Oxidative and Reductive Bleaching of Secondary Fibers

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Historically pulp bleaching was studied for its application to virgin pulps and mill generated broke. The current demand for increased recycled fibre content has expanded bleaching research in order to optimise applications to secondary fibre. This has been further complicated by the environmental restrictions placed on mills, limiting their dependence on the typical chorine based bleaching agents. Industry experts have risen to the challenge by continuing to provide bleaching solutions to meet their customer's needs. The paper tries to provide an alternative bleaching process of secondary fibre.

INTRODUCTION

Now a days the source of secondary fibre as a surplus is becoming limited due to their wide usage by various countries to save forests and to keep ecological balance.

Apart from availability of secondary fibre in the form of waste paper of different grades are also highly polluted by unacceptable contaminants and eventually the plant gets disturbed by using such contaminated waste paper and such type of waste paper likely to come to developing countries to full fill the gap between demand & supply.

In this case the solution is to develop chemical and equipment technology to sustainable usage of contaminated waste paper and the most important factor is bleaching and colour stripping of recycled fibres to obtain suitable brightness for graded papers for marketing especially from Dinked pulp.

Oxidation

Oxidation attempts to modify the lignin either making it soluble for removal in washing stage or in case of peroxide by changing its color to white.

Reduction

Reduction modifies the chemical structure of dyes present in the pulp causing them to appear colorless. Because this colour change or removal process is often carried out as a separate stage and the term "Colour stripping" is used.

Bleaching Agents

Hydrogen peroxide: It is colorless liquid typically transported as an aqueous solution of 50% or 70% concentrations. As it decomposes rapidly when it comes in contact with contaminants, it must be stored in dedicated containers made of Aluminum, Stainless steel or plastic carboys. While peroxide solutions are not flammable, they can ignite flammable materials. Certain contaminants such as heavy metals, their salts or caustic soda cause rapid exothermic decomposition resulting the formation of oxygen gas and water. It is because of these relatively harmless products of decomposition that the use of hydrogen peroxide has gained much favour in recent years in paper industry.

Chemical Reaction

In an aqueous solution, hydrogen peroxide dissociates as

$$H_2O_2 + H_2O = H_3O + O_2H$$

The perhydroxyl ion, O_2H is thought to provide the bleaching action of Peroxide. The concentration of perhydroxyl ion concentration depends on alkalinity of the solution, so peroxide bleaching is carried out under alkaline conditions. Peroxide decomposes when in the presence of the metals and must be stabilised before being added to pulp and Sodium Silicate is most commonly used as stabiliser.

Advantages

Hydrogen Peroxide has been used in alkaline condition of both in pulper and in bleached tower to provide brightness gain to secondary fibre furnishes. Fig. 1 and 2 show the brightness gain with hydrogen peroxide in Tower bleaching and after Floatation repectively.

Limitations

Hydrogen Peroxide is only marginally effective in colour stripping dyes from the furnish and in often used in conjunction with reductive bleaching stage using Hydrosulphite or FAS.

Effective peroxide bleaching of Secondary fibre requires proper equipment. High consistency, good mixing and proper stock preparation are essential for succ ssful bleaching performance.

Oxygen

Chemical reaction - Oxygen as a strong, naturally occurring oxidizing agent, has been found to be useful for bleaching of secondary fibre. Molecular oxygen has a strong tendency to react with organic substances in pulp to form intermediates like peroxides and other radicals. These intermediates however are very non-specific and can degrade the cellulosic fibre if not properly controlled.

Oxygen bleaching can be considered as consisting of two simultaneous general reactions, a desirable delignification reaction and an undesirable and closely related carbohydrate degradation reaction.

Advantages

Pulp brightness is increased as result of the lignin oxidation that takes place during oxygen bleaching. Cleaner pulp is most significant benefit of oxygen bleaching of secondary fibre. The delignification of the brown fibres in the pulp is the primary reason for brightness improvement. Brightness gains of 9-13 points are reported for various grades of secondary fibres. Oxygen has been proved to be very good color striper of both ledger and wood containing furnishes. The use of oxygen bleaching also improves the responsiveness of pulp to Hypochlorite bleaching and it also helps prevent color reversion.

Limitations

Because of delignification takes places during oxygen bleaching usage limited to low ground wood content furnishes. The effect of oxygen on strength properties of chemical pulp remains a concern. Severe degradation of fibre occurs if intimidate bleaching reactions are not properly controlled.

Ozone

Chemical reaction - Ozone is a powerful oxidizer that is typically produced on site by electrical discharge through oxygen. It is a powerful bleaching chemical and is one of the best in destroying the chromophoric compounds usually present in the pulp.

Advantage

Brightness gains of 6-10 points have noticed with wood free deinked pulp with a single ozone

Table -1 Peroxide bleaching:- Typical application rates and bleaching conditions

Consistency	pH	Temp.	Time	Application	References
15%	-	50-70°C	30-90 min	1-2.5% H_2O_2	1
15%	10.5	70°C	30-90 min	2% H_2O_2 0.3% NaOH 0.2% DTPA 2% Silicate	9
10-25%	9.5-11.5	50-75°C	20-180 min	0.5-3% H_2O_2 0.3-2. 3% NaOH 3% Silicate	10

Table -2 Oxygen bleaching :- Typical application rates and bleaching condtions

Consistency	pH	Temp.	Time	Application	References
12-15%	9-12	100-115^{0}C	30 min	1-3 O_2 3-5% NaOH	12

Table -3 Ozone bleaching :- Typical application rates and bleaching condtions

Consistency	pH	Temp.	Time	Application	References
30-35%	2.5	26^{0}C	30 min	1% O_3	9
40-45%	2.4	30-55^{0}C	1-5 min	0.2-1% O_3	11

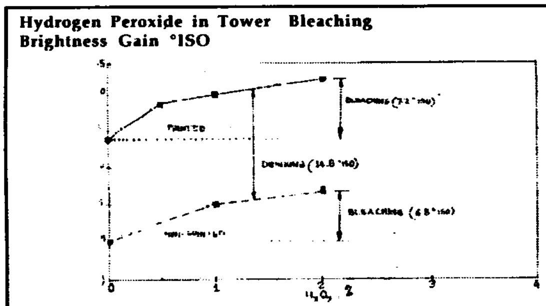

Fig. 1 Bleaching and Deinking in the Pulper with printed (Initial Brightness43.2° ISO) and Non-Printed (Initial Brightness = 64.6° ISO)

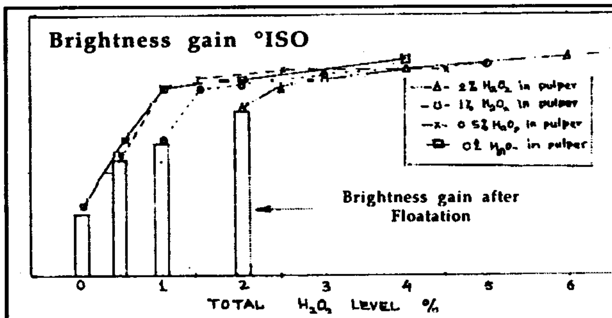

Fig. 2 Effect of Pulping of H_2O_2 Gain Intial Brightness 44.1° ISO

bleaching stage, with peroxide brightness gains of nearly 14-15 points. Ozone bleaching is most effective when pulp is acidified to pH-4 prior to the addition of ozone gas. Reaction time is only 2-5 minutes. Ozone bleaching technology is receiving great deal of interest because of its strong oxidation potential.

Limitation

Ozone bleaching is a delignifying process, which limits its use with mechanical fibre. There is generally no brightness gain when it is applied to mechanical pulp. It is not yet very much commercialized because of its limitation of usage and the high cost.

Reductive bleaching

Sodium Hydrosulphite (Dithionite) generally sodium hydrosulphite is shipped as a solid powder in metal container of 50 kgs. Hydrosulphite as a solid powder in metal container of 50 kgs. Hydrosulphite decomposes rapidly when exposed to air. When dissolved in water, it liberates sulfur gases that tend to be corrosive to equipment and building. Some times the aqueous solution is typically stored in closed tanks with a nitrogen pad. When mixed with pulp slurry sodium hydrosulphite under goes three competing reactions.

$Na_2S_2O_4$ + H_2O + Pulp - bleached pulp + $NaHSO_3$ = H_2O

The sodium bisulphate produced protects pulp-

Table -4 Sodium hydrosulphite, typical application rates and bleaching conditions.

Consistency	pH	Temp.	Time	Application	References
3-5%	5-9	40-70^{0}C	20-70 min	0.25-1.25% (Hydro)	1
3-5%	7-10	60-70^{0}C	45-60 min	0.25-1.25% (Hydro)	15
4%	6-5	55^{0}C	45-60 min	1% (Hydro)	9

Table -5 Formamidine sulfinic acid (FAS), Typical application rates and bleaching conditions.

Consistency	pH	Temp.	Time	Application	References
15%	8-11	60°C	60 min	0.3-1% FAS 0.05-0.5% NaOH	1
15-30%	7-8	70°C	15-90 min	0.2-0.8% FAS 0.1-0.4% NaOH	15

preventing reversion. At the same time two competing reactions take place which require proper measures to control

$Na_2X_2O_4 + H_2O + O_2 = HaHSO_3 + NaHSO_4$

This oxidation reaction consumes Hydrosulphite with no bleaching effect.

$Na_2S_2O_4 + H_2O = Na_2S_2O_3 + NaHSO_3$

This decomposition reaction forms sodium thiosulfate, which can cause pitting corrosion.

Hydrosulphite reacts rapidly with pulp, so rapid and through mixing is essential. Iron, Aluminum and copper ions are particularly detrimental to brightness response.

Advantages

Sodium hydrosulphite is an excellent bleaching agent for colour striping many dyes. As reductive bleaching process, there is no loss of yield in bleaching stage. It offers 19-12 points brightness gain in a tower application. The pH is closer to neutral, making it compatible with other bleaching agents.

Limitations

Secondary fibre containing ground wood pulp is subject to alkali darkening if sodium hydrosulphite bleaching occurs at high alkalinity. Also because of the tendency of hydrosulphite to decompose with exposer to the to the entrained air.

Formamidine sulfinic acid (FAS)

Chemical reaction

FAS generally called thiorurea is an odorless, crystalline powder packed in fibre drums or super sacks. In solution, the FAS solution, the FAS bleach liquor is very unstable so it is typically prepared on a continuous basis and fed directly to the process. In alkali conditions, the sodium sulfinate is oxidized during bleaching process to urea and sodium bisulphate.

$NH_2C(NH)SOOH + NaOH == (NH_2)_2CO + NaHSO_3$

The bisulfate is further oxidised to bsulfate

$NaHSO_3 = NaHSO_4$

The required alkali is normally provided by caustic soda in a 2:1 ratio (FAS:NaOH) in the bleach liquor.

Advantages

FAS is an effective reductive bleaching agent, finding many applications in the secondary fibre mills. It is especially effective as an alternative to hypochlorite for colour stripping coloured broke in the pulper where the objective is to eliminate hypochlorite. FAS is most effective at medium consistency and at high temperature.

Limitations

FAS requires a solid metering system to properly make down bleach liquor. FAS is only slightly soluble in water, so proper agitation of the bleach is critical for the most efficient bleaching response. The high cost and low application rate of the raw material restircts the use of FAS.

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