

Utility of Nitrogen Compounds as Inhibitors of Pulp Degradation in Hypochlorite Stage of Bleaching

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SUMMARY

The results of laboratory trials on the effect of added nitrogenous compounds like Urea, Ammonium Chloride, Ammonium Sulphamate and Sulphamic Acid in the Hypochlorite stage of CEH bleaching of bamboo-mixed tropical hardwood pulp, on the optical properties as well as the strength properties of final bleached pulp are presented. The results of plant trial on the addition of a wellknown industrial nitrogenous compound, viz. Melamine in the hypochlorite stage of bleaching of bamboo-mixed tropical hardwood pulp are also presented in this paper.

It has been well established in literature that use of nitrogen additives in chlorination as well as hypochlorite stages of bleaching will minimise the degradation of cellulose resulting in pulp of good strength¹⁻⁶. The nitrogenous compounds were basically amines or amine derivatives. The amine group present in these additives react with hypochlorous acid (HOCl) or hypochlorite Ion (OCl⁻) formed in bleaching stages, producing chloramines which have less oxidising power than either HOCl or OCl⁻ and result in reduced oxidative degradation of cellulose.

The literature survey by us has revealed that the most popular nitrogen compound which has been subjected to extensive investigation has been sulphamic acid²⁻⁵. Although the use of other nitrogenous compounds such as urea, ammonium chloride and melamine (a commonly available amine derivative) had been suggested by Aldrich¹, we found that very little is on record on the utility of these compounds as degradation inhibitors in the hypo-chlorite stage of bleaching. We feel that this is important, as in Indian Mills, the bleaching sequence involves the extensive use of hypochlorite and the necessity of preserving the strength properties by using degradation inhibitors is of paramount importance.

We report in this paper the results of our studies on the effect of addition of the following nitrogenous additives on the properties of bleached pulp.

- Urea
- Ammonium Chloride
- Ammonium Sulphamate
- Melamine

EXPERIMENTAL

Bamboo (*Dendrocalamus Strictus*) and tropical mixed hard wood (TMHW) (60 : 40) blended pulps were used in these investigations. For the ammonium chloride, ammonium sulphamate and urea studies, alkali extracted pulps were collected from Mills bleach plant and were treated with the required dosage of calcium hypochlorite as per the permanganate number of the alkali extracted pulps. Dilute solutions of these chemicals (1% wt/vol) were added to hypochlorite solution prior to its treatment with the pulp.

In case of urea, fertilizer grade urea was used in these experiments and the other two chemicals viz. ammonium chloride and ammonium sulphamate were

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of Analar grade. In the case of ammonium chloride and urea, the dosage of these chemicals in Hypochlorite stage varied from 0.1 to 0.75% on oven dry pulp basis, without the addition of regular buffering agent, (sodium hydroxide), keeping the other bleaching conditions same. But, in the case of ammonium sulphamate the dosage was 0.1% on O.D. pulp basis, in addition to regular buffer (sodium hydroxide).

The melamine was tried on plant scale with CEHH sequence, by adding the dilute solution (3 gpl) at the repulper of alkali extraction stage washer along with hypochlorite and alkali buffer in Hypo-I stage at a dosage of 0.24% on O.D. pulp basis.

The bleaching conditions, chemical dosages and the final bleached pulp properties are presented in the Tables—1 to 5.

TABLE—1
EFFECT OF UREA IN I-HYPO STAGE BLEACHING

| Sl.No. | Particulars | Set I | | | Set II | | |
|--------|----------------------------------|---------|------|------|---------|------|------|
| | | Control | Urea | Urea | Control | Urea | Urea |
| 1. | Chlorine as Hypo, % | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 |
| 2. | Buffer as NaOH, % | 1.35 | Nil | Nil | 1.40 | Nil | Nil |
| 3. | Urea on pulp basis, % | Nil | 0.15 | 0.20 | Nil | 0.50 | 0.75 |
| 4. | End pH of pulp | 8.5 | 7.4 | 7.4 | 8.6 | 7.7 | 7.9 |
| 5. | Residual Chlorine, mg/lit | 14.0 | 28.0 | 36.0 | 7.1 | Nil | Nil |
| 6. | I-Hypo pulp brightness % Elrepho | 76.0 | 76.0 | 76.0 | 74.0 | 47.5 | 41.5 |
| 7. | Viscosity, (0.5% CED) cps | 7.6 | 7.2 | 7.1 | — | — | — |

| | Set I | Set II |
|------------------------------|--------|-------------------------|
| Alkali Extracted Pulp K. No. | 7.0 | 7.5 |
| Bleaching conditions : Cy. : | 10.0 % | Temperature : 43 ± 2°C; |
| Retention Time : 3 hrs. | | |

TABLE—2
EFFECT OF AMMONIUM CHLORIDE IN I-HYPO BLEACHING

| Sl. No. | Particulars | Ammonium Chloride | | | |
|---------|---------------------------|-------------------|-------|-------|-------|
| | | Control | 0.10% | 0.15% | 0.20% |
| 1. | Chlorine as Hypo, % | 5.0 | 5.0 | 5.0 | 5.0 |
| 2. | Buffer as NaOH, % | 1.68 | nil | nil | nil |
| 3. | pH at the end of 3 hrs. | 9.0 | 7.0 | 7.0 | 7.0 |
| | 4 hrs. | 8.4 | 7.0 | 7.0 | 7.0 |
| 4. | Residual chlorine, mg/lit | | | | |
| | after 2 hrs. | 185 | 135.0 | 191.0 | 195.0 |
| | after 3 hrs. | 14.0 | 21.0 | 53.0 | 67.0 |
| | after 4 hrs. | 7.1 | 7.1 | 21.0 | 28.0 |
| 5. | Brightness % Elrepho | | | | |
| | after 2 hrs. | 76.0 | 77.5 | 77.0 | 75.0 |
| | after 3 hrs. | 77.0 | 78.5 | 78.5 | 78.5 |
| | after 4 hrs. | 75.0 | 76.5 | 76.5 | 77.5 |
| 6. | Viscosity, (0.5% CED) cps | | | | |
| | after 2 hrs. | 9.5 | 7.3 | 7.6 | 7.6 |
| | after 3 hrs. | 8.6 | 7.2 | 7.3 | 7.4 |
| | after 4 hrs. | 7.5 | 6.3 | 6.3 | 6.4 |

Bleaching conditions : Cy=10.0% ; Temperature=43 ± 2°C
Retention time = 4.0 hrs.

TABLE—3
EFFECT OF AMMONIUM SULPHAMATE AND SULPHAMIC ACID IN I-HYPO
STAGE BLEACHING

| Sl. No. | Particulars | Control | Ammonium Sulphamate 0.1% | Sulphamic Acid 0.1 % |
|---------|-------------------------------------|---------|--------------------------|----------------------|
| 1. | Chlorine as Hypo, % | 4.0 | 4.0 | 4.0 |
| 2. | Buffer as NaOH % | 1.30 | 1.16 | 1.22 |
| 3. | Residual chlorine, mg/lit | 28.0 | 163.0 | 242.0 |
| 4. | End pH | 8.3 | 8.4 | 8.4 |
| 5. | Brightness % Elrepho | 76.5 | 76.0 | 76.5 |
| 6. | Viscosity (0.5% CED) cps | 6.5 | 8.8 | 8.8 |
| 7. | Strength properties at 40°SR | | | |
| a) | Burst Index, K pa.m ² /g | 3.05 | 3.23 | 3.09 |
| b) | Tear Index, mN.m ² /g | 7.3 | 7.0 | 7.3 |
| c) | Breaking length, km | 5.44 | 5.60 | 5.63 |
| d) | Double folds, Nos. | 7 | 12 | 12 |

Bleaching conditions :

Cy = 10.0% ; Temperature = 43 ± 2°C; Retention time = 2.5 hrs.

TABLE—4
EFFECT OF AMMONIUM SULPHAMATE AND SULPHAMIC
ACID IN-HYPO STAGE BLEACHING OF CEHH

| Sl. No. | Particulars | Control | Ammonium Sulphamate 0.1% | Sulphamic Acid 0.1% |
|----------------------|-------------------------------------|---------|--------------------------|---------------------|
| I—HYPO STAGE | | | | |
| 1. | Chlorine as Hypo, % | 2.5 | 2.5 | 2.5 |
| 2. | Retention time, hrs | 3.5 | 3.5 | 3.5 |
| 3. | Buffer as NaOH, % | 1.35 | 1.00 | 0.95 |
| 4. | Residual chlorine, mg/lit | 7.0 | 14.0 | 57.0 |
| 5. | Brightness % Elrepho | 66.5 | 66.5 | 67.0 |
| 6. | Viscosity (0.5% CED) cps | 9.7 | 11.1 | 11.4 |
| II HYPO STAGE | | | | |
| 1. | Chlorine as Hypo % | 2.0 | 2.0 | 2.0 |
| 2. | Retention time, hrs. | 3.0 | 3.0 | 3.0 |
| 3. | Buffer as NaOH % | 0.45 | 0.50 | 0.45 |
| 4. | Brightness % Elrepho | 77.5 | 77.5 | 77.5 |
| 5. | Residual chlorine, mg/lit | 326 | 412 | 625 |
| 6. | Viscosity (0.5% CED) cps | 7.6 | 8.8 | 9.2 |
| 7. | Strength Properties at 40°SR | | | |
| a) | Burst Index, K pa.m ² /g | 2.95 | 2.98 | 3.04 |
| b) | Tear Index, mN.m ² /g | 8.3 | 8.3 | 8.2 |
| c) | Breaking Length, km | 5.10 | 5.10 | 5.13 |
| d) | Double folds, Nos. | 8 | 10 | 12 |

TABLE—5
EFFECT OF MELAMINE COMPOUND IN I-HYPO STAGE OF BLEACHING

| Sl.No. | Particulars | Control | Additive |
|--------|-------------------------------------|---------|----------|
| I | Alkali Washer Pulp Kappa No. | 25.3 | 24.9 |
| II | Viscosity, (0.5% CED) cps | 20.3 | 20.2 |
| III | I-HYPO STAGE | | |
| 1. | Cl ₂ as Hypo % | 2.90 | 2.90 |
| 2. | pH | 7.3 | 8.4 |
| 3. | Residual chlorine, mg/lit | 51.1 | 92.3 |
| 4. | Brightness % Elrepho | 75.5 | 67.7 |
| 5. | P. C. No. (16 hrs) | 6.5 | 6.0 |
| 6. | Copper No. | 2.46 | 1.0 |
| 7. | Viscosity, (0.5% CED) cps | 7.5 | 9.1 |
| IV | II-HYPO STAGE | | |
| 1. | Cl ₂ as Hypo % | 1.3 | 3.2 |
| 2. | pH | 8.1 | 8.5 |
| 3. | Residual chlorine, mg/lit | traces | 6.0 |
| 4. | Brightness, % Elrepho | 77.7 | 78.3 |
| 5. | P.C. No. (16 hrs) | 6.6 | 5.9 |
| 6. | Viscosity, (0.5% CED) cps | 6.3 | 5.9 |
| 7. | Strength Properties at 40°SR | | |
| a. | Burst Index K pa. m ² /g | 2.67 | 2.95 |
| b. | Tear Index mN . m ² /g | 4.7 | 5.0 |
| c. | Breaking length, km | 4.76 | 4.34 |

RESULTS AND DISCUSSION

A—EFFECT OF UREA

A perusal of the results, vide Table—1, shows that the addition of urea 0.15—0.20% without buffer there is not much change in brightness compared to the addition of regular buffer (sodium hydroxide); with higher dosages, the brightness development was impeded drastically. This may be due to the lowering of the oxidizing capacity of the bleach liquor abnormally and thereby slowing down the rate. With 0.2% urea, there is a slight decrease in viscosity. This may be due to lower terminal pH (7.4) compared to the terminal pH with sodium hydroxide buffer (8.5) and more residual chlorine left behind after 3 hrs. retention time.

B-EFFECT OF AMMONIUM CHLORIDE

With 0.1% ammonium chloride addition there is perceptible improvement (1.5 points) in pulp brightness but a decrease in viscosity value, over control set vide Table—2. By increasing the dosage to 0.2%, no

improvement either in pulp brightness or in viscosity is observed. With the addition of ammonium chloride (0.15 to 0.20%) instead of regular sodium hydroxide buffer there is a slight decrease in bleach chemical consumption.

To study the effect of retention time on the pulp properties in Hypo stage with and without addition of ammonium chloride, pulp samples were tested after 2 hrs, 3 hrs. and 4 hrs. for brightness and viscosity. Perusal of results shows that, upto 3 hrs. there is an increasing trend in brightness and thereafter starts decreasing. However, the brightness development is better with ammonium chloride addition compared to sodium hydroxide buffer. In case of viscosity, there is decreasing trend continuously.

C—EFFECT OF AMMONIUM SULPHAMATE

A comparison was made on the effect of ammonium sulphamate with that of sulphamic acid in Hypo—I

stage at same dosage (0.1%). In these experiments, the buffer, sodium hydroxide was added to maintain the pulp pH above 8.3.

Perusal of results, vide Tables—3 & 4, shows that the addition of 0.1% ammonium sulphamate along with sodium hydroxide buffer slightly reduces the chlorine consumption for getting the same degree of brightness with improved viscosity. The improvement in viscosity is comparable to that of 0.1% sulphamic acid addition. Except tear, there is slight improvement in strength properties. The advantages likely to be achieved by switching over to ammonium sulphamate from sulphamic acid, are—

- i) The ease of preparation of the solution because of its high solubility (200.2 g/100 g water at 20°C)⁷ compared to sulphamic acid (47.08g/100g water at 80°C)⁷.
- ii) The high pH of its aqueous solution (5% solution pH is 5.2)⁷ compared to sulphamic acid (1% solution pH is 1.18)⁷ solution will be added advantage as these additives are being used in alkaline system. However, the final selection depends upon the cost and availability of the material.

D—EFFECT OF MELAMINE COMPOUND

A plant trial was conducted with a melamine compound in C E H H bleaching of bamboo, mixed hardwood blend pulp. As the additive has low solubility (about 4 gpl at 20°C), a solution of 3 gpl. was prepared and added at a constant rate at the repulper of alkali extraction stage washer along with hypochlorite and sodium hydroxide buffer.

A perusal of results from Table-5 reveals that the use of 0.24 additive in I-Hypo stage improves the I-Hypo overflow pulp properties i. e., increase in viscosity and drop in copper number but retards the brightness development. But, after the completion II-Hypo stage without additive, properties of the final bleached pulp (viscosity and post colour number) are almost similar to that of control pulp. However, the strength properties burst index and tear index are slightly higher when additive was used. The lower copper number and

P. C. number indicates the effectiveness of melamine additive in reducing cellulose degradation during bleaching, though it retards the brightness development because of slower reaction.

CONCLUSIONS :

From the above finding it is evident that the nitrogenous compounds are helpful to certain extent in reducing the cellulose degradation when they are used in small quantities, 0.1—0.2%.

The degree of effectiveness depends upon the nature of the nitrogenous compound and the pulps.

Among urea, ammonium chloride, ammonium sulphamate and melamine compound, ammonium sulphamate gives better results comparable to that of sulphamic acid. This indicates that the sulphamic acid functional group is more active in controlling the cellulose degradation without hindering the brightness development. To retain the benefits achieved in I-Hypo stage, the additives should be added along with the normal caustic buffer in Hypo-II stage also in a CEHH sequence bleaching.

However, the final choice depends upon the individual mill conditions and economics as sulphamic acid and ammonium sulphamate are costlier than urea.

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