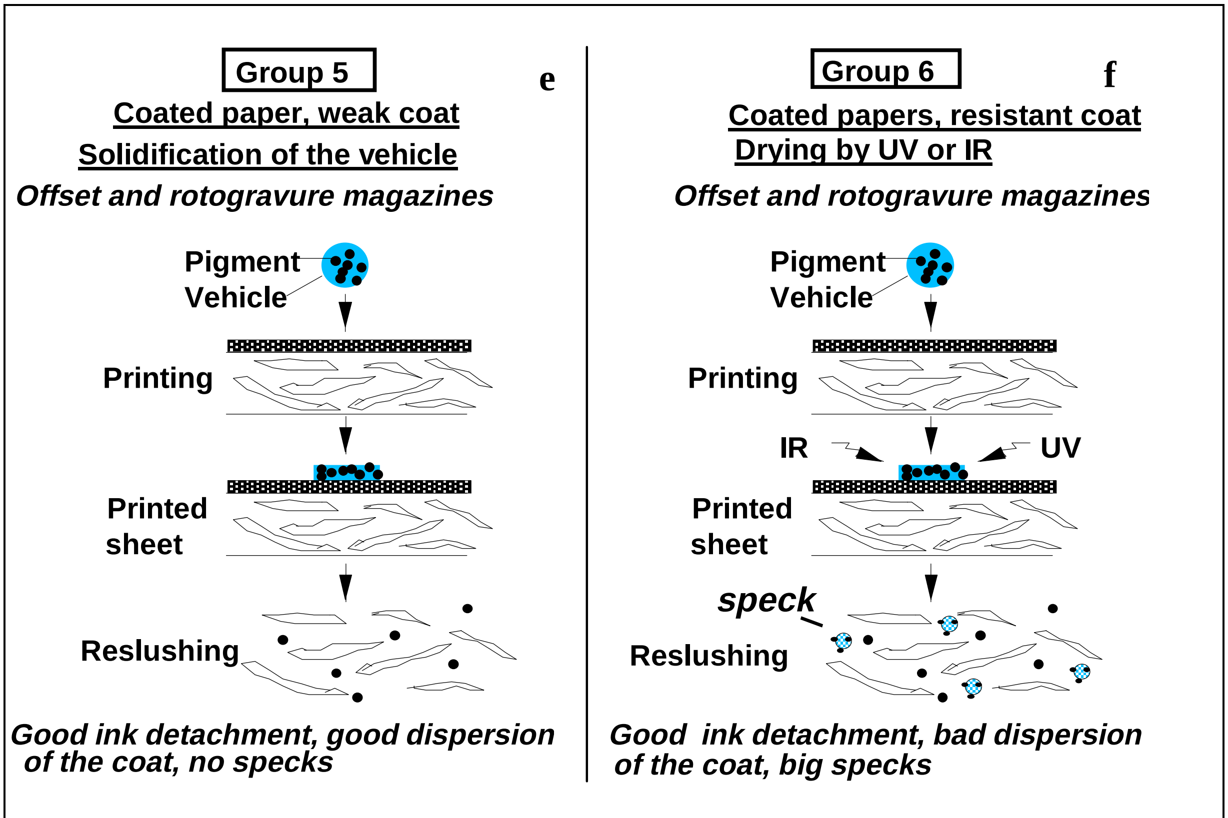
Figures 1a–g proposes seven models summarizing the main deinkability behavior vs. the paper surface and the type of ink, printing process, and aging.



Figures 1a and 1b. Deinkability trend vs. paper surface and printing processes—Groups 1 and 2



Figures 1c and 1d. Deinkability trend vs. paper surface and printing processes—Groups 3 and 4



Figures 1e and 1f. Deinkability trend vs. paper surface and printing processes—Groups 5 and 6

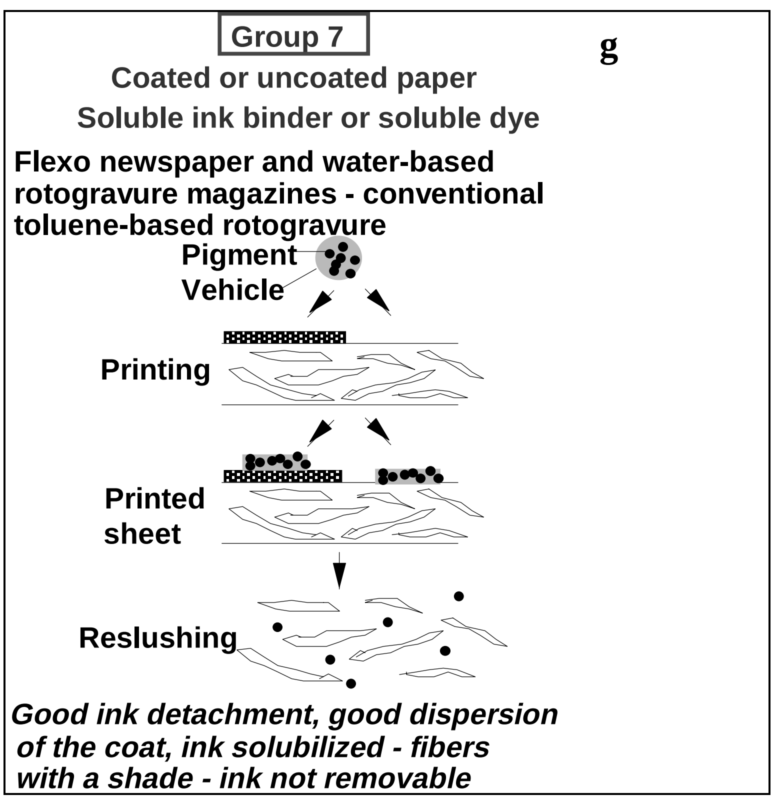


Figure 1g. *Deinkability trend vs. paper surface and printing processes—Group 7*

The main parameter concerning the influence of the surface of the paper is whether or not it is coated. As seen in Figs. 1a–1f (Groups 1–6), most of the ink detachment difficulties (aged offset, sheet-fed offset, offset heat-set, toners) arise when the ink is directly fixed onto the fibers. As soon as the paper is coated, ink detachment from fibers becomes easier. For lightweight coated (LWC) paper, ink detachment problems can still be present, depending on the coverage of the coat. This deinkability difference—depending on whether the paper is coated or not—has long been known. However, it must be mentioned that inked fillers from the coat seem to float better than noninked fillers. It may thus also be important to try to detach the ink from fillers to achieve a better quality and a higher yield. This is discussed in detail later in this paper under the heading "Deinkability of heat-set printed papers."

None of these conclusions applies when discussing soluble dye and ink broken down into small pigments (Fig. 1g, Group 7), such as for water-based flexo ink for newsprint (repulped in alkaline conditions), water-based rotogravure, and soluble dye added in the formulation of conventional toluene-based rotogravure ink. In this case, the paper surface is not a crucial parameter.

DEINKABILITY OF VEGETABLE-OIL-BASED OFFSET NEWSPRINT

Substitution of vegetable oil for mineral oil in the formulation of offset ink for newsprint has been said to degrade deinking ability. The oxidation of unsaturated oil with aging explained this behavior. However, work has been performed in the framework of a European project (**Programme AIR - 3 - CT94 - 2272**) with two suppliers—Trenal, an ink supplier, and Kao, a deinking chemical supplier—and two research centers (PIRA and CTP) to improve the formulation of these inks and achieve a good deinkability.

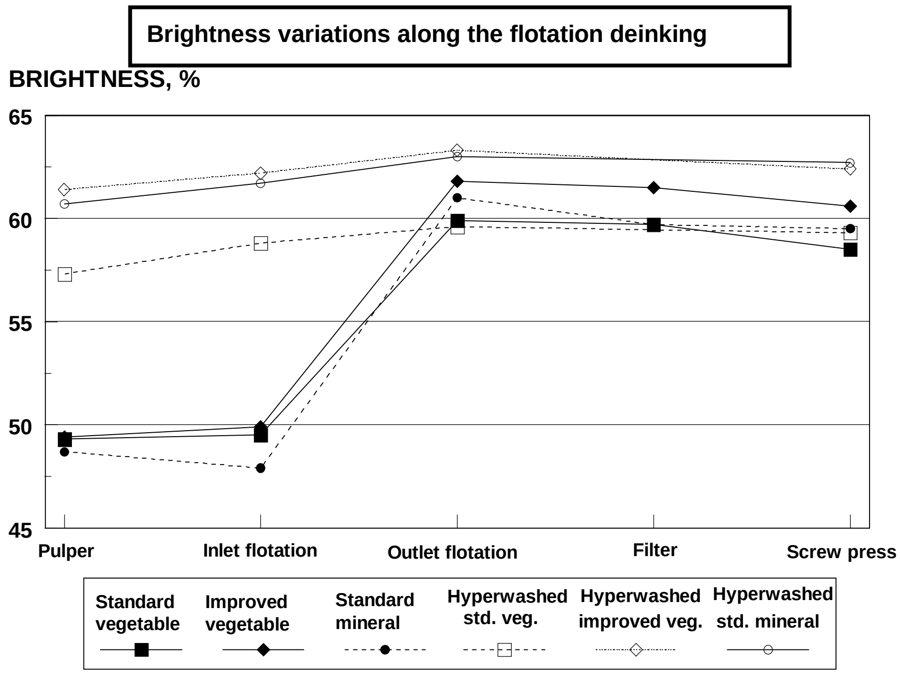
The goal of that project was to study the effect of the different components of the ink formulation on deinkability. It was shown that not only the vegetable oil but also the type of resin could induce a strong oxidation. This explains why even some purely mineral-oil-based inks for newsprint can show a very poor deinkability because of other oxidative components present in the ink formulation. Moreover, experiments showed that some vegetable oils with a low oxidation rate with aging could provide deinkability equal to that of mineral-oil-based ink.

Some experiments are recalled below.

RESULTS

EFFECTS OF CONVENTIONAL FLOTATION DEINKING

All of the experimental conditions are given in the Appendix at the end of this paper. Values are represented as curves in the following figures:

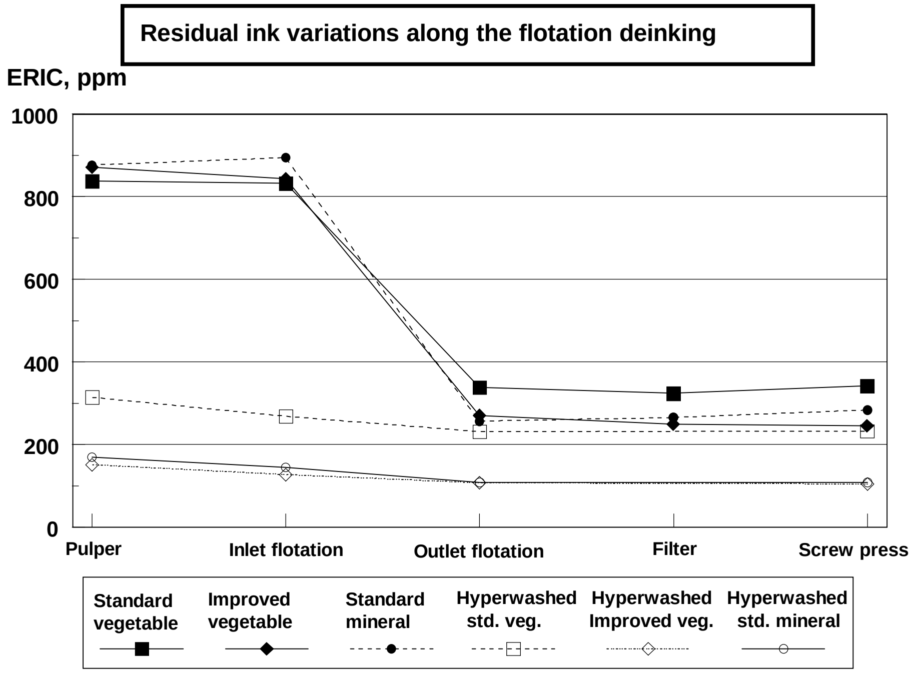


<u>Figure 2.</u> Brightness variations along a conventional flotation deinking process for three newsprint inks on whole and hyperwashed pulps

Brightness after pulping, as reported in **Fig. 2**, illustrates mainly the print fragmentation due to the shear delivered in the pulper. Brightness variations also illustrate differences in hydrogen peroxide bleaching. However, because the paper composition is identical for each print, there should be no differences due to yellowing or bleaching. The main trends are as follows:

- Brightness differences after pulping illustrate variations in ink fragmentation. The differences are small, which means that ink fragmentation is similar whatever the type of ink.
- On the other hand, small differences are observed on brightness after flotation. Higher brightness gains (and final brightness around 62) are obtained with the newly “improved vegetable” ink. Good results are also obtained for the standard mineral ink (final brightness of 61), whereas the lowest results are obtained for the standard vegetable ink (final brightness just below 60).
- Looking at brightness values on hyperwashed pulp, variations in ink detachment can be seen. There are two main behaviors. A rather good ink detachment is obtained for both “improved vegetable” and “standard mineral” inks. Hyperwashed brightness is around 61 just after pulping. On the other hand, the hyperwashed brightness obtained for the “standard vegetable” ink is much lower, around 57 after pulping.
- The hyperwashed brightness values increase slightly along the deinking process, mainly because shear delivered by the different pumps helps to increase ink detachment. Hyperwashed brightness for “standard mineral” and “improved vegetable” inks increases up to 63, whereas hyperwashed brightness for “standard vegetable” increases up to nearly 60.
- Reformulation of the “standard vegetable” ink formulation toward the “improved vegetable” ink by changing the type of resin enables at least identical deinkability (in terms of brightness) as a “standard mineral” ink to be achieved.

The brightness results can be controlled by residual ink measurements, reported in **Fig. 3**.



<u>Figure 3.</u> Variation in effective residual ink concentration (ERIC) along a conventional deinking process for three newsprint inks on whole and hyperwashed pulps

Residual ink concentrations reported in Fig. 3 corroborate the brightness trends observed in Fig. 2:

- Similar ink fragmentation during pulping, better ink removal, and much better ink detachment for "improved vegetable" and "standard mineral" inks
- These residual ink measurements are logical. They follow the brightness variations because the base paper (newspaper) is composed of the same fibers (same amount of mechanical and deinked pulps).

Apart from final brightness, ink removal, and ink detachment, an important characteristic of deinkability is the tendency to form black specks. This has been measured by image analysis, and the results are presented in **Table II**.

	Standard vegetable ink	***Improved vegetable ink***	***Standard mineral ink***
Speck contamination after flotation, specks/m²	**780.690**	**253.156**	**266.851**
Speck contamination after flotation, mm²/m²	**12.780**	**3.423**	**3.711**

<u>Table II.</u> Black speck contamination after a conventional flotation deinking process for three newsprint inks (measurements performed on hyperwashed pulp)

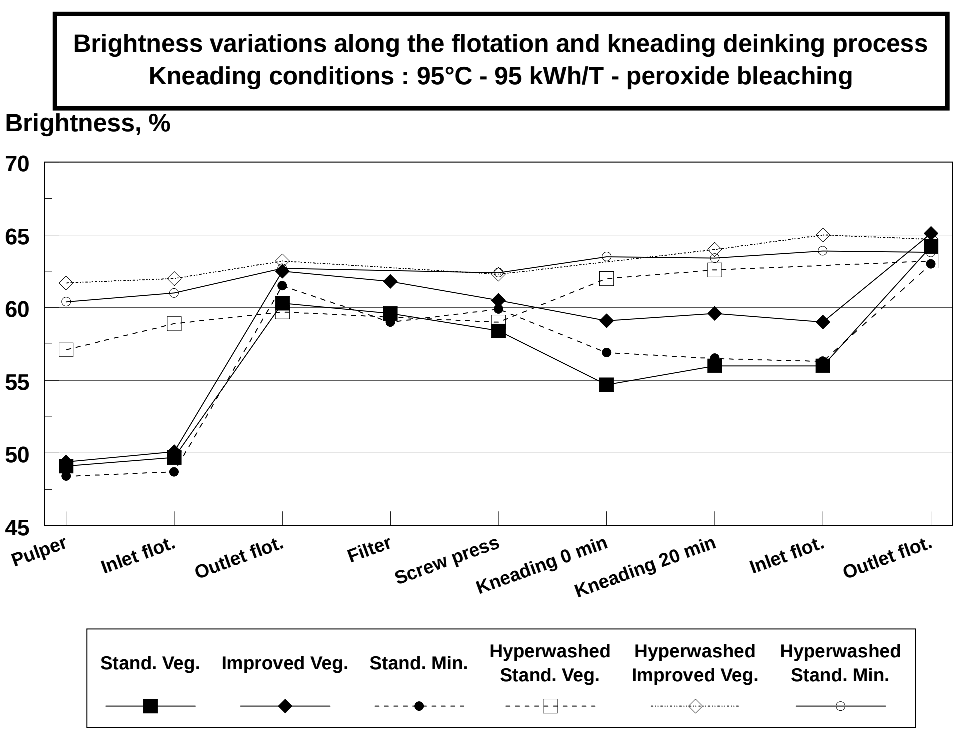
Table II clearly shows that there are wide differences among the inks. The most noticeable point is the very high speck contamination in the floated pulp issued from the recycling of the "standard vegetable" ink newspaper. Both counts, in terms of number and surface are very high, nearly three times higher than the results obtained with the "improved vegetable" and "standard mineral" inks. Considering brightness, residual ink content, and speck contamination, the "deinkability" results obtained with the new "improved vegetable" ink are thus very encouraging.

The next results illustrate the effect of mechanical treatment, kneading, and a second deinking loop on further improving the deinkability of the newly developed vegetable ink.

EFFECT OF FLOTATION, KNEADING, AND POST-FLOTATION DEINKING ON THE DEINKABILITY OF VARIOUS INKS

New deinking processes nowadays implement an additional stage of flotation after the dispersing stage in order to remove the ink that has been detached during dispersion. This whole treatment has been studied in a pilot plant after different kneading conditions. Only the best results are reported (kneader with hydrogen peroxide bleaching at high energy and temperature).

The results for brightness, residual ink and ink detachment, and speck contamination are presented in **Figs. 4 and 5** and **Table III**, respectively.



<u>Figure 4.</u> Brightness variations along a double-loop deinking process for three newsprint inks on whole and hyperwashed pulps (kneading conditions: 95 kW·h/metric ton at 95°C; peroxide bleaching)

In the presence of peroxide during kneading, results show that all final brightness values, either on whole or hyperwashed pulp, are similar whatever the kneading conditions. Ink not detached during pulping was detached during alkaline kneading, and final brightnesses after flotation are thus not too different among all the inks (biggest difference nearly 1.5 points). Results on final hyperwashed brightness are also rather similar. With a difficult-to-detach ink during pulping, an alkaline kneading stage followed by a post-flotation leads to an acceptable brightness.

Measurements of residual ink content and ink detachment reported in Fig. 5 confirm these brightness results.

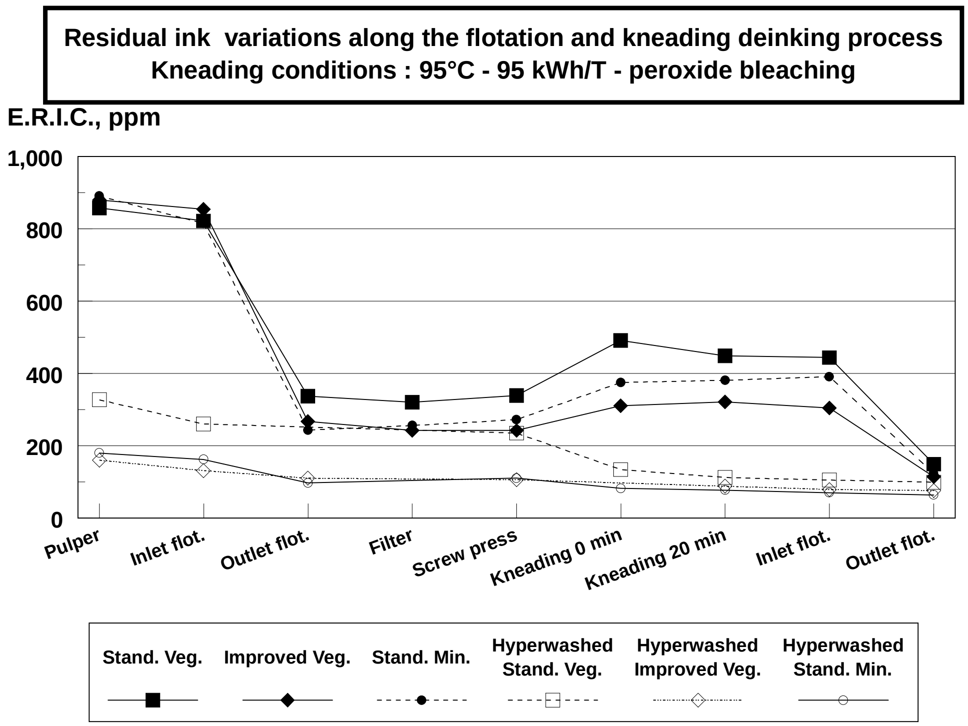


Figure 5. Residual ink and ink detachment variations along a double-loop deinking process for three newsprint inks on whole and hyperwashed pulps (kneading conditions: 95 kW·h/metric ton at 95°C; peroxide bleaching)

Looking at final residual ink content when kneading has been performed with peroxide at high energy and temperature, good results are obtained for all inks. In these conditions, results given by the “standard vegetable” ink are quite similar to the two others.

	“Standard vegetable” ink	***“Improved vegetable” ink***	***“Standard mineral” ink***
Speck contamination after kneading and post-flotation, specks/m²	**173.665**	**125.981**	**96.417**

Speck contamination after kneading and post-flotation, mm²/m²	**1890**	**1832**	**1068**

Table III. Black speck contamination after a conventional flotation, kneading, and post-flotation deinking process for three types of ink (measurements performed on hyperwashed pulp; kneading at high energy and temperature in presence of peroxide)

When looking at the results in Table III, it appears that the initial speck contamination observed after the first flotation (Table II) is the leading parameter when looking at the final contamination. "Standard vegetable" ink, which gives the strongest contamination after the first flotation, never gives a similar final speck contamination after kneading and post-flotation. Speck contamination differences for the two other inks are nevertheless reduced but not to a similar level.

Speck contamination is slightly lower for the "standard mineral" ink than for the "improved vegetable," although the difference is small. Based on the number of specks/mm², the standard vegetable-oil-based ink leads to the worst results. This means that while kneading at high energy and temperature and post-flotation are sufficient to achieve a similar brightness as the improved vegetable- and the mineral-oil-based inks, the speck contamination remains higher.

CONCLUSION

It appears that equally good deinkability results can be obtained with an "improved vegetable" ink as with a "standard mineral" ink. The deinkability of the conventional "standard vegetable" ink has been much improved by changing the type of resin. Compared with the "standard mineral" ink, the "improved vegetable" ink gives better results (in terms of brightness and ink content) and slightly similar results (for speck contamination) along each step of a deinking process composed of a single flotation, or flotation and kneading, or flotation, kneading, and post-flotation stages.

Concerning the "standard vegetable" ink, results are markedly lower after a single flotation and after flotation and kneading. However, differences are reduced after applying an additional post-flotation, although speck contamination remains greater than for the other two inks. Kneading conditions must be optimized: high energy and temperature, concurrently with alkaline bleaching, will help to detach the residual ink, giving a final deinked pulp of rather good quality. The main problem is that very few mills have a process including both kneading (and bleaching) and post-flotation. The cost of such a process is indeed very expensive, and the corresponding yield is reduced.

DEINKABILITY OF RED ROTOGRAVURE PRINTS

Among the various problems faced by papermakers producing deinked pulps, one of the most vexing is the appearance of red color in the deinked pulp. Some work on this problem has been performed by Frank *(5)*, who studied the influence of red offset ink on this phenomenon in the framework of an INGEDE research project. Using pigment red 57:1, a standard pigment for process magenta offset inks, test series were made of different binder compositions and other pigment classes. Results showed deinked pulp of a more or less reddish color that could not be improved by subsequent bleaching trials. Frank *(5)* concludes with the following sentence: “All these results clearly defeat frequent claims that the reddish color solely originates from the poor alkali resistance of pigment red 57:1. Additional studies will be necessary for clarification.” Frank *(6)* also studied the effect of colored ink on deinking. He concludes that “comparable proportions of the 3 primary color inks are removed in the flotation deinking process so that their deinkability may be rated as identical. However, concerning the red ink, both whiteness and brightness were adversely affected. Although the red ink content of deinked stock is comparable quantitatively it is distinctly more conspicuous visually and in measurements.” The problem is thus still not solved, and more investigations are needed.

The deinkability of red offset ink has thus already been tested without any final conclusion and solution. However, red offset ink may not be the right ink to study because the pigment is mixed with more resin and oil in offset than in rotogravure formulations. The same pigment is also present in red rotogravure ink with a lower amount of resin and without oil. Moreover, this phenomenon seems to be much more pronounced when deinking rotogravure magazines than offset. A wide series of tests have thus been performed with red rotogravure ink partly in collaboration with Sun Chemical. The work was based on the same red 57:1 Rubine lithol pigment because it has indeed a poor alkali resistance and may dissolve during alkaline pulping. The first objective of our work was to identify the deinking pulping conditions that emphasize the problem. The second objective was to look at the effect of different red ink formulations (different pigments and resins but also the presence of red dye) on bleeding. The final objective was to investigate bleaching or color-stripping solutions to remove this reddish shade. Results for the two last objectives are reported here.

EFFECT OF SEVERAL INK FORMULATION ON BLEEDING

Given that the red shade is mainly due to the type of pigment and dye, experiments have been conducted in cooperation with Sun Chemical, manufacturer of rotogravure inks.

OPERATING CONDITIONS

Sun Chemical formulated different red inks with different resins to prepare the ink as well as rhodamine dyes prepared in different ways. **Table IV** shows the red rotogravure ink formulations.

Sample	Pigment	Dye	Resin
1	PR 57	NO	Resinate
2	PR 57	NO	Hydrocarbon
3	PR 57 + Additive	NO	Resinate
4	PR 57	SALT	Resinate
5	PR 57	IN RESIN	Resinate
6	PR 57	SALT	Hydrocarbon
7	PR 57	IN RESIN	Hydrocarbon
8	PR 48	NO	Resinate
9	PR 53	NO	Resinate

Table IV. Red rotogravure ink formulations

Samples of the different red inks were printed onto a supercalendered (SC) paper and deinked under the following conditions:

Pulping:

100% of red printed papers were pulped in a laboratory Hélico pulper at 12% consistency and floated in a Voith laboratory flotation cell at 1% consistency. Pulping and flotation conditions were as follows:

Laboratory Hélico pulper
Pulping time: 20 min
Pulping temperature: 50°C
Consistency: 12%
Pulping chemistry: 1% NaOH, 1% H_2O_2, 2.5% silicate, 1% soap, 0% DTPA
Pulping water: Tap water with nearly 70 mg/L of Ca^{2+} adjusted to 600 mg/L of Ca^{2+} with $CaCl_2$.

Flotation parameters:

Voith laboratory flotation cell
Flotation time: 10 min
Flotation temperature: 35°C
Consistency: around 1%
Dilution waters: tap water with 70 mg/L of Ca^{2+} adjusted to 600 mg/L of Ca^{2+} with $CaCl_2$.

CONTROLS PERFORMED

Bleeding was followed by measuring brightness, residual ink, and *L*, *a*, *b*, on entire and hyperwashed pulps after pulping and flotation.

RESULTS

Results are given only in terms of *a** color of the floated pulp and hyperwashed fibers and in terms of transmittance or absorbency on the pulping waters to control the presence of the pigment or dye in the water.

All the results, firstly with different formulations based only on pigments (different pigment and/or different resins) and secondly based on pigments and dyes with different ways of preparing the dye are presented in **Figs. 6–9**. (Note that HL indicates hyperwashed pulp.)

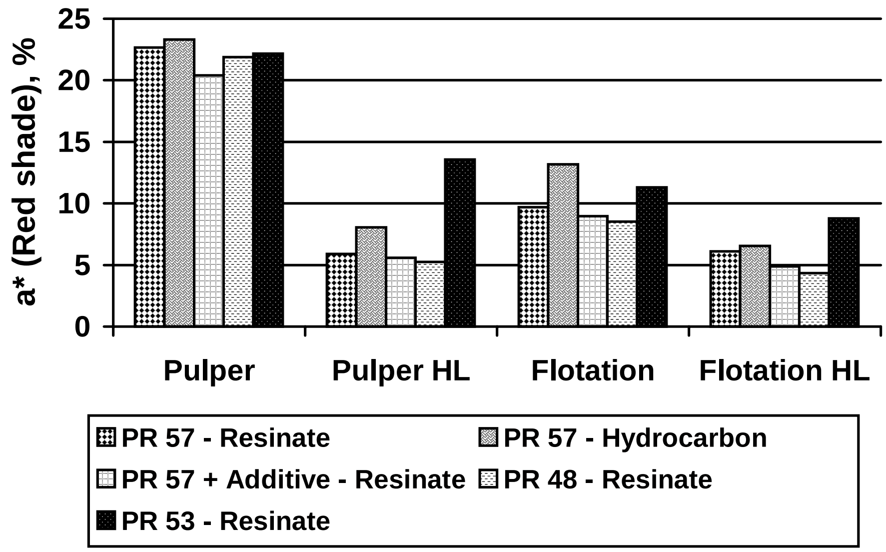


Figure 6. Influences of resin type and pigment on pulp shade for inks without dye

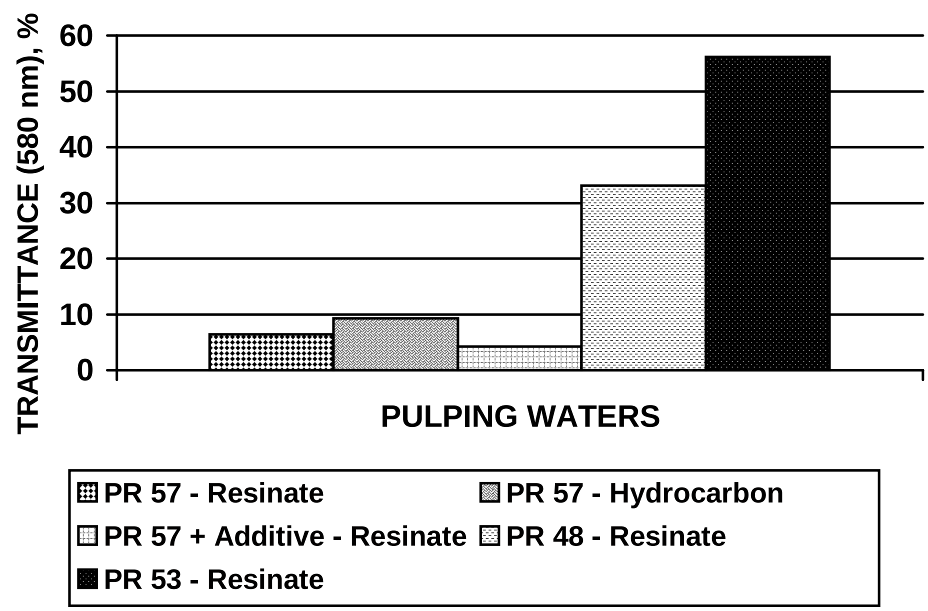


Figure 7. Influences of resin type and pigment on pulping water color for inks without dye

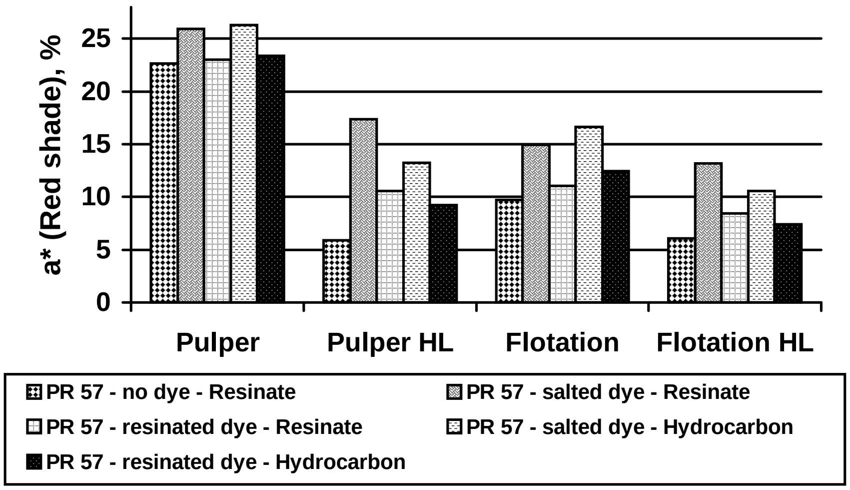


Figure 8. Influences of resin type and dye formulation on pulp shade for inks with dye

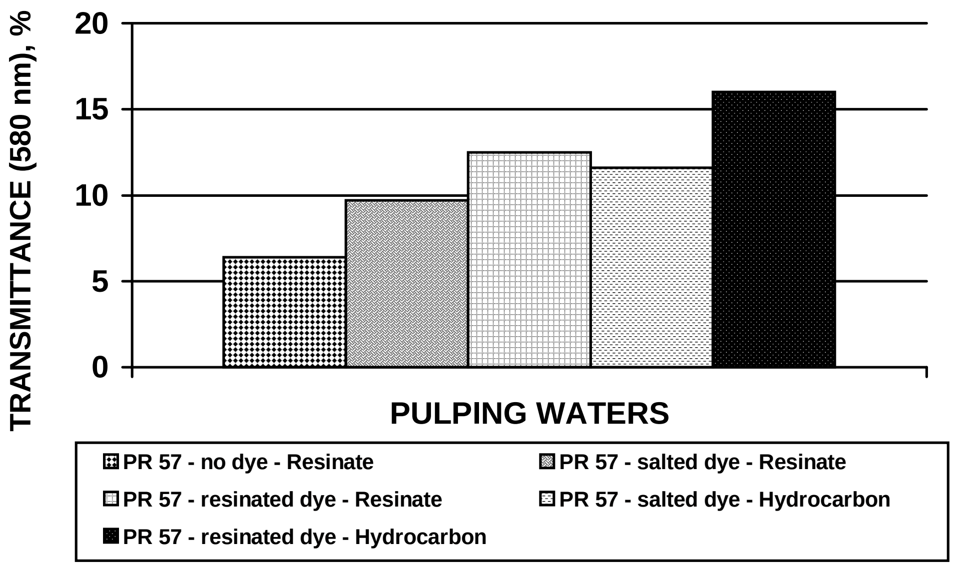


Figure 9. Influences of resin type and dye formulation on pulping water color for inks with dye

From the results shown in Figs. 6–9, the following points can be made:

- The substitution of pigment PR 57 Rubine lithol by pigment PR 48 or PR 53 does not reduce the red shade on either the floated pulp or the hyperwashed fibers, nor in the pulping waters. Pigment PR 48, without dye, gives a nearly similar red color as PR 57 with the additive on fibers and in the floated pulp, but the release is slightly higher in the pulping waters. PR 53 gives an orange color that is even more detrimental than the color given by PR 57. Clearly, these changes in formulation for these pigments did not solve the problem of red color in the deinked pulp. Additional trials with less alkali-sensitive pigments would be necessary, but it will also be necessary to check whether this is technically possible and economically viable for printers and ink suppliers.

- A positive point is that it has been clearly demonstrated that resinate gives a lower red color release than hydrocarbon resin. It is thus preferable to prepare the pigment with resinate, which may transfer to the pigment a slightly higher resistance to alkali and temperature.
- Concerning ink formulations containing rhodamine dye, the presence of this dye clearly increases the red shade of the floated pulp, the fibers, and the pulping waters. However, the effect of resinate compared with hydrocarbon resin has been confirmed, and it has also been pointed out that the dye prepared with a resin gives lower bleeding than when it is prepared as a salt. More work is also needed in this field.

EFFECT OF COLOR STRIPPING ON REMOVAL OF RED SHADE

As no definite solution was identified to reduce the red shade release, neither through pulping conditions nor through special ink formulation, another possibility was investigated to try to solve this bleeding problem: color stripping.

OPERATING CONDITIONS

Since we had samples of printed papers with different pigments or dye, color-stripping sequences were tested on two different pigments and on rhodamine. The ink formulations tested are listed in **Table V**.

Sample	Pigment	Dye	Resin
1	PR 57	NO	Resinate
2	PR 53	NO	Resinate
3	NO	In resin	-

Table V. Red rotogravure ink formulations studied for color stripping

As in previous tests, samples of the different red inks were printed on a SC paper and deinked under the following conditions before being thickened and bleached:

Pulping:

20% of red printed papers, mixed with 80% of the unprinted SC paper were pulped in a laboratory Hélico pulper at 12% consistency and floated in a Voith laboratory flotation cell at 1% consistency. Pulping and flotation conditions were as follows:

Laboratory Hélico pulper
Pulping time: 20 min
Pulping temperature: 50°C
Consistency: 12%
Pulping chemistry: 1% NaOH, 1% H_2O_2, 2.5% silicate, 0.1% nonionic surfactant, 0% DTPA.
Pulping water: tap water with nearly 70 mg/L of Ca^{2+}, adjusted to 600 mg/L of Ca^{2+} with $CaCl_2$.

Flotation parameters:

Voith laboratory flotation cell
Flotation time: 10 min
Flotation temperature: 35°C
Consistency: around 1%
Dilution water: tap water with 70 mg/L of Ca^{2+}, adjusted to 600 mg/L of Ca^{2+} with $CaCl_2$.

Bleaching conditions:
Bleaching treatments were performed after flotation and thickening. The bleaching treatments and the conditions used were as follows:

Hydrosulfite bleaching in closed jar:
Consistency: 3%
Temperature: 80°C
pH 7
Bleaching time: 60 min
1% or 2% of hydrosulfite

Peroxide bleaching in plastic bag:
Consistency: 15%
Temperature: 80°C
Bleaching time: 60 min
1% or 2% of peroxide in the bleaching liquor: 1% NaOH, 2.5% silicate, 0.3% DTPA.

These bleaching treatments were carried out with waters saturated or not in calcium ions.

CONTROLS PERFORMED

Bleeding was followed by measurements of brightness, residual ink, and *L*, *a*, *b*, on entire and hyperwashed pulps after pulping and flotation. The red color of the bleached pulp water was also checked through absorbency measurements.

RESULTS

Results are given only in terms of *a** color of the floated pulp and hyperwashed fibers and also in terms of transmittance or absorbency on the bleached pulp waters to control the removal of the pigment or dye shade in the water.

All the results are represented in **Figs. 10–12**.

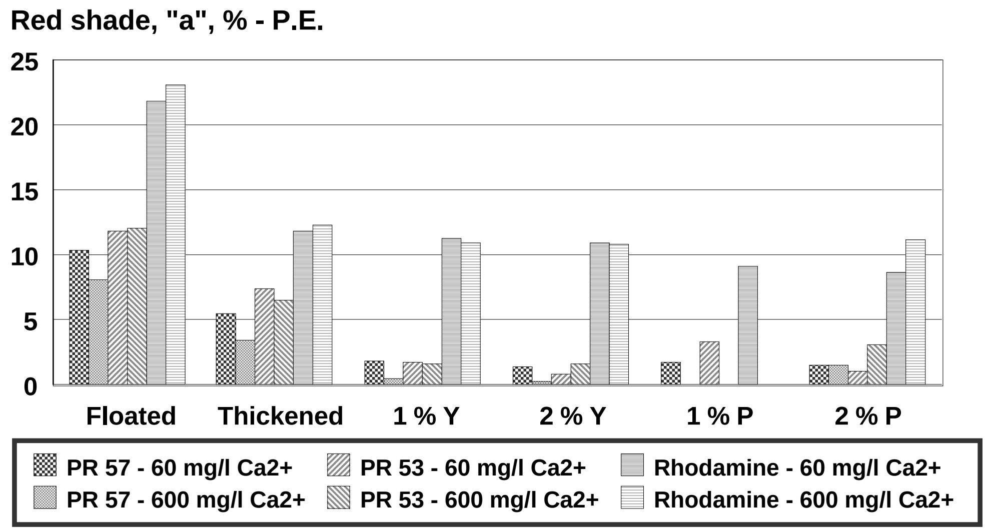


Figure 10. Color stripping: effects of peroxide (P) and hydrosulfite (Y) on pigments PR 57, PR 53, and rhodamine dye removal on entire pulp

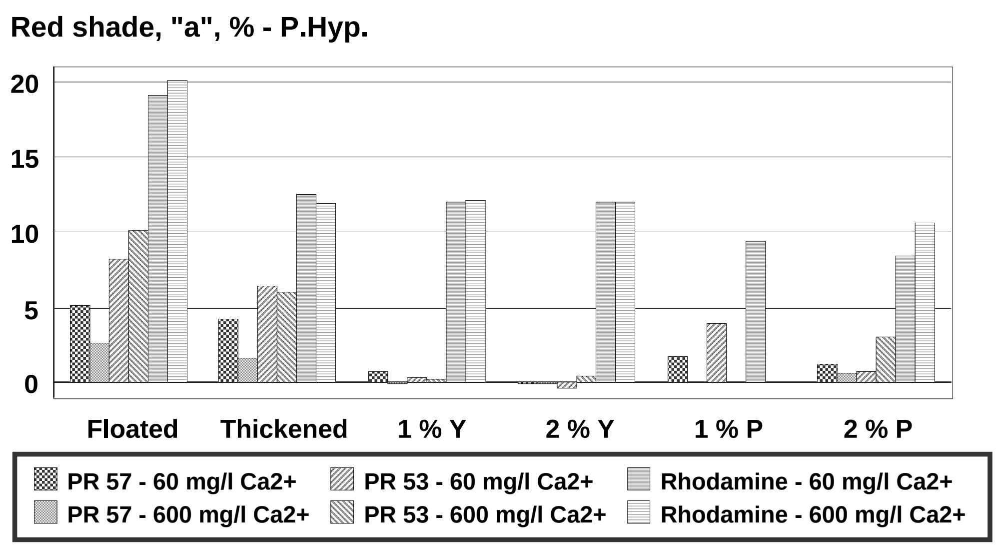


Figure 11. Color stripping: effects of P and Y on pigments PR 57, PR 53, and rhodamine dye removal on hyperwashed pulp

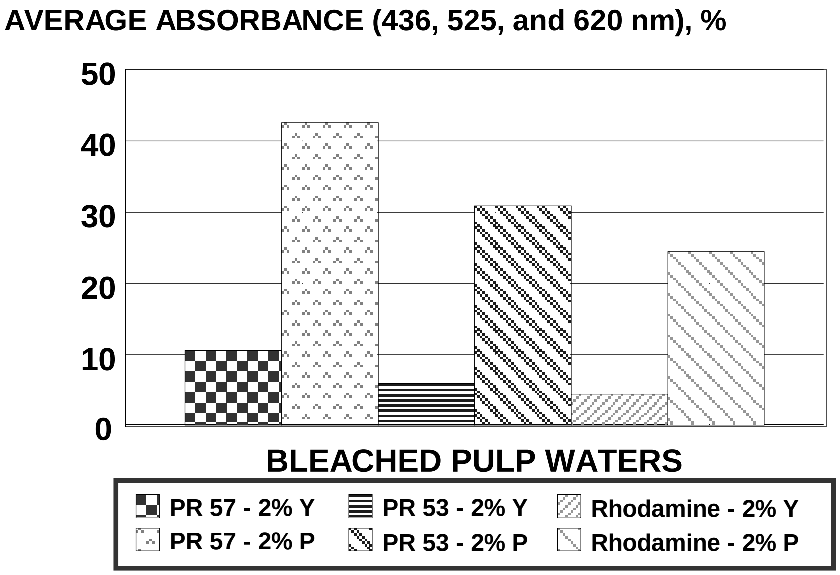


Figure 12. Color stripping: effects of P and Y on pigments PR 57, PR 53, and rhodamine dye removal in bleached pulp waters

From the results given in Figs. 10–12, the following comments can be made:

- From all the figures, it is obvious that a reductive treatment is able to remove the red shade both on the floated pulp, on the fibers, and in the water when the red shade comes from Rubine lithol (PR 57) or PR 53 pigment. Good removal is also obtained with peroxide bleaching but with a lower efficiency.
- On the other hand, neither the reductive hydrosulfite bleaching nor the peroxide oxidative bleaching were able to remove the red shade from the rhodamine dye. A solution remains to be found for the latter, perhaps with a stronger oxidative treatment.

DEINKABILITY OF OFFSET HEAT-SET PRINTED PAPERS

With the increasing amount of advertising, we find in our mailbox a number of uncoated or coated papers that have often been printed by the offset heat-set process. The deinkability of these prints has been investigated by several authors *(7–10)*, and the results showed that when deinking uncoated offset heat-set papers, especially aged prints, it was difficult to recover a sufficient brightness, and moreover, there were some specks contaminating the pulp. Investigations have been performed at CTP for some years on this problem, and the results show a strong decrease of deinkability with aging due to increased attachment of the ink onto fibers along with an increasing number of specks. Experiments were also performed to look at different ink formulations and emphasize wide differences in deinkability according to the presence of drying components in the ink. However, problems were not solved, and more investigations are still needed. Papermakers, especially during the summer, must face up to this difficult raw material. Progress has been made with the use of dispersion and post-flotation *(11)*, but this does not always work, and it reduces yield.

The objectives of the experiments reported here were twofold: first to investigate the effect of some paper properties (wood containing, manufacturing pH, coated or uncoated) on deinkability and secondly to look at the effect of some printing parameters (type of heat-set ink, temperature of the heat-set oven after the press, amount of ink deposited, aging) on deinkability.

EFFECT OF DIFFERENT LWC PAPER AND INK TYPES ON DEINKING

Only results with different LWC papers are reported. These, with increasing coating, were printed with two commercial offset heat-set inks before being deinked.

The deinking results for these different LWC papers are reported in **Figs. 13 and 14**. (Note that HL indicates hyperwashed pulp.)

All the printing and deinking conditions are reported in the Appendix.

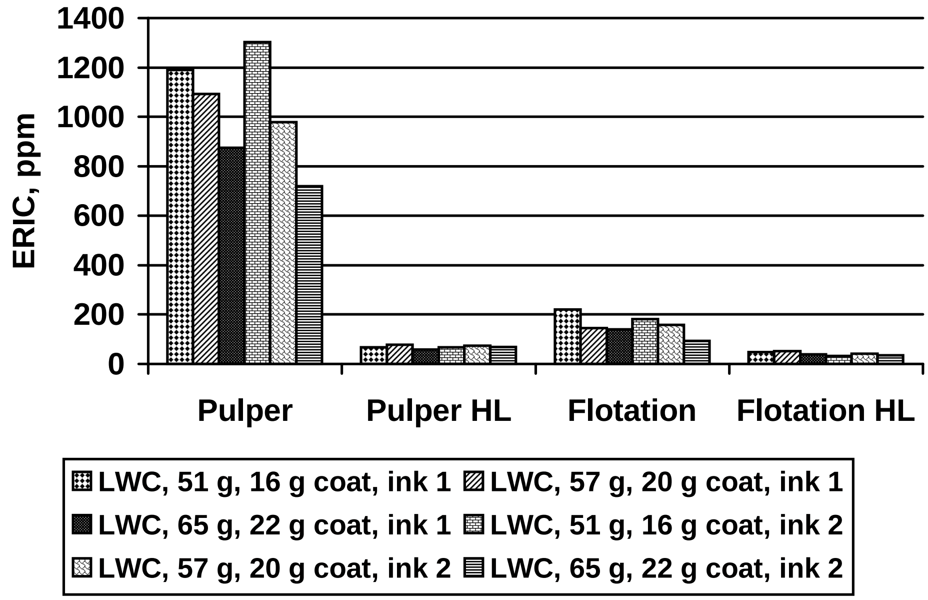


Figure 13. Effect of different LWC paper on deinkability; residual ink

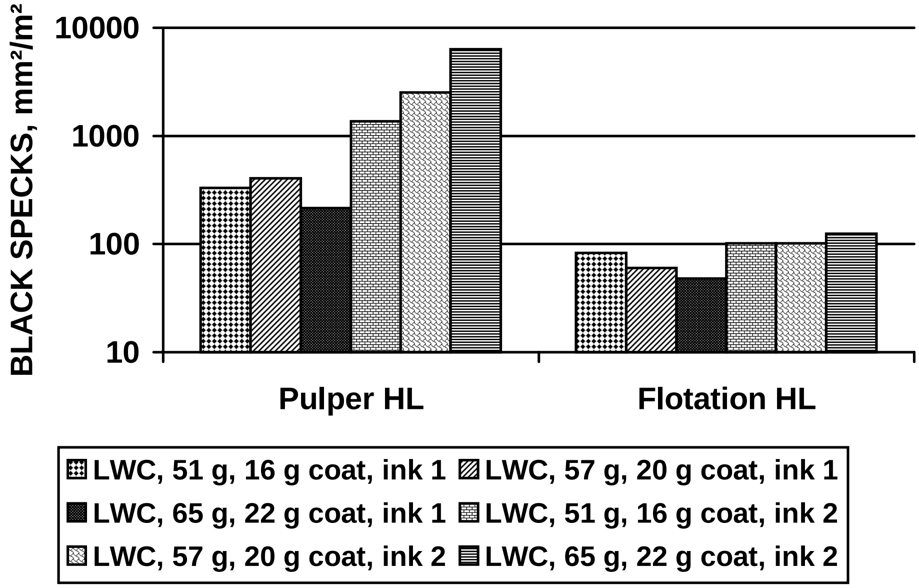


Figure 14. Effect of different LWC paper on deinkability; speck contamination

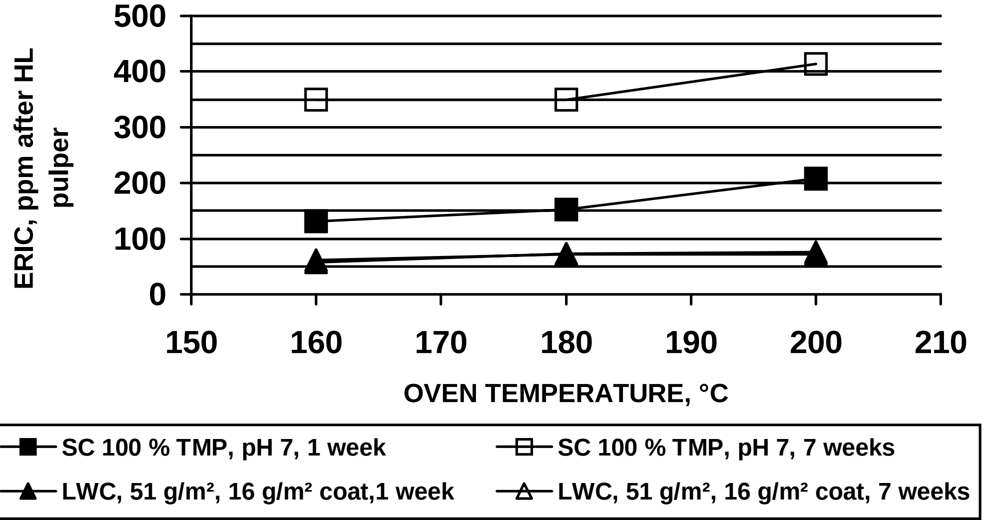
The results reported in Figs. 13 and 14 show the following interesting points:

- The first major point is the large deinkability difference depending on the type of ink, mainly in terms of speck contamination (Fig. 14), especially after pulping. The link between ink 2 and the coating (mainly thick coating) seems to be much stronger than with ink 1.
- Apart the large difference in terms of speck contamination, the LWC type of paper shows less difference in terms of residual ink content or attached ink on fibers. However, a thick coating does seem to improve the ink removal efficiency during flotation.

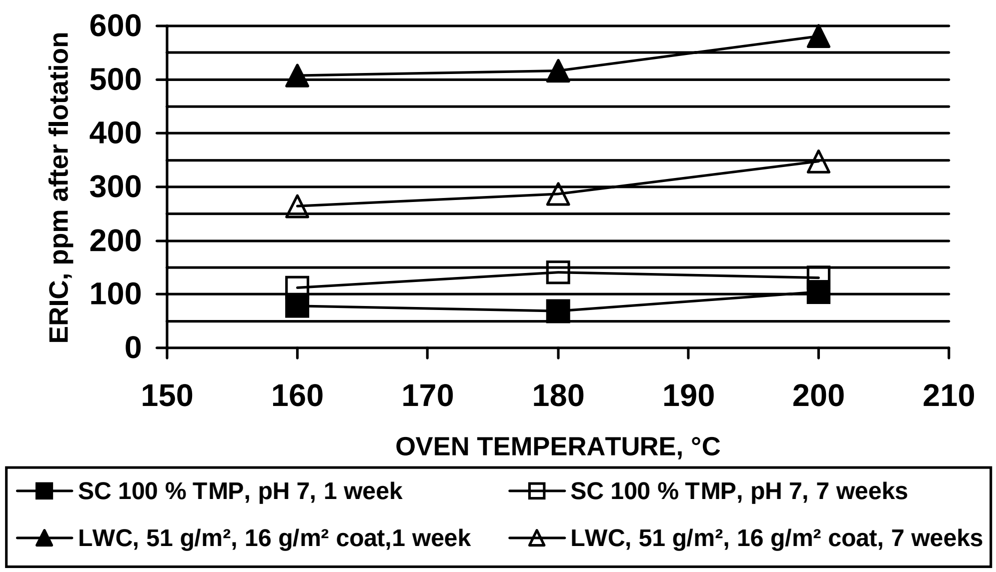
Out of all the measurements, small deinkability differences are due to the weight of the coating (8–11 g/m²). This implies that 8 g/m² may be sufficient to efficiently cover all the fibers. Most of the differences are due to the ink type, i.e., the ink formulation. Ink 2 seems to be more cohesive, which gives a higher speck contamination after pulping, but this difference is strongly reduced after flotation.

INFLUENCE OF HEATING TEMPERATURE DURING DRYING IN THE HEAT-SET OVEN ON DEINKABILITY

As explained previously, heating temperature in the heat-set oven was varied from 160 to 200°C. The impact of this drying difference and the impact of aging are compared in terms of deinkability. **Figures 15–17** illustrate these effects. (Note that HL indicates hyperwashed pulp.)



<u>Figure 15</u>. Effects of aging and drying temperature on residual attached ink on fibers



<u>Figure 16</u>. Effects of aging and drying temperature on residual ink after flotation

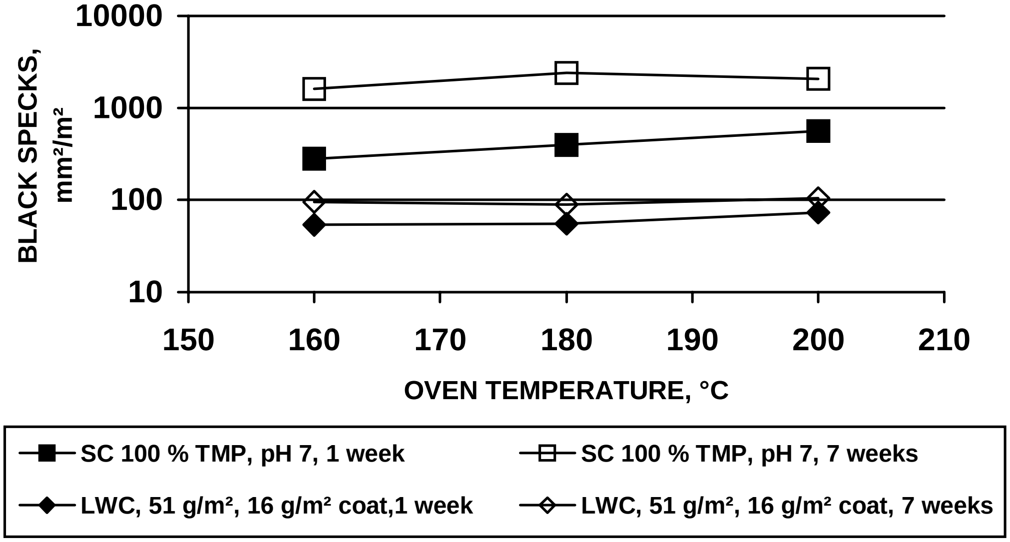


Figure 17. Effects of aging and drying temperature on speck contamination

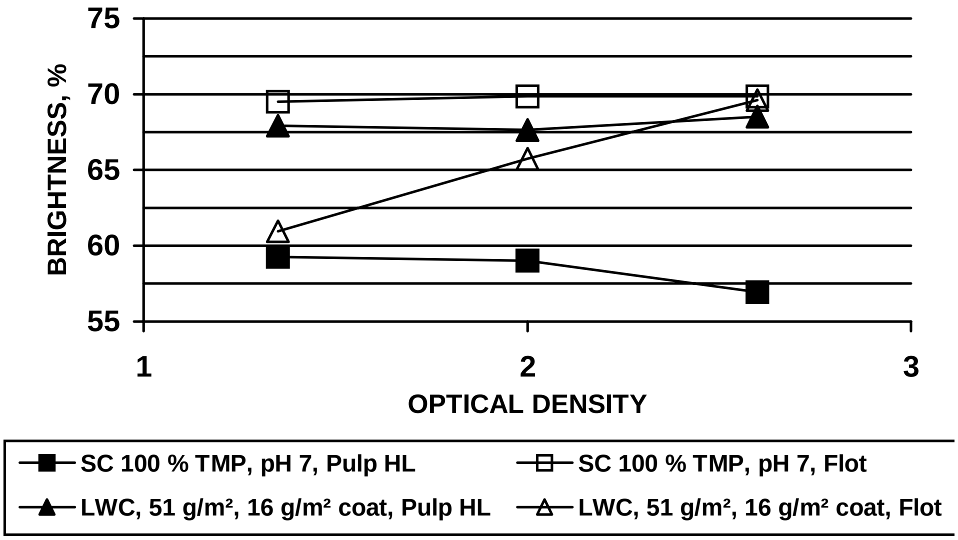
Figures 15–17 show the following points:

- Increasing the drying temperature induces a small increase in the bond between the ink and the fibers, as shown by both the residual attached ink (on hyperwashed pulp, Fig. 15, SC paper after one week of aging) and the speck contamination (Fig. 17, SC paper after one week of aging). After seven weeks of aging, the effect of drying temperature is still slightly visible on the amount of attached ink but is less pronounced on speck contamination. Aging smoothes the differences between drying temperature and aging. In terms of deinkability, aging time seems much more important than drying temperature.
- On the other hand, increasing the drying temperature does not seem to affect ink detachment so much when deinking LWC printed papers. This is logical, since ink is not in direct contact with fibers during printing of coated papers. Thus the amount of ink attached to fibers after pulping is much lower than that observed with SC paper. With this type of LWC paper, aging and drying temperature have a small impact on ink detachment and speck contamination.
- Residual ink values after flotation (Fig. 16) are much more interesting (and surprising!). Residual ink content was indeed lower when deinking SC papers. Brightness differences observed when deinking LWC or SC paper can be up to 15 points ISO (500–100 ppm ERIC, respectively) after one week of aging, decreasing to 4 points (250–100 ppm ERIC, respectively) after seven weeks of aging. As residual ink content on fibers (Fig. 15, hyperwashed fibers) varies in the opposite direction, the only explanation lies in the fact that with LWC paper, ink fixed onto coating particles (mineral fillers) is not easily removed and may not be well detached. In that case, mineral fillers would be more or less gray and would not increase brightness. This is not the case with fillers from SC paper, which are only partly in contact with ink during printing and are thus clean and bright.
- Although it was already known that deinkability decreased with aging for uncoated paper, the trend seems to reverse for coated paper, at least with the offset heat-set prints used.

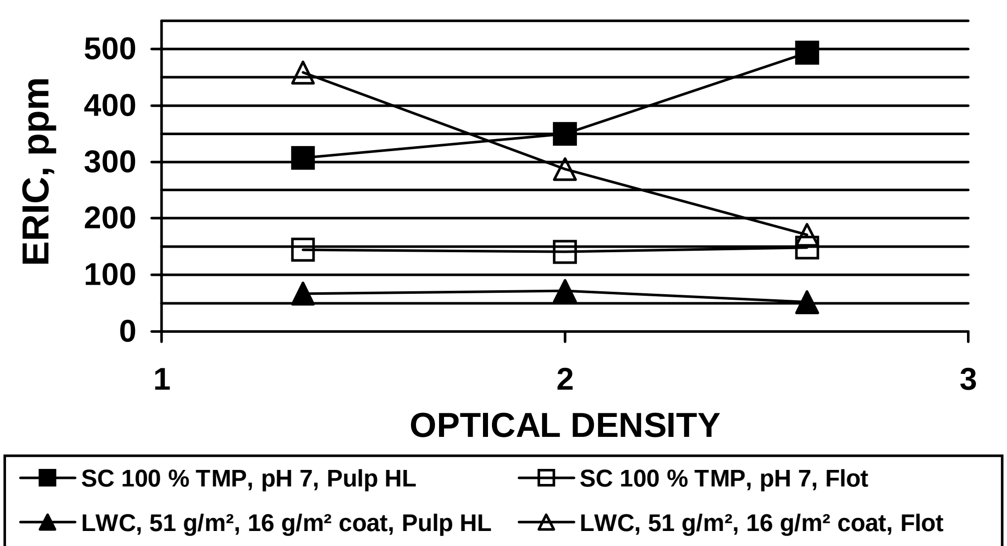
INFLUENCE OF INK THICKNESS (THROUGH OPTICAL DENSITY) ON

DEINKABILITY

Dorris and Sayegh *(12)* showed that for toner prints, the flotation removal efficiency was better for thick ink particles. **Figures 18–20** show the trends for offset heat-set ink. (Note that HL indicates hyperwashed pulp.)



<u>Figure 18</u>. Effects of base paper and ink thickness (through optical density) on brightness of hyperwashed fibers and on brightness after flotation



<u>Figure 19</u>. Effects of base paper and ink thickness (through optical density) on residual attached ink (hyperwashed fibers) and on total ink content after flotation

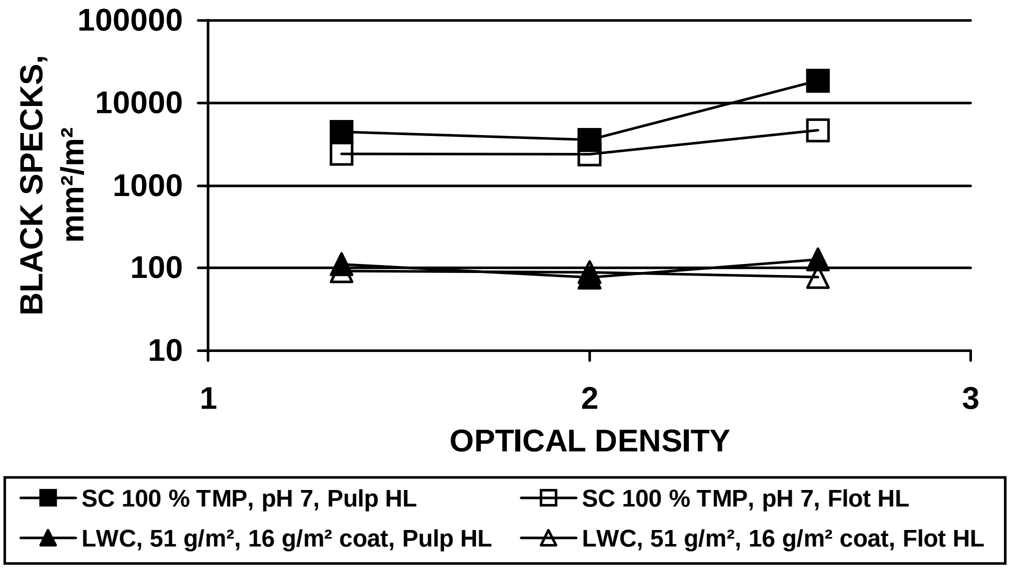


Figure 20. Effects of base paper and ink thickness (through optical density) on speck contamination for hyperwashed pulp and after flotation

Figures 18–20 show the following points:

- Increasing the thickness of the ink layer deposited on SC paper induces a small decrease in ink detachment, visible in the results for both brightness and residual attached ink on hyperwashed pulp. However, this decrease in ink detachment does not induce any reduction of brightness or increase in ERIC on the floated pulp, which remains bright, with brightness around 70%. On the other hand, this increase in ink thickness induces a small increase in speck contamination on the pulp, which is reduced after flotation. Taken as a whole, an increase in the ink thickness does not cause too much deterioration of the deinkability of SC paper.
- Concerning LWC paper, it can logically be observed that increasing the ink layer thickness does not degrade ink detachment or increase speck contamination. Ink is fixed on the coating and not on the fibers, so this result is logical. Moreover, it can be seen that the coating is not very resistant, because no specks remain after flotation.
- A more interesting result is the variation of the flotation efficiency with the ink film thickness deposited on LWC paper. This efficiency is indeed not high when the ink film is thin (brightness of the floated pulp around 61%), whereas it increases markedly when the ink film thickness is higher (brightness around 70% at an optical density of 2.5). When the ink film is thin, ink deposited on coating fillers would be more difficult to detach and remove by flotation. On the other hand, when the ink film is thick, ink detachment would be easier due to the stronger cohesiveness and the larger size of ink particles. This would facilitate removal of the ink and keep the fillers clean in the deinked pulp.
- When observing brightness of deinked pulp issued from SC or LWC printed papers, it can once more be seen that higher brightness is obtained with SC papers, except when the ink film on LWC paper is sufficiently thick, in which case brightness is similar. However, speck contamination is always higher with SC papers compared with LWC.

Out of all the preceding results, it can be said that increasing the ink film thickness causes a slight reduction in ink detachment and increase in speck contamination when deinking SC paper. On the other hand, a thick ink film on LWC paper will induce good ink detachment and thus good flotation removal of the ink, which is attached to mineral fillers of the coat. This leads to higher brightness after flotation (around nine brightness points difference, depending on the ink film thickness). Final brightness after flotation is higher overall with SC than LWC paper, but speck contamination is worse.

CONCLUSIONS

VEGETABLE-OIL-BASED OFFSET INK FOR NEWSPRINT

It appears that equally good deinkability results can be obtained with an "improved vegetable" ink as with a "standard mineral" ink. The deinkability of the conventional "standard vegetable" ink has been much improved by changing the type of resin. Compared with the "standard mineral" ink, the "improved vegetable" ink gives better results (in terms of brightness and ink content) and similar results (for speck contamination) along each step of deinking processes composed of either a single flotation, or flotation and kneading, or flotation, kneading, and post-flotation stages.

Concerning the "standard vegetable" ink, results are markedly lower after a single flotation and after flotation and kneading. However, differences are reduced when applying an additional post-flotation, although the difference in speck contamination remains. Kneading conditions must be optimized: High energy and temperature, concurrently with alkaline bleaching, will help to detach the residual ink, giving a final deinked pulp of rather good quality. The main problem is that very few mills have a process including both kneading (and bleaching) and post-flotation. The cost of such a process is indeed very expensive, and the corresponding yield is reduced.

BLEEDING DUE TO RED ROTOGRAVURE INK

Firstly, concerning the effect of red ink formulation, some conclusions can be drawn to slightly reduce the bleeding. For red ink containing only pigment PR 57:1 and varnish, without dye, it appears that hydrocarbon resin leads to a higher release of red color than resinate. Moreover, it appears that other pigments, PR 53:1 and PR 48:1 (both barium salts), lead to poorer results than PR 57:1, especially for PR 53:1, which gives a strong orange color both on the fibers and in the deinking process waters. Concerning red ink, which also contains the rhodamine dye, it appears firstly that the presence of rhodamine increases the red shade of the deinked pulp and secondly that the way of preparing the dye has an effect on bleeding. Using rhodamine dye prepared with a resin induces less bleeding than using the salt form of the dye. Efforts to reduce bleeding by modifying red ink formulations have not been successful, and much progress remains to be made.

Secondly, concerning the effect of color stripping of the red shade, experiments have been performed with H_2O_2 and sodium dithionite. It appears that all of the pigments tested—PR 57:1, PR 53:1, and PR 48:1—are efficiently discolored with a reductive bleaching and slightly less efficiently discolored by H_2O_2. On the other hand, the rhodamine dye is not discolored at all with any of these treatments.

DEINKABILITY OF HEAT-SET OFFSET PRINTS

The trials conducted in the course of this study showed the effect of several parameters on deinkability. The investigated parameters were the type of paper (uncoated or coated), the type of ink, as well as the influence of different offset heat-set printing parameters. In terms of final brightness, it appears that the deinkability of an SC paper is better than that of an LWC paper. For LWC, attached ink fixed on the fillers of the coating is not easily removed during flotation, and this induces poor brightness after flotation. However, coated papers have an advantage in that there is no residual ink on fiber, in contrast to uncoated papers, where ink is applied adheres directly to the fibers. On SC papers, residual attached ink on fibers induces poor cleanliness of the floated pulp, but the presence of ink-free fillers from the base paper strongly increase the brightness. Deinkability also varies strongly with the type of ink, especially in terms of speck contamination when printing has been performed on uncoated paper. The highest impact on deinkability, however, is aging. It has been shown that aging of uncoated printed papers leads to poor ink detachment from the fibers as well as high speck contamination. On the other hand, it has been shown that aging is good for deinking coated printed papers. The ink attached to coating fillers oxidizes with aging, thus improving ink detachment from the coating fillers as well as its removal during flotation, leading to higher brightness levels.

Additionally, it has been shown that increasing the drying temperature in the heat-set oven slightly accelerates drying, and thus the bond between ink and fibers. However, this effect appears small compared with aging.

Finally, it has been shown that the ink film thickness on an LWC printed paper has a strong impact on deinkability. The smaller the thickness, the worse is the flotation efficiency, whereas the higher the thickness, the better the ink removal will be. The impact of this parameter on the deinkability of uncoated paper is different, inducing a small effect on final brightness but a higher impact on speck contamination after flotation.

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APPENDIX

EXPERIMENTAL CONDITIONS FOR DEINKING TRIALS WITH VEGETABLE-OIL-BASED NEWSPRINT INK

MATERIALS AND METHODS

Materials

A paper usually employed to print newspaper was used to test three different inks:

- Conventional vegetable-oil-based offset ink
- Improved vegetable-oil-based offset ink
- Conventional mineral-oil-based offset ink

The main difference between these different inks is that the newly developed vegetable ink contains a hydrocarbon resin instead of a phenolic one. Of course, the mineral-oil-based ink is made with a 100% mineral oil.

The resulting newspapers were deinked nearly two months after printing, which is not a long aging time compared with the time frame used during the preliminary studies but which corresponds to realistic average aging time.

Methods

Old newspapers were disintegrated in conventional conditions in the Hélico pulper. In order to get a realistic composition, 75% newspapers were mixed with 25% magazines (mixture of French magazines: *Paris Match, VSD, Prima, Avantages*).

The flow sheet for the processes studied is presented in **Fig. A-1**. Initially, only the first loop of the process was used. Later, both loops of the deinking process were applied.

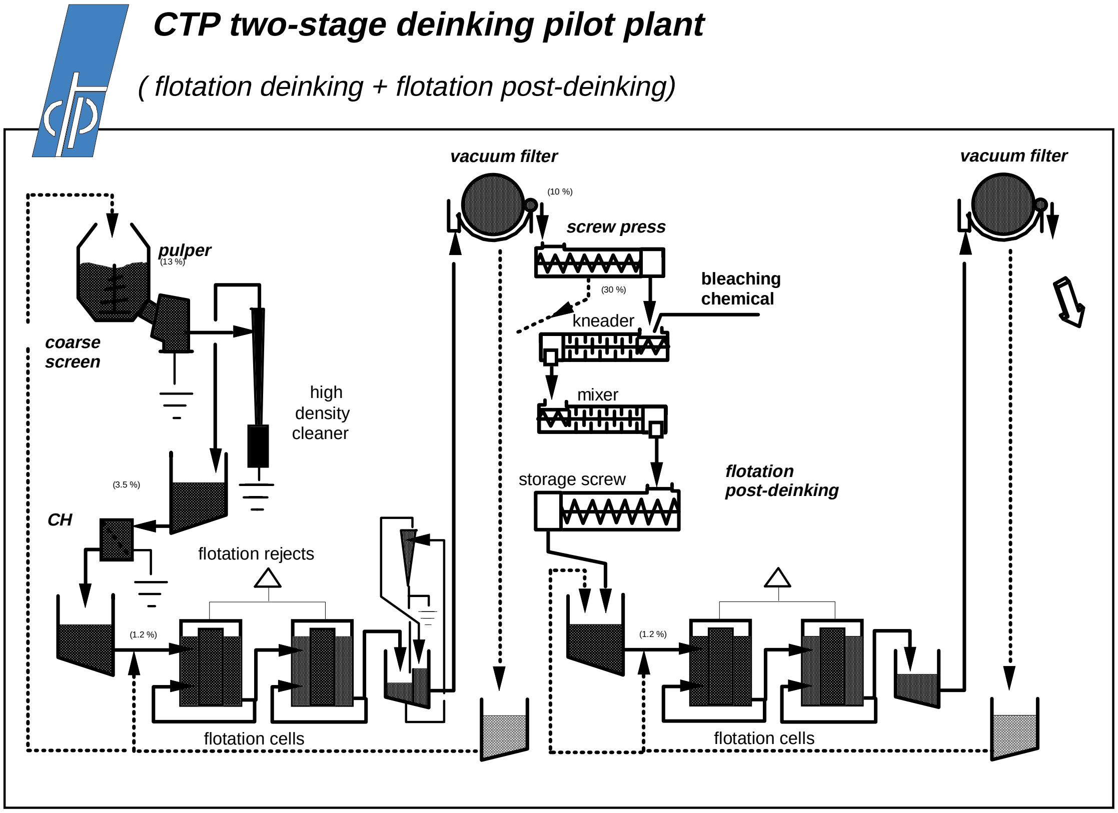

Figure A-1: Flow sheet of conventional flotation deinking process

The conventional pulping conditions are as follows:

Pulping time: 15 min
Pulping temperature: 40°C
Pulping consistency: around 12%
Pulping chemistry:

- 1% sodium hydroxide
- 1% hydrogen peroxide
- 2.5% sodium silicate
- 0.45% surfactant (DI 140)

Kao DI 140 was identified in trials by Kao Chemicals as the most suitable surfactant for deinking vegetable-oil-based sheet-fed offset ink.

Ink fragmentation was controlled after the pulping stage thanks to brightness and residual ink content (ERIC measurements).

Residual ink content was then controlled after flotation and thickening through brightness and ERIC measurements.

Ink detachment estimation was controlled after the pulping and flotation stages through brightness and ERIC measurements on hyperwashed pulp. Hyperwashing is a strong washing on a 100-µm screen performed until the washing waters are completely clear. This removes all of the detached ink particles, with only the attached ink particles remaining on the fibers.

In addition to the previous measurements, a control of the number and surface of black specks after pulping and flotation was performed (on hyperwashed pulp). After aging, these black specks indeed sometimes appear, and they must be controlled.

The presence of black specks was estimated through image analysis with a SIMPATIC image analysis device developed at CTP. The minimum size of black specks counted was 50 µm. The thresholding is made at 15% gray level difference, compared with the average gray level of the background. This control is performed on hyperwashed handsheets made after pulping and flotation. Performing this measurement on hyperwashed pulp accentuates the contrast between black specks and the background. Results are expressed in number of counted particles per m² as well as in mm² of black specks per m².

The kneading conditions were varied according to the following values:

Kneading without chemical:

- 65 kW·h/metric ton at 65°C
- 95 kW·h/metric ton at 65°C
- 65 kW·h/metric ton at 95°C
- 95 kW·h/metric ton at 95°C

Kneading concurrently with alkaline H_2O_2 bleaching:

- 65 kW·h/metric ton at 65°C
- 95 kW·h/metric ton at 65°C
- 65 kW·h/metric ton at 95°C
- 95 kW·h/metric ton at 95°C

The bleaching liquor was composed of the following chemicals:

- 1% NaOH
- 2.5% silicate
- 0.3% DTPA
- 1% H_2O_2

However, only the results obtained with peroxide liquor in the kneader at high temperature and energy are reported.

EXPERIMENTAL CONDITIONS FOR DEINKING TRIALS WITH OFFSET HEAT-SET PRINTS

TRIALS PERFORMED

The different papers employed for the offset heat-set printing were as follows:

SC papers:

- SC paper, 56 g/m² basis weight, with 85% TMP and 15% chemical pulp, containing 30% clay, manufactured in acidic conditions at pH 4.8.
- SC paper, 56 g/m² basis weight, with 100% deinked pulp, manufactured in neutral conditions at pH around 7.

- SC paper, 56 g/m² basis weight, with 100% TMP, and essentially clay, manufactured in neutral conditions at pH around 7.

LWC papers:

- LWC paper, basis weight 51 g/m² for the base paper and 16 g/m² for the coat (8 g/m² per side), woodfree paper.
- LWC paper, basis weight 57 g/m² for the base paper and 20 g/m² for the coat (10 g/m² per side), woodfree paper.
- LWC paper, basis weight 65 g/m² for the base paper and 22 g/m² for the coat (11 g/m² per side), woodfree paper.

For all three LWC papers, coating color was made up of 65 parts of $CaCO_3$ and 35 parts of clay. Latex was a styrene butadiene.

Inks:

The two commercial offset heat-set inks were Challenge (black + C + M + Y) from Sun Chemical and Jaguar (black + C + M + Y) from Coates Lorilleux.

Printing conditions: fixed and variable parameters:

Fixed parameters:

Prints were made on an offset heat-set press by CTP (P. Piette and C. Trehoult) at the "Nord Est" printing shop.

The press was a HARRIS M 90 with four printing units. The maximum printing speed is 30,000 copies/hour, although the printing speed used during the trial was 10,000 copies/hour because of the low basis weight (51 g/m²) paper, which gives runnability problems at higher speeds.

Variable parameters:

A first trial run was performed with the Challenge ink on all six papers. The same experiment was initially planned with the Jaguar ink, but the runnability was too poor. The trials with the Jaguar ink were thus only performed with the three LWC papers.

Printing conditions for the first trial were: four-color printing, 10,000 copies/hour, heat-set oven at 180°C, optical density fixed at 2.00.

Afterwards, a second run of trials was performed to look at the effects of some printing press parameters: the heat-set oven temperature was adjusted to 160, 180, and 200°C; the amount of deposited ink was also varied through three optical densities: 1.5, 2.0, and 2.5. The whole run was realized with the Jaguar ink on SC paper (100% TMP manufactured at neutral pH) and on one of the LWC papers (lowest grammage, thinnest coat).

DEINKING CONDITIONS

For most of the printed samples, deinking was performed after six weeks of aging, which corresponds to about the average industrial aging.

Deinking procedure:

- Repulping with a Hélico pulper for 20 min at 45–50°C and 12–13% consistency, conventional chemistry (1% NaOH, 2.5% silicate, 1% peroxide, 1% soap)

- 30-min soaking to complete peroxide reaction
- Flotation in a Voith laboratory cell at 1% consistency
- Hyperwashing of the pulp after pulper and flotation.

Controls carried out:

Deinking such types of print generally gives specks and a poor ink detachment. All the following characteristics were measured.

- Brightness and ERIC on entire and hyperwashed pulps after pulper and flotation
- Speck contamination on hyperwashed pulp handsheets after pulper and flotation.