Improvement of Paper Properties

Part I: Application of different techniques using gelatin-hexamine mixture to bagasse pulp.

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Sizing of paper is a treatment primarily designed to reduce the rate of penetration of liquids. Sizing treatments are applied either by internal precipitation on the fibers in the beater (in-pulp) or by surface treatment on the web of the paper by two different techniques namely: dipping and spraying. This study shows the effect of treatment of unbleached and bleached bagasse pulp with gelatin-hexamine mixture according to mentioned methods to compare the changes that occurred in water resistance and permeability.

INTRODUCTION

Since high water resistance is desirable in some types of paper with a reasonable strength properties, so a gelatin-hexamine mixture was used, which resulted in a decrease of permeability.

The presence of the gelatin molecules, which are like those of other proteins, composed of about 18 different amino acid radicals linked together with several kinds of possible structures [1]. Among the proposed theories are those based on the peptide linkage, the diketopiperazine structure, the protamine nucleus, and the cyclol structure .Also, two other possible linkages through a nitrogen atom have been suggested:

a) CH_2 - NH - CH_2 -, a stable linkage found in proline and hydroxy- proline, and b) - CH_2 - NH - C = NH, found only in arginine. However, the behavior of gelatin indicates a fundamental arrangement in which the amino acid radicals are joined together by peptide linkages, - CO - NH -, in chains of varying lengths and molecular weights.

The presence of low concentration of the gelatin solution (0.5%) leads to a low viscosity of the coating solution which can penetrate more easily through the pores of the paper sheet and precipitates as an insoluble film on the fibre. Due to cross linking formed through formaldehyde, which is liberated as a result of hexamine degradation, rendering the soluble gelatin to an insoluble form [2].

The rate of penetration is affected by several factors among them the type of fiber used, where paper is a layered material, consisting of a network of cellulose fibers bonded together. Each of fiber-fiber contact is held together by intermolecular forces, Van der Waals; hydrogen bonding, which are very sensitive to water. The extent of bonding decreases slowly as the water content of the paper increases[3].

The degradation of hexamine can be noticed from the fact that the hexamine is formed from the evaporation on the steam bath of a solution of formaline (37% formaldehyde) and ammonium hydroxide. This reaction is partially reversible [4] i.e. the presence of hexamine with water (hexamine' solution) and at presence of heat during the drying process of the sheet, thus the formaldehyde can be liberated.

In certain industrial applications, the viscosity of the water solution of gelatin is as important as the ability of the solution to form a gel. So a more important characteristic property of gelatin is its ability to form a gel or jelly in aqueous solution at temperatures below 35°C. At higher temperatures, the system exists as a solution. The gelatin <=> solution system is heat reversible. The melting temperature being slightly higher than the setting point.

Proposed mechanisms for cross - linking

The presence of hexamine (C_6H_{12} N_4) is to improve the water resistance of the papers. This effect can be attributed either to one or both of the following reasons:

1) The degradation of the hexamine in presence of water during the drying process of the sheet formation and the liberation of formaldehyde, which is a cross-linking agent. In this case, the liberated formaldehyde reacts with gelatin (- CO - NH -) with an equilibrium reaction:

$$-CO-NH + CH_2O \quad \Leftrightarrow \quad -CO-N-CH_2OH \quad (5)$$

If more concentration of gelatin is present, the reaction continues on to form methylenebisamides.

$$-CO-N-CH_2-OH + -CO-NH \rightarrow -CO-N-CH_2-N-CO- + H_2O$$

Since a low concentration of gelatin ,0.5%, is present, the reaction will stop at the first step. Then it will continue as a cross- linking agent with the cellulose according to the following mechanism:

$$CO-N-CH_2OH + R\,cell.OH \Leftrightarrow -CO-N-CH_2-O-R\,cell. + H_2O$$

2) The second mechanism can be elucidated from the presence of lone pair of electrons on the nitrogen atoms of hexamine which can form bonding with the cellulose and hence it reacts as a cross-linking agent with the cellulose molecules.

Experimental

In this study, three different pulps were used, namely, unbleached, bleached bagasse pulps with 3% potassium permanganate and ,bagasse pulp bleached with 4% hydrogen peroxide.

A preliminary experiment was carried out to determine the suitable concentration of gelatin-hexamine mixture to be used as a water repellent mixture. It was found that a suitable mixture in the present study was 0.5% gelatin with 0.2 -1.0% hexamine (based on pulp weight). The following procedure is carried out: 0.5g accurately weighed gelatin, cut into small pieces was left to swell in 20 cm^3 of water for 30 minutes. The gelatin was allowed to dissolve on a water bath at 100°C, then completed to 100 cm^3 with water and left to cool. Hexamine was dissolved in the previous solution in five different concentrations, namely 0.2, 0.4, 0.6, 0.8 and 1.0% based on the dry weight of pulp. The mixture was then applied to the pulp or to the paper sheets through three different techniques:

1. In pulp

where the previously prepared gelatin-hexamine mixture was added on the unbleached and/or bleached pulps ,and left for 30 minutes in a water bath at 60°C. Then the content was stirred with water to prepare it for sheet formation.

2. Spraying

where the previously prepared hand - sheets were coated with the mentioned mixture using an atomizer, left to dry in the air and before complete drying, a hydraulic pressure was used without heating to prevent paper wrinkle. The samples were placed in a rotating drum at 60°C for 30 minutes.

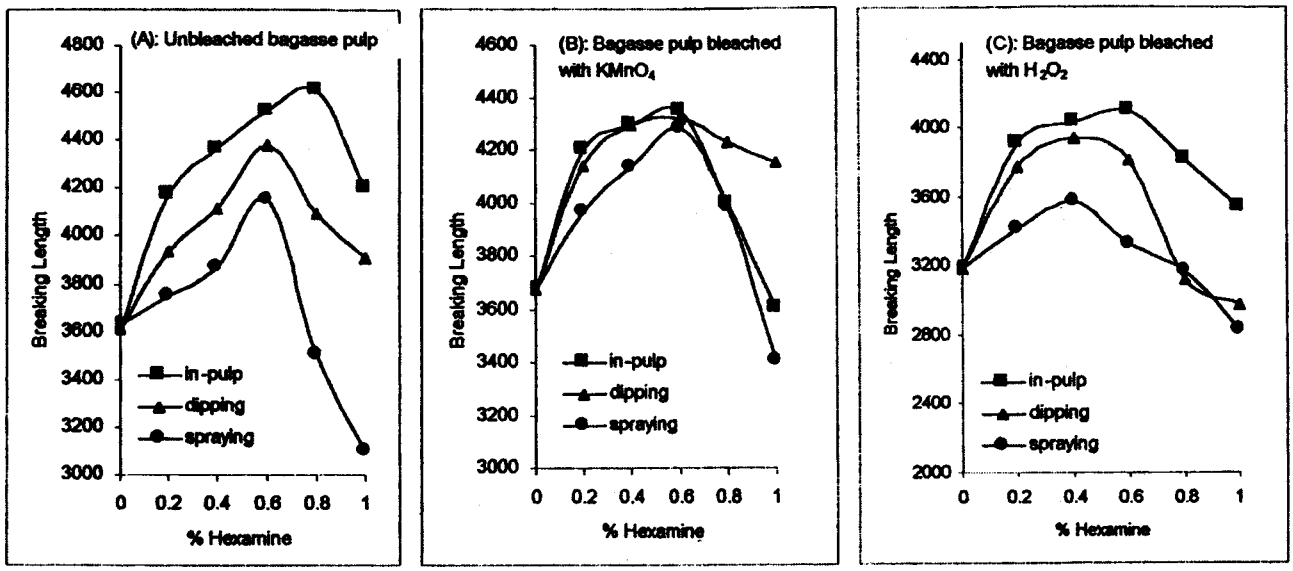

Fig.1: Effect of treatment with gelatin-hexamine on breaking length of unbleached and bleached bagasse pulps

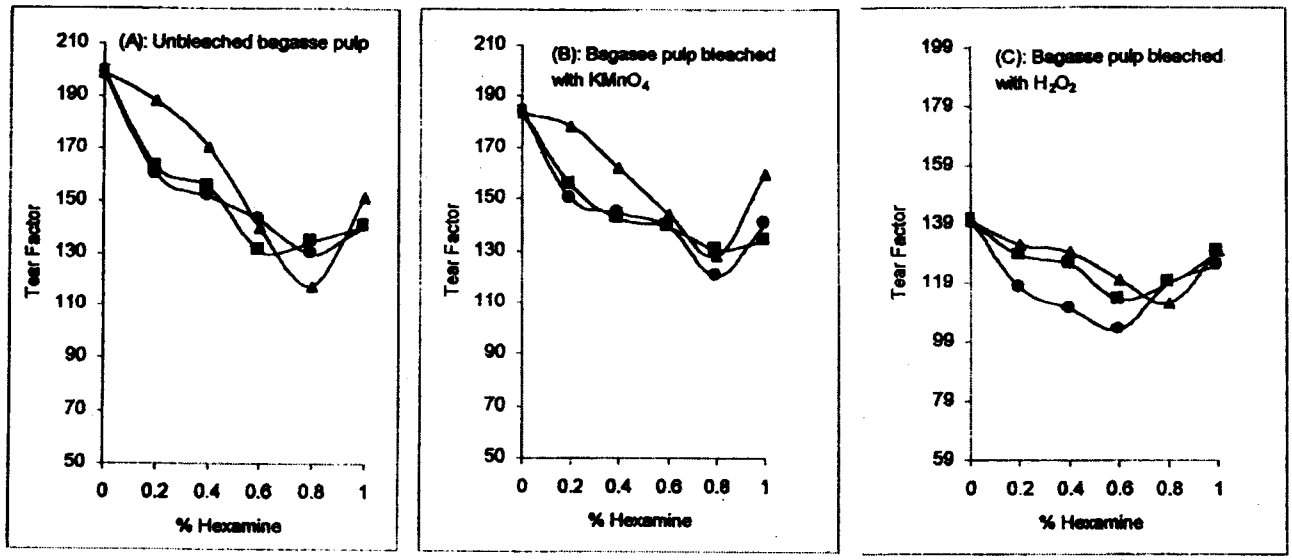

Fig.2: Effect of treatment with gelatin-hexamine on breaking length of unbleached and bleached bagasse pulps

3. Dipping

where the previously prepared hand - sheets were dipped in the mentioned mixture for 1 minute each sheet. The sheets were left to dry in the air and then treated in the same manner mentioned in step 2.

Permeability tests

In this work, permeability of all samples treated with gelatin - hexamine mixture was tested on "Toyoseiki Permeability Tester, Japan" at a pressure of 12.7 mm water. Also, the mechanical properties of .the resulting paper sheets were tested according to standard method [6].

RESULTS

Effect of treatment with gelatin-hexamine mixture on breaking length

The effect of treatment with gelatin-hexamine mixture on breaking length of unbleached and bleached bagasse

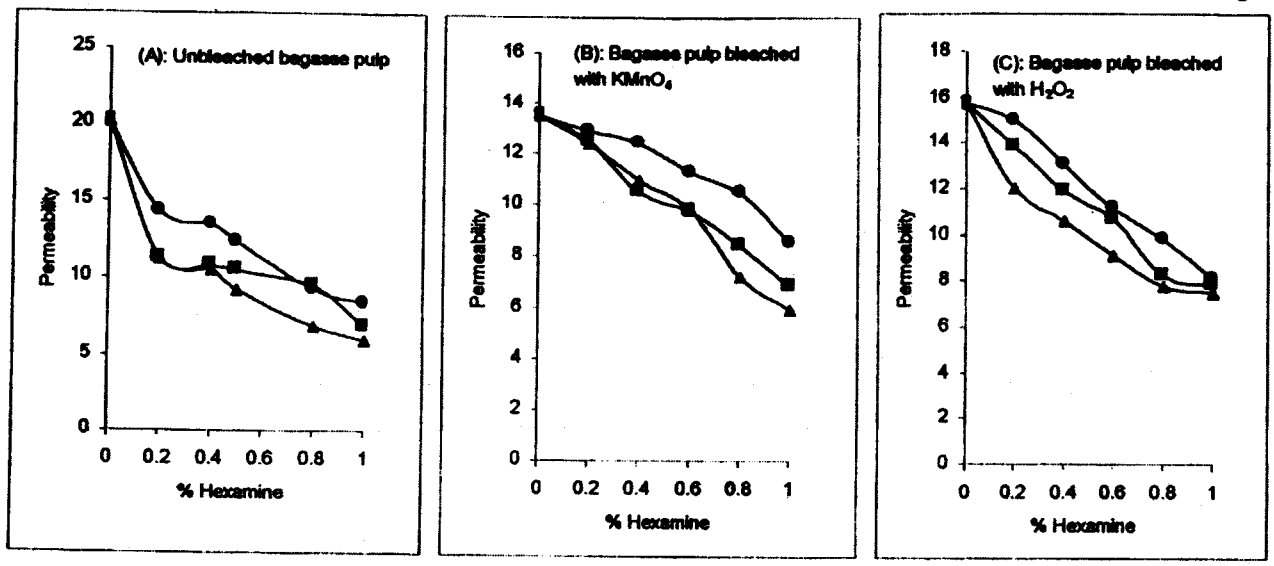

Fig.3: Effect of treatment with gelatin-hexamine on permeability of unbleached and bleached bagasse pulps

hydrogen peroxide is presented in figure1: A,B&C respectively. It is clear that, for all pulps, the addition of gelatin-hexamine using the three different techniques leads to an increase in the breaking length at low hexamine concentrations (0.2-0.6%), but as the hexamine concentration increases (0.6-1.0%), the breaking length starts to decrease. This may be explained on the basis that at low hexamine concentrations, hexamine works as strengthening agent. As the hexamine concentration increases, brittleness of the fibres occurs leading to decreased breaking length.

For unbleached bagasse pulp, fig.l:A, it can be noticed that, by increasing the hexamine concentration, there is a gradual increase in the breaking length in case of unbleached bagasse pulp treated by the in pulp technique, reached a maximum value of 27% at 0.6% hexamine concentration. Samples treated with the dipping method show lower increase in the breaking length, 20.8% , at the same hexamine concentration. The samples sprayed with gelatin-hexamine mixture show the lowest increase (15%). In all samples, as the hexamine concentration increases (above 0.6%), a drop in breaking length occurs reaching minimum values.

The bleaching of bagasse pulp either with potassium permanganate or with hydrogen peroxide affected to different extents the breaking length, since the effect of bleaching agents on the fibers differs from one method to another. It should be noted that the samples bleached with potassium permanganate and treated with different concentrations of hexamine in different ways show slightly higher breaking length than those bleached with hydrogen peroxide (fig.l:B&C).

From fig.l:A,B&C, it is clear that the breaking length of unbleached and bleached bagasse pulps treated with gelatin-hexamine by the in pulp technique shows the highest increase in the breaking length, followed by samples treated by dipping, while the lowest values of breaking length are those of the sprayed samples. These results can be explained on the basis that the cellulose fibers are totally impregnated in the gelatin-hexamine solution when the in pulp technique was used leading to a great number of cross-links between the fibers. In case of dipping, where the surface of the fibres is only exposed to the mixture the cross links on the surface are limited (partial impregnation). The sprayed samples show the lowest breaking length as the external fibre surface is only exposed to the gelatin-hexamine mixture.

2. Effect of treatment with gelatin-hexamine mixture on tear factor

Fig.2:A,B&C shows the effect of treatment with different concentrations of gelatin-hexamine on the tear factor of unbleached and bleached bagasse pulps. It is noticed that the behavior of all the pulps is completely the contrary of breaking length. In other words the values of tear factor of all samples gradually decrease with the increase of hexamine concentration, as the tear factor depends mainly on the fibre length. The rate of decrease is the highest in case of unbleached bagasse pulp, than pulp bleached with potassium permanganate and finally that bleached with hydrogen peroxide.

Comparing the tear factor values using different techniques in case adding different hexamine concentrations, it can be concluded that the minimum deterioration occurs when the in pulp technique was used, then dipping and finally spraying techniques.

3. Effect of treatment with gelatin-hexamine mixture on permeability

The effect of treatment of unbleached and bleached bagasse pulps with different hexamine concentrations is presented in fig.3:A,B&C. In all samples, it is clear that the permeability of the pulps highly decreases, as the hexamine amount increases.

From the same figure, one can notice that the rate of decrease of permeability is nearly the same for all pulps, showing from 40-45% decrease of the original values.

CONCLUSION

1. In-pulp technique produced paper sheets with the highiest breaking strength than the other two techniques, but unfortunately tear factor deteriorated.

2. The permeability of the pulps highly improved by increasing gelatin concentrations in all studied techniques, which rendered these sheets suitable for water resistance purposes.

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