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The Reclamation of Fibers from Blueprint Stock

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The Reclamation of Fibers from Blueprint Stock

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by

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OBJECT

A method of reclaiming the fibers from blueprint paper after it has been used in the photocopying precess and the subsequent bleaching of these fibers is sought.

THE BLUEPRINTING PROCESS(1)

In the blueprinting process the "raw stock", untreated paper, is coated with a sensitized solution by a series of rolls. Then the paper is dried at 200 degrees Fahrenheit and continues to the printing operation.

The paper is exposed to an arc or mercury vapor lamp through the tracing or drawing original. The exposed sheet is washed with water spray and completely emersed in water. This removes undesirable chemicals and stimulates the reactions which produce the images. An oxidizing solution (usually bichromate or peroxide) is used to fix the chemicals followed with a final wash. The print is dried at a high temperature. This produces a print with white lines and a blue background.

CHEMISTRY OF PHOTOCOPYING PROCESS

The coating solution contains a soluble ferricyanide and ferric salt. Upon exposure to light the ferric salt is reduced and insoluble Prussian Blue is formed.(2) Below are two formulas for such sensitizing solutions:

Standard Formula

Solution "A"

Water 8.5 oz. or 50cc.

Iron and Ammonium citrate 1.7 oz. or 10gm

Solution "B"

Water 8.5 oz or 50cc.

Potassium Ferricyanide 1.4 oz. or 8gm

Filter the two solutions separately. They may be preserved, separately for sometime and are best kept in the dark. For use, mix in a dark room, or by an artificial light of low intensity, equal quanities of the two solutions.(3)

New Formula (4)

4 parts Potassium ferricyanide

4 parts Ferrous ammonium oxalate

5 parts neutral hydrolyzable sodium hexametaphosphate

The first formula is the one used most and the general reaction for its employment are:

Ferric salt plus light $\longrightarrow$ Ferrous salt

Ferrous salt plus Ferricyanide $\longrightarrow$ Prussian Blue (2)

The opaque lines on the tracing of the original drawing prevent the light from reaching the sensitized layer. The Prussian Blue precipitates wherever the light reaches the sensitized layer.

RAW STOCK

Chemically the stock must be non-reactive with respect to the blueprint coating. This means no reducing substance can be present in the rosin, beater sizing, starch, glue, or tub siz-

ing. Rag or cotton linters make up 50 percent of the fiber content with the remainder being bleached sulphite. Some grades contain only 25 percent rag and an appreciable quanity have an all wood furnish. Higher rag content results in better permancy.(5)

Normally raw stock has two basis weights, 17 and 20.5 pounds 17" x 22" 500. High wet strength and high folding endurance are a must. Good tearing characteristics and the right amount of absorption are strived for. The stock gives best results after two to three months aging. Opacity is gained by loading the sheet with titanium oxide and clay.(1)

CONTENTS OF SPENT BLUEPRINT

In summation bleached sulphite fibers, iron complex salts, Prussian Blue, rag fibers, titanium oxide, rosin, size, bichromate, peroxides, wet strength resins, and clay may be present in the treated sheet. In the pulping of second grade rags oxalic acid is employed to remove undesirable iron compounds. (6) This fact may prove useful in reaching the desired point of brightness.

DEFIBERING AND DEINKING PULP

The wet strength must be destroyed by adding 5 percent alum to the hydrapulper and raising the temperature to 200 degrees Fahrenheit. Then the stock is cooked for two hours and pumped to the stock chest. From the stock chest it continues to the flat screens and dirtex for removal of unwanted objects. A final washing is given to the stock before bleaching begins.(8)

BLEACHING OF RAGS

Several methods of bleaching may be used:

1. Bleaching powder
2. Sodium chlorite activated with hypochlorite
3. Sodium chlorite activated with chlorine
4. Zinc hydrosulphite

BLEACHING POWDER(9)

Bleaching powder, $CaCl(OCl)$, and wash water are agitated in a tank. After settling, the required degree of Baume' is reached by using either liquor or water. This controls the hypochloritel content.

The roll and washing cylinder are raised before the bleach liquor is added to the washing engine. Alum may be used as an accelerator at this time. After the desired coloriis reached the excess chlorine is washed out. Any residual chlorine will give a positive starch-iodine indicator test.

SODIUM CHLORITE AND HYPOCHLORITE(6)

Alum is employed to maintain a pH of 8.5-9.0. This sodium chlorite reacts with the hypochlorite as shown here:

$$2NaClO_2 + NaOCl \longrightarrow 2ClO_2 + Na_2O + NaCl$$

The active bleaching agent is the ClO_2. Excess chlorine is washed out and tested as above. Advantage is taken of the inability of chlorite and hypochlorite to react at high pH values to prepare stable stock solutions of the mixture in the optimum proportions required for bleaching.(10) This method of bleaching results in:

1. A high brightness obtained with less degradation.
2. Chlorine dioxide replacing 50 percent of the chlorine.
3. Chlorine costs one-fourth of the original amount.
4. The viscosity of the bleached pulp being equal to or greater than the unbleached pulp.
5. The copper number being reduced from .40 to .15, hypochlorite to sodium chlorite.

SODIUM CHLORITE AND CHLORINE(7)

Bleaching with this method produces ClO_2 as the active agent in a similiar reaction to the one above. Alum is used as above and the results are about the same.

ZINC HYDROSULPHITE(11)

Zinc hydrosulphite has proven sucessful in the bleaching of mechanical, kraft and certain other pulps. The big difference in this method is that the process is carried out between a pH of 5.0 and 6.5. The temperature is between 140 and 160 degrees Fahrenheit during this bleaching operation which requires one hour. One percent zinc hydrosulphite is mixed along with one-half percent sodium polyphosphate. This powder mixture is added directly to the mixing apparatus. This method has also been used for the stripping of dyed fabrics and for the deinking of paper stock.

EXPERIMENTAL PROCEDURE

WET STRENGTH REMOVAL

Steam injection was employed together with five perbent alum to remove the wet strength. A temperature of 98 degrees Centigrade was reached while the pH remained near 3. The consistency was five percent (oven dry*) and after one hour treatment with an Atlas drill press, 800 revolutions per minute, it had dropped to 1.6 percent due to the steam condensation. The disintegrated stock was washed with cold water to remove all of the soluble chemicals.

DEINKING OF THE DEFIBERED STOCK

The pulp was pressed to remove excess water and then the consistency was adjusted to five percent. Five percent caustic soda was added and the same treatment as employed in the wet strength removal was used again. The only difference being the pH. The resulting pulp was a cream color and was screened with a 100 mesh wire laboratory screen to remove unbeaten fiber. The stock was washed again with excess water to wash out residual chemicals. Brightness pads were made according to TAPPI standards. TAPPI standards were used throughout this research work.

IDENTIFICATION OF FIBERS IN STOCK

Microscopic slides were made with the deinked stock and the following fibers were found:

1. Rag(cotton)
2. Bleached sulphite
3. High Alpha cellulose

*All consistencies used are on oven dry basis.

HYPOCHLORITE BLEACHING

From the above results it was conclude that calcium hypochlorite could be employed to bleach the pulp. It was added to the pulp at a consistency of 10 percent and the hypochlorite was added based on three percent available chlorine. Prior to this the bleaching solution was saturated with lime to maintain a basic pH. The pulp was bleached in polyethylene bags for five hours at 40 degrees Centigrade. Brightness pads were made from this stock. Then .25 percent sodium hydroxide was used for two hours at 125 degrees Fahrenheit with the pulp at a consistency of 12 percent. The yellow color still remained.

SODIUM CHLORITE

Some of this bleached pulp was treated with sodium chlorite activated with hypochlorite. One percent sodium chlorite was added along with three percent chlorine as calcium hypochlorite. The pH was maintained between 8.5 and 9.0. The reaction continued for 1½ hours and the yellow color was still present.

REPEATED CAUSTIC EXTRATION

A sample of the yellow bleached pulp from the hypochlorite treatment was extracted with one percent caustic soda for three hours at 41 detrees Centigrade. This was repeated again and the yellow color still remained.

ZINC HYDROSULPHITE

From the above results it seems logical that zinc hydrosulphite would work because it bleaches cellulose near a pH of five. It is employed in the stripping of dyed fabrics.

Blueprint fibers have been subjected to this bleaching method. The results were unfavorable. (12)

ACID HYPOCHLORITE

The bleaching process was repeated with acid extraction replacing the caustic extraction. Sulphuric acid (4N) was employed and a pH of two was reached. The time of the reaction was one hour and the temperature held at 100 detrees Fahrenheit. The bleached pulp was washed with water and brightness pads were made as before.

This time, the yellow color had been removed and the pulp appeared much brighter.

OXALIC ACID

Some of the deinked stock was washed with a solution of 2.5 percent oxalic acid. The stock was at a temperature of 20 degrees Centigrade and the consistency was 10 percent. Some of this same solution was used again on more deinked stock. Both times the stock immediately turned white. The yellow color produced by the comples iron salts was washed away.

TREATMENT OF RESULTS

A sample from each process was evaluated by means of a Photovolt brightness test. The results are given in table I. Then the color in the samples was determined by bristimulus excitation method; the purity of these samples' colors along with the corresponding wave lengths were determined.(13) A little blue added to the oxalic acid pulp would improve the brightness.

TABLE I

Treatment	Apparent color	Average Photovolt brightness	Wave length	Corresponding color	Percent purity
Wet strength removal	blue		577	yellow	29.2
Deinking with caustic soda	pale yellow	58	563	greenish yellow	28.6
Hypochlorite & caustic extraction	pale yellow	63	576	yellow	10.6
Repeated caustic extraction	pale yellow	64	553	greenish yellow	9.2
Acid hypochlorite	white	70	567	Greenish yellow	7.2
Oxalic acid	white	74	582	yellow	5.0

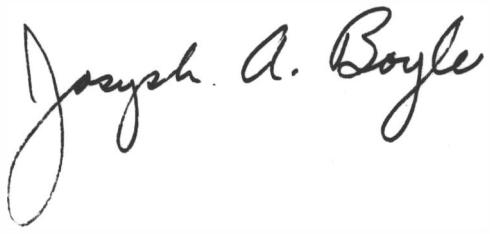
SUMMARY

This study of the pulping of blueprint paper revealed that the wet strength had to be removed before any more progress could be made. With this defibered pulp it was found that five percent caustic destroyed the characteristic blue color. Normal hypochlorite and caustic extraction failed to remove the yellow color. Acid hypochlorite together with high temperatures bleached the pulp best. This pointed to an acid treatment to accomplish the desired result. Therefore a 2.5 percent oxalic acid solution was tryed as a wash for the deinked stock. As seen in table I, this brought out the white color quickly. The color investigation revealed that the oxalic acid treated sheet had the lowest percent purity and also showed that some blue coloring would improve the appearance.

CONCLUSIONS

Blueprint stock contains a high rag content which could prove useful in making book grades and other related grades. However the complex iron salts formed in the blueprinting process are not removed by any standard bleaching process. High hydrogen ion concentrations and high temperatures along with the normal hypochlorite treatment could be used to extract this yellow iron complex color. This could reduce the strength properties of the treated pulp. Oxalic acid at normal temperatures, proved sucessful in accomplishing this result faster and therefore probably with less degradation of the pulp. For such a process few equipment changes would be necessary. In

the near future the spent blueprint rag fibers may end up in a sheet of paper similiar to the one upon which this conclusion was written.



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