Ozone bleaching of recycled paper

Michel Muguet and Jack Kogan

ABSTRACT: Chlorinated bleaching chemicals, notably chlorine and hypochlorite, are still being used to bleach deinked, woodfree pulps. Increasing environmental concern about the use of these chemicals—coupled with the industry's efforts to increase the use of recycled fibers—highlight the need to develop better techniques for producing high-quality deinked pulp. Results presented in this report suggest that deinked fibers can be treated with ozone followed by a peroxide bleaching stage to produce a high-quality pulp.

KEYWORDS: Ozone bleaching, ozonization, peroxides, reclaimed fibers, recycling.

The secondary-fibers industry is undergoing a period of high growth in North America. Growth is being driven primarily by the need to reduce the flow of waste to landfills. Chlorine and hypochlorite are still being used to bleach certain wood-free post-market papers. Given the growing concern about the environmental effects of chlorinated organic compounds in effluents from pulp and paper mills, it is likely that the use of these bleaching agents will be phased out in the near future.

Ozone bleaching is one of the most promising of the emerging technologies striving to make chlorine-free bleaching of kraft pulp a reality. This report examines the basic considerations involved in application of ozone bleaching for deinked pulp. Also presented are the results of a study comparing the optical and mechanical properties of pulps after bleaching with ozone or conventional bleaching agents.

Ozone as a strong oxidizer

Ozone has one of the highest oxidation potentials (2.07 V), second after fluorine (2.87 V) but greater than chlorine (1.36 V) or chlorine dioxide (1.15 V). Ozone has been used to treat drinking water since the turn of the century *(1)*. Industrial applications started in the early 1950s *(2)*, ranging now from fine-chemicals synthesis and kaolin bleaching to wastewater effluent treatment.

Ozone reacts very easily with inorganics (cyanides, sulfides, nitrites) as well as organic materials. Its affinity toward unsaturated hydrocarbons, amines, or more specifically aromatic compounds makes ozone a chemical of choice for removing lignin from wood pulps.

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Ozone as a bleaching agent

Deinked, woodfree, secondary fibers traditionally are bleached with chlorine and hypochlorite. Different bleaching sequences can be used, depending on the brightness of the unbleached pulp. The most common bleaching sequences are CH or CEH, and brightness up to 80% GE is easily obtained *(3)*.

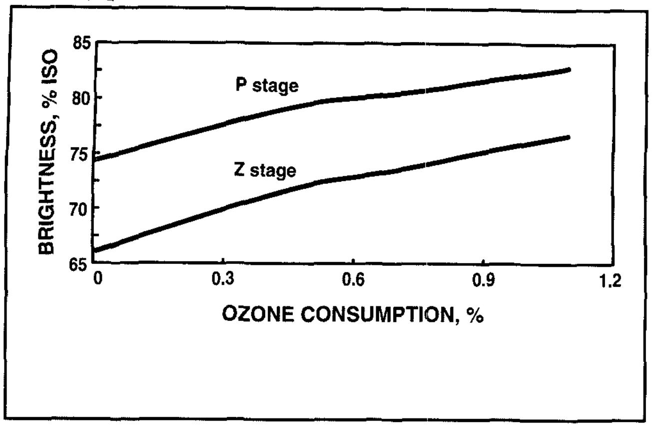
The move to chlorine-free bleaching sequences for deinked pulp represents an interesting challenge, and experience gained in the bleaching of chemical pulps must be kept in mind. Lachenal *(4)* proposed a classification to evaluate the potential of using ozone and other chemicals in a kraft pulp bleaching sequence. Chemical-reactivity considerations showed clearly that the C stage (chlorine) can be efficiently substituted by a Z stage (ozone), while the H stage (hypochlorite) could be replaced by a P stage (hydrogen peroxide). The next logical step was to try a ZP bleach sequence on a standard wood-free composition of secondary fibers.

ZP sequence: alternative to CH?

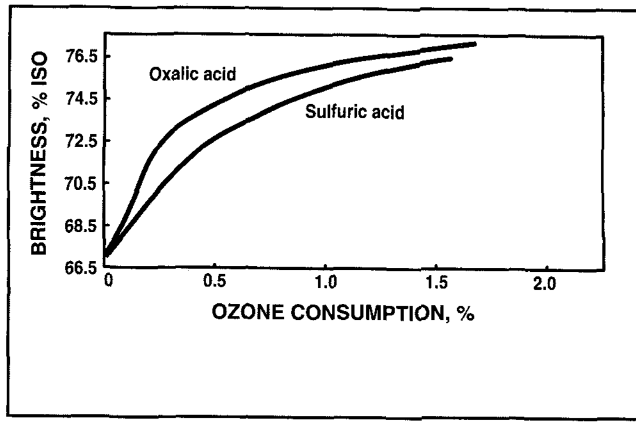
Figure 1 shows brightness after Z-stage and P-stage bleaching of a typical ledger furnish with an initial brightness of 66.5% ISO. At 0.5% O_3 consumption, the Z-stage treatment raised the brightness by 6.1 points to 72.6% ISO. The P stage (1.5% H_2O_2) gave an additional 7.5-point increase, up to 80.1% ISO. Brightness of 75% ISO was obtained at approximately 1% ozone consumption.

From the standpoint of brightness development, it appears that a ZP

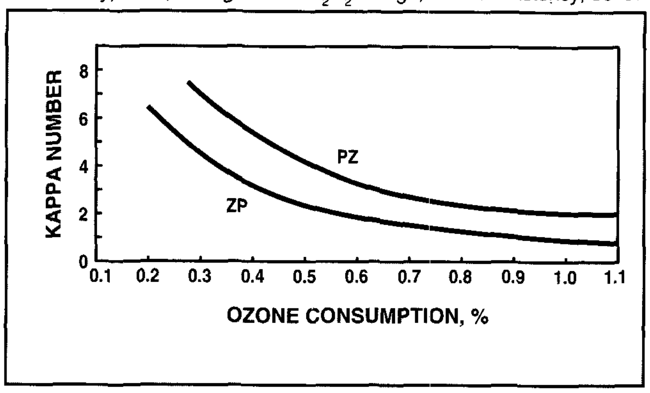
1. Brightness as a function of O_3 consumption for recycled deinked pulp after ZP bleach sequence. Z stage: no preacidification; P stage: 1.5% H_2O_2 charge.



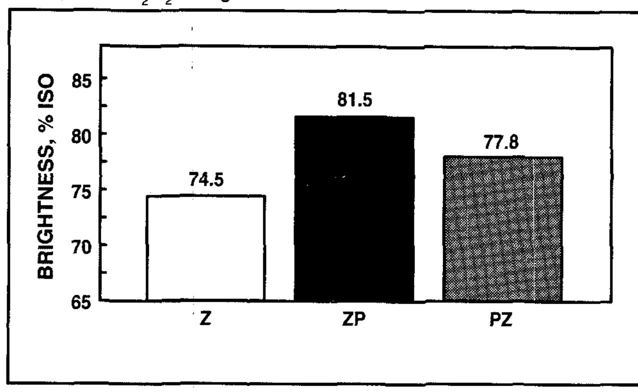
2. Brightness as a function of O_3 consumption for recycled deinked pulp after Z-stage bleaching. Preacidification to pH 2.5 using either oxalic acid or sulfuric acid.



3. Kappa number as a function of O_3 consumption for softwood kraft pulp after ZP or PZ bleach sequences. Z stage: preacidification to pH 2.5, 3.5% consistency, 25°C; P stage: 1.5% H_2O_2 charge, 10% consistency, 80°C.



4. Brightness of wood-free recycled deinked furnish after Z, ZP, or PZ bleach sequences. Initial brightness, 65% ISO; O_3 consumption, 0.7%; 1.5% H_2O_2 charge.



bleach sequence represents a potential alternative to chlorine-based bleaching. Thus it is imperative to define the conditions under which ozone treatment is most efficient.

Guidelines for efficient use of O_3

This discussion does not pretend to be a detailed exploration of the boundaries for ozone bleaching of virgin pulp. Rather, the discussion simply highlights some general conclusions based on our experience.

Ozone stability. Despite its good solubility in water, ozone has a tendency to decompose easily, giving birth to a variety of intermediates like peroxides and hydroxyl radicals. This effect is accelerated in the presence of trace amounts of transition-metal ions *(5)*. Generally, acidic conditions prevent rapid decomposition of ozone in aqueous media, and a pH of 2–2.5 is highly recommended at the beginning of an ozone treatment applied on kraft or sulfite pulp *(6)*.

The same trend is apparent when bleaching recycled pulp. As seen in **Table I**, acidification prior to the Z stage produced a 1.9-point brightness advantage compared with no acidification. A standard P stage was added at the end of the ozone treatment at peroxide charges of 1% and 1.5%. Again, better brightnesses were obtained when the ozone process was carried out in acidic conditions: 75.7% ISO compared with 74.7% ISO, and 76.6% ISO compared with 75.2% ISO, respectively.

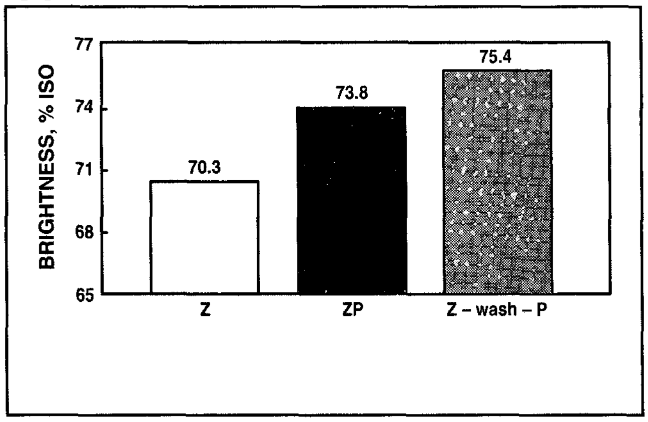
Type of acid used. Preacidification was carried out using two different acids, oxalic acid, and sulfuric acid. **Figure 2** compares the efficiencies of the

I. Brightness after Z-stage bleaching and after a ZP bleach sequence with and without acidification before the Z stage[a]

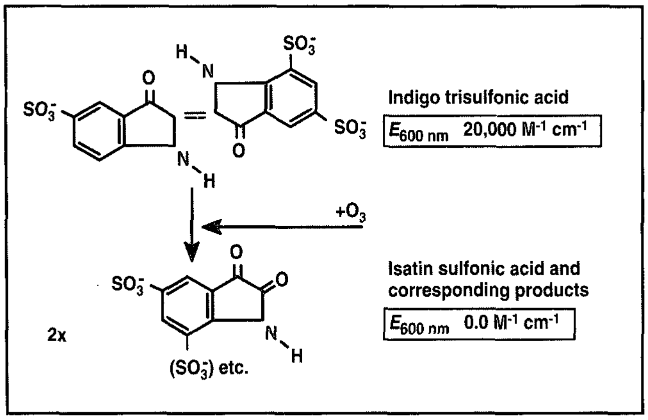
Bleach sequence	*H_2O_2 charge, %*	*Brightness, % ISO[b]* No preacidification	*Brightness, % ISO[b]* Preacidification
Z[c]		69.5	71.4
ZP	1.0	74.7	75.7
ZP	1.5	75.2	76.6

[a]Bleaching conditions are described under the heading "Experimental procedures."
[b]Reference brightness = 65.5% ISO
[c]Ozone consumption = 0.3%

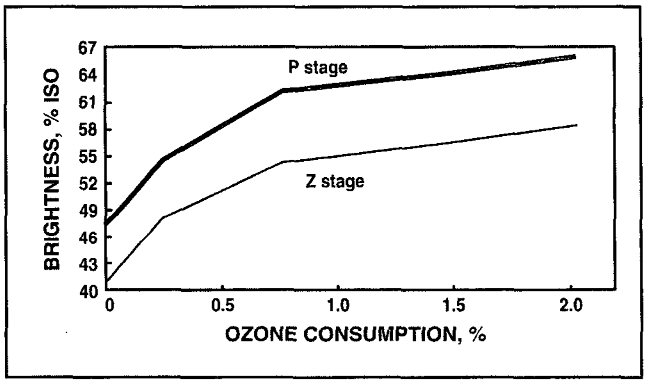
5. Brightness of deinked pulp after Z, ZP, or Z–wash–P bleach sequences. Initial brightness, 65% ISO; O_3 consumption, 0.3%; 1.5% H_2O_2 charge.



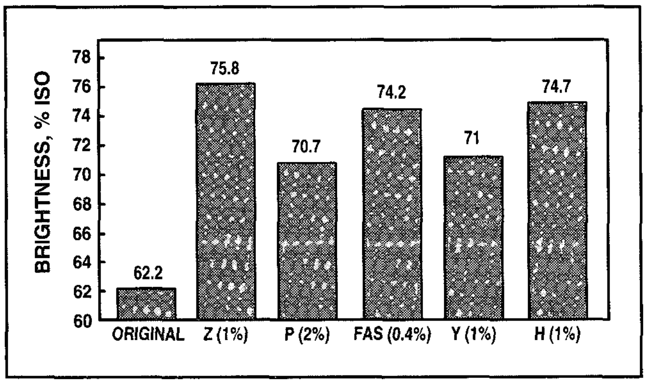
6. Ozone–indigo blue dye reaction



7. Brightness as a function of O_3 consumption for low-grade recycled pulp after ZP bleach sequence. P stage: 2.0% H_2O_2 charge.



8. Brightness of recycled furnish (91.5% office papers, 8.5% colored ledger) after Z, P, FAS, Y, or H bleaching stages



II. Treatment conditions for five bleach stages

	Z	*P*	*FAS**	*Y*	*H*
Charge, %	1.0	2.0	0.4	1.0	1.0
Additives, %					
NaOH	...	0.3	0.2	...	0.3
DTPA*	...	0.2	...	...	...
Na_2SiO_3	...	2.0	...	...	...
Consistency, %	35	15	5	4	12
Temperature, °C	23	70	65	55	40
Initial pH	2.5	10.5	7.0	6.5	11.0

*FAS = formamidine sulfinic acid; DTPA = diethylenetriamine pentaacetic acid

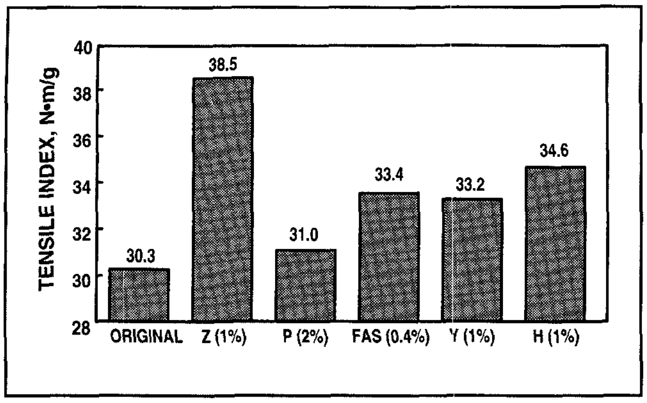
two acids at equivalent ozone consumption. Oxalic acid has been shown to be effective in ozone bleaching of kraft pulp *(7)*, and the results in Fig. 2 show that this is also true for ozone bleaching of deinked recycled fibers. For ozone consumptions between 0.3% and 0.9% on pulp, the pulp acidified with oxalic acid was more than 1 point brighter than the pulp acidified with sulfuric acid. The pH of the acidified pulps was 2.5 in both cases. The greater efficiency of oxalic acid can be attributed to the more extensive elimination of metal ions in the filtrate when the pulp is dewatered for ozone treatment at 30% consistency.

ZP or PZ bleach sequence?

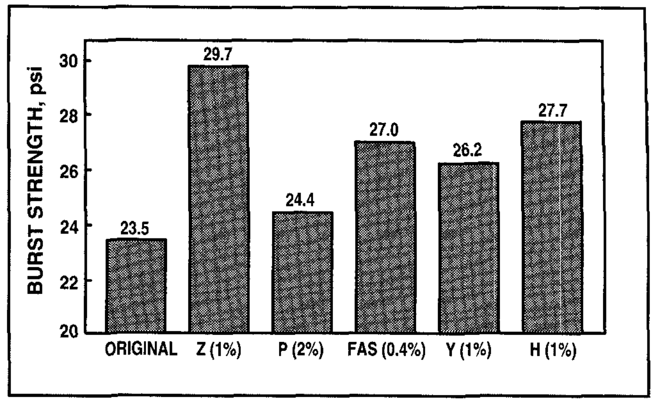
Lachenal *(8)* studied the efficiency of ZP and PZ sequences for a kraft pulp. The ZP sequence provided superior delignification, as seen in **Fig. 3**. Lower kappa number and higher brightness were obtained when ozone was applied first.

Parallel behavior can be established in the case of wood-free secondary fibers, as seen in **Fig. 4**, which shows that the ZP sequence provided a pulp of 81.5% ISO, far brighter than the 78% ISO for the pulp treated in a PZ sequence.

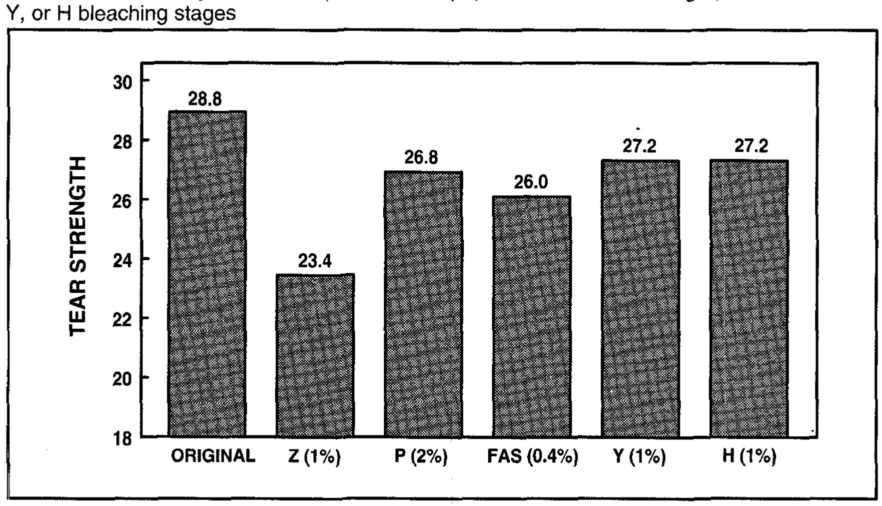
9. Tensile index of recycled furnish (91.5% office papers, 8.5% colored ledger) after Z, P, FAS, Y, or H bleaching stages



10. Burst index of recycled furnish (91.5% office papers, 8.5% colored ledger) after Z, P, FAS, Y, or H bleaching stages



11. Tear index of recycled furnish (91.5% office papers, 8.5% colored ledger) after Z, P, FAS, Y, or H bleaching stages



Washing after Z stage?

From an industrial-process standpoint, it would be desirable to avoid washing the pulp after the ozone stage. **Figure 5** shows the brightnesses obtained with and without a wash stage, with other conditions held constant. The effluent from this wash stage displays low values of COD, BOD, and color, as previously described by Van Lierop *(9)*. Nevertheless, the wash stage has a significant impact on the following peroxide stage. After washing, the P stage increased brightness by 5.1 points. In the absence of a wash stage, brightness after the P stage increased by only 3.5 points. Although installation of an intermediate wash stage between the Z and P stages would require a higher investment, it also would provide a substantial reduction in chemical costs.

Ozone as an alternative to chlorine-based chemicals

Ozone is a plausible alternative to chlorine-based bleaching chemicals. Moreover, ozone seems to fit very well in a ZP sequence, since preacidification and the subsequent washing stage provide good control of metal-ion content and prepares the pulp for a peroxide bleaching process. In addition, ozone is also well known to react on dyes, as shown in **Fig. 6**. Its high selectivity toward indigo blue makes this reaction a useful and precise titration method of ozone in liquid phase *(10)*.

Thus, a ZP process should provide some good color stripping, as already suggested by several authors, while providing a good bleaching effect on highly contaminated furnishes. **Figure 7** shows the brightness evolution of a low-grade recycled paper with an initial brightness of 41% ISO. A dramatic 17-point increase was obtained at 2% ozone consumption. In a subsequent stage, 2% hydrogen peroxide gave an additional 7 points, up to 65.5% ISO, making this ZP sequence extremely powerful.

Ozone vs. other bleaching or color-stripping agents

A comparative study between ozone and several other chemicals known as bleaching or color-stripping agents was carried out. These chemicals were hydrogen peroxide, formamidine sulfinic acid (FAS), sodium hydrosulfite (Y stage), and sodium hypochlorite (H stage). Results were obtained by measuring the optical and mechanical properties of the bleached pulps.

The pulp used was a recycled deinked pulp that was a mixture of 91.5% mixed office waste and 8.5% colored ledger. The total mechanical pulp content of this mixture was 5%. This mixture, having an initial brightness of 62.2% ISO, simulates pulp used by mills producing tissue products from recycled fibers. **Table II** lists the conditions for treatment with the various bleaching agents. Chemical dosages were typical of those that would be used in a single bleaching stage.

Optical properties

Brightness evolutions are given in **Fig. 8**. The ozone treatment produced the best result, a 13.6-point brightness increase to 75.8% ISO. Formamidine sulfinic acid (FAS) and hypochlorite were next, with 74.2% ISO and 74.7% ISO, respectively. Despite the relatively high charge, hydrogen peroxide and hydrosulfite were less efficient, with 70.7% ISO and 71% ISO.

Strength properties

There are legitimate concerns about the impact of ozone on pulp strength. Oxidative degradation of cellulose can severely reduce the viscosity of kraft pulps.

All five treatments produced higher tensile index. Surprisingly, the highest tensile index was obtained on the pulp treated with ozone, as seen in **Fig. 9**. Similar results are apparent in **Fig. 10**, which shows that the ozone-treated pulp had the highest burst index. In both cases, strength increased by 30% following ozone treatment. All treatments reduced tear index, as seen in **Fig. 11**. Ozone produced the lowest results. However, all obtained values were still acceptable for tissue production.

These results indicate that ozone is a very powerful bleaching agent that can compete with the conventional chemicals that are currently used to bleach deinked pulp for tissue manufacturing. Substantial brightness gain is achieved after an ozone stage, while pulp strength is not adversely affected. Indeed, the improved tensile and burst values are important figures for the quality of the final product and for the runnability of the paper machine.

Conclusion

Major mills in Scandinavia and Canada will soon begin phasing out their use of molecular chlorine by bleaching with ozone. It appears that ozone will become an essential chemical in future chlorine-free bleaching sequences. Results presented in this report suggest that ozone can be used with hydrogen peroxide in a combined ZP sequence to treat recycled paper, particularly wood-free paper.

The recent development of better process equipment is helping to make ozone a routine bleaching agent in treatment of virgin pulps. This, in turn, has made ozone a strong candidate for use in bleaching recycled deinked pulp.

Experimental procedures

Fiber

Experiments were carried out on different wood-free recycled papers with an initial brightness varying slightly around 65% ISO.

Ozone stage

Before ozone bleaching, the furnish was diluted to 3% consistency and the slurry was acidified to pH 2.5 with the appropriate acid. After dewatering, pulp was then centrifuged to reach 30–40% consistency and fluffed before ozone reaction.

An LN 103 Ozonia generator (7 g/h capacity) supplied ozone at a concentration of 3.5% in O_2. This gas was directed to flow through the fluffed pulp (at ambient temperature) in a rotating glass reactor. Exposure times were set according to O_3 charges. O_3 consumptions were determined by measuring the remaining ozone in the outlet gases.

Peroxide stage

A standard peroxide stage was applied using the following conditions: consistency, 15%; temperature, 66°C; time, 150 min; NaOH, 0.3%; H_2O_2, 1%–1.5%; DTPA, 0.2%; Na_2SiO_3, 2%.

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