Polymer Bulletin 4, 219–223 (1981)

Polymer Bulletin

Treatment of Wood Pulp with Nitrogen Dioxide Before Oxygen Bleaching

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Summary

Pretreatment of kraft pulp with nitrogen dioxide and oxygen before conventional oxygen bleaching with magnesium sulfate as protector leads to markedly decreased lignin contents after a given duration of the oxygen bleaching. An increased temperature during the pretreatment favours the delignification. The most striking effect of the pretreatment is that it leads to a suppressed rate of depolymerization of the cellulose during the oxygen bleaching.

Introduction

A two-stage method for bleaching of wood pulp in which the first stage is a pretreatment with nitrogen dioxide followed by washing and oxygen bleaching has been reported in recent patent applications. We here report on the delignification and depolymerization of the carbohydrates during pretreatment with nitrogen dioxide plus oxygen at varying temperatures followed by washing and oxygen bleaching at high consistency with addition of magnesium sulfate to suppress the depolymerization of the carbohydrates.

Experimental

A commercial kraft pulp from pine, corresponding to 40 g of dry pulp was impregnated with water and centrifuged to a pulp consistency of 41%. The pulp was torn into pieces by hand and introduced into a glass flask with a volume of 2000 ml. After evacuation liquid dinitrogen tetroxide was evaporated in 3 portions into the flask. After 5 min oxygen was introduced in 4 portions with an interval of 1 min so that the nitrogen oxide formed as an intermediate was consumed almost completely and atmospheric pressure was attained (ABRAHAMSSON, LÖWENDAHL, SAMUELSON in press).

After 10 min the NO_2/O_2 treated pulps were washed with cold water. After impregnation with magnesium sulfate solution and then sodium hydroxide the pulp consistency was 3.8%. The impregnation liquor was filtered off and the pulp pressed to a consistency of 30%. The pulp contained 2% NaOH and 0.2% Mg calculated on the dry weight of the pulp.

0170-0839/81/0004/0219/$01.00

Kappa number which is a measure of the lignin content in the pulp and intrinsic viscosity in copper ethylenediamine solution were determined according to SCAN methods. The unbleached pulp had a kappa number of 30.4 which corresponds to 4.5% lignin and an intrinsic viscosity of 1190 dm^3/kg.

Results and discussion

Plots of the kappa number of the oxygen bleached pulp as a function of the duration of the oxygen bleaching under otherwise constant conditions showed that the NO_2/O_2 pretreatment led to decreased lignin contents in the final pulp (Fig. 1). One factor which contributes to the observed results is the dissolution of lignin before the oxygen bleaching. A small fraction was removed during the pretreatment while a larger proportion was dissolved during the impregnation of the pretreated pulp with sodium hydroxide and removed during the concentration of the pulp from 3.8 to 30% consistency before the oxygen bleaching. The higher pH during the oxygen bleaching of pretreated pulps, indicated in the figure, will contribute to an increased rate of delignification in this stage. This increase in pH can in part be explained by the removal of wood compounds before the oxygen stage. When no pretreatment is carried out, these compounds give rise to acids which consume alkali during the oxygen bleaching.

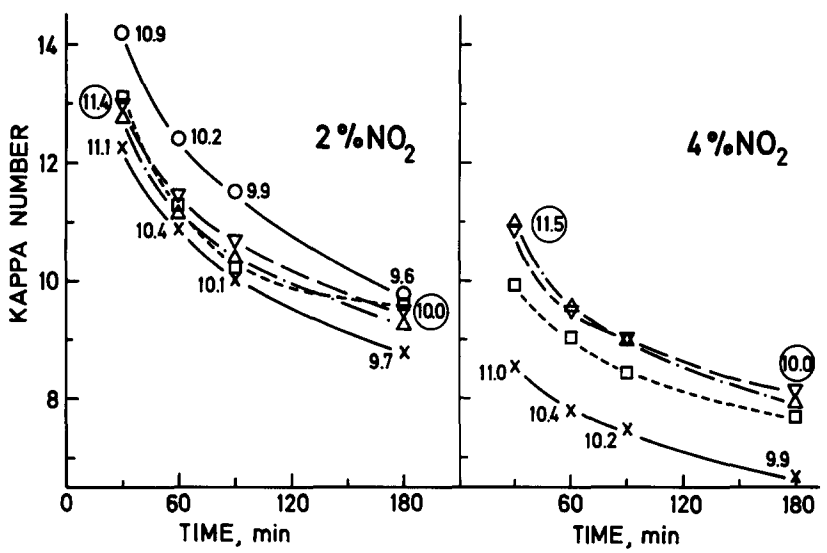

Fig. 1. Kappa number of oxygen bleached kraft pulps (initial kappa number 30.4) versus the duration of the oxygen bleaching
Blank without pretreatment O
Pretreatment at ▽ 25°C; △ 40°C; □ 55°C; X 68°C.
Values in the diagrams refer to the pH of spent liquors from the oxygen bleaching. The values within circles refer to pulps pretreated at 25°C. The other values refer to blanks and pulps pretreated at 68°C.

The pH in the spent liquors after the oxygen bleaching was affected only slightly when the addition of NO_2 was increased from 2 to 4% compared at the same temperature during the pretreatment. Hence, the differences in pH cannot explain the decrease in kappa number observed independent of the pretreatment temperature when the addition of NO_2 was doubled. A larger dissolution of lignin during impregnation with sodium hydroxide is one important factor but probably other factors, such as a more extensive modification of the lignin during pretreatment with the larger addition of NO_2, have an effect as well.

An increased temperature from 25°C to 55°C had no significant effect on the pH after the subsequent oxygen bleaching while a slight decrease was observed when the temperature was increased to 68°C. This was true both for the smaller and larger additions of NO_2. Independent of the NO_2 addition the change in temperature from 25 to 40°C had no detectable effect on the final kappa number. When 4% NO_2 was used pretreatment at 68°C led to a large decrease in the final kappa number while an increase from 25°C to 55°C led to a small but significant decrease in kappa number. In the experiments with 2% NO_2 the dependency on temperature was less. A decrease, confirmed in experiments with another pulp, was obtained when the temperature was raised to 68°C.

The pH of the spent pretreatment liquor was approximately 1.8 in these experiments compared to 1.5 in the experiments with 4% NO_2. An increased concentration of nitric acid is responsible for the difference.

The most striking effect of the NO_2/O_2 pretreatment was an enhanced viscosity compared at the same reaction time in the oxygen bleaching (Fig. 2). The results show that the pretreat-

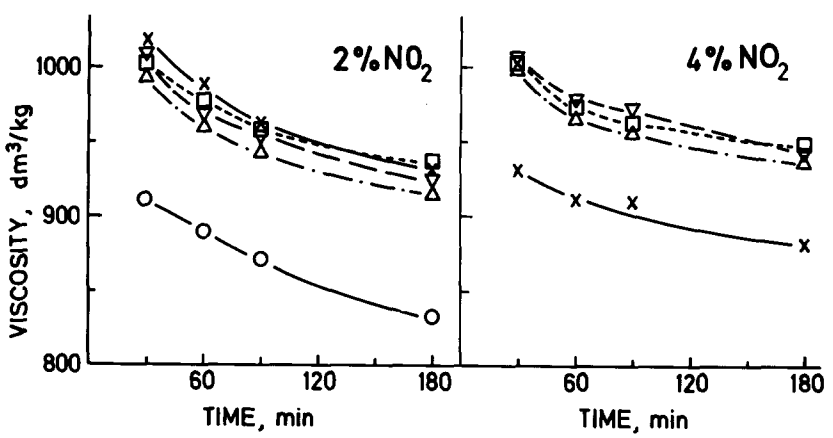

Fig. 2. Viscosity of oxygen bleached kraft pulps (initial viscosity 1190 dm^3/kg) versus duration of the oxygen bleaching
Blank without pretreatment O
Pretreatment at ▽ 25°C; △ 40°C; □ 55°C; X 68°C

ment leads to a suppressed rate of depolymerization of the cellulose during the oxygen bleaching. A very large effect was obtained already for pulps subjected to oxygen bleaching for 30 min. For the pulp pretreated with 2% NO_2 temperature variations during the pretreatment within the range 25°C - 68°C had a slight influence only. With the larger addition of NO_2 the change in temperature from 25°C to 55°C had no significant effect on the viscosity after any given duration of the oxygen bleaching. On prolonged oxygen bleaching the retarding effect of the pretreatment on the depolymerization of the carbohydrates was larger for the experiments with 4% NO_2 than in those with 2%. An increase in temperature to 68°C with the larger addition of NO_2 led to lower viscosities although the pH during the oxygen stage was lower. A significant depolymerization of the carbohydrates occurred during this pretreatment. This was confirmed in separate experiments in which pulp pretreated under identical conditions was dried rapidly in a stream of air after a careful washing and the viscosity determined immediately afterwards. The loss in intrinsic viscosity was 60 dm^3/kg for the pulp pretreated at 68°C while the loss observed at 55°C was insignificant.

Plots of viscosity versus kappa number (not reproduced here) show that a superior selectivity, defined as the viscosity of the final pulp at any given kappa number, was obtained when the pulp was pretreated with NO_2/O_2 at 25-55°C with 4% NO_2 compared to 2% NO_2. Table 1 shows that, at the final kappa number of 10, the viscosity was 840 dm^3/kg for the blank. Pretreatment at 68°C with 2% NO_2 gave an improvement of 120 dm^3/kg and a shortening of the duration of the oxygen bleaching from 165 to 90 min. The increase in selectivity by pretreatment with 4% NO_2 at the most favorable temperature (55°C) was 160 dm^3/kg. It is noteworthy that the gain in selectivity was much larger than that obtained by the presence of magnesium compounds which are generally used during commercial oxygen bleaching. The time required in the oxygen stage to obtain kappa number 10 decreased to 20% of that required in the blank.

TABLE 1

Influence of pretreatment with NO_2/O_2 on the intrinsic viscosity at kappa number 10 and the duration of the oxygen bleaching to kappa number 10 (interpolated values)

NO_2, % on pulp	Temp °C	Viscosity at kappa number 10 dm^3/kg	Duration of bleaching min
0	-	840	165
2	25	940	135
2	40	930	120
2	55	950	110
2	68	960	90
4	25	990	45
4	40	980	45
4	55	1000	30

Acknowledgements

The financial support from the Swedish Board for Technical Development and the 1959 Års Fond för Teknisk och Skoglig Forskning samt Utbildning is gratefully acknowledged.

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Received January 24, 1981
Accepted January 27, 1981