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The Influence of Single, Two, and Three Stage Bleaching on the Opacity of Deinked Stock

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THE INFLUENCE OF SINGLE, TWO, AND THREE STAGE BLEACHING ON THE OPACITY OF DEINKED STOCK

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"Bleaching may be defined as the alteration of coloring matter in such fashion as to cause it to reflect more true white, or the solubilizing of such coloring matter to make it possible to wash out the color substance, or both." (2) The most common method of bleaching is the oxidation of the coloring substance although reduction with ZnS_2O_4 is sometimes used with ground-wood. This discussion will be limited to bleaching by means of oxidizing agents namely: chlorine and calcium hypochlorite.

The early method of bleaching was with $Ca(OCl)_2$ in open tanks. Since the method was not too successful, Hollander type beaters replaced the tanks and because of the agitation a much better bleach was obtained. The bellmer bleacher which was designed for the sole purpose of bleaching improved the bleaching action still more by using steam for heat which speeds up the bleaching process. These bleachers were of the low density type (5-7% consistency). About 1920 high density systems (10-30% consistency) came into use. These high density bleaches allow the pulp to be bleached faster and also save on the amount of bleach consumed due to the law of mass action(the higher the bleach liquor concentration, the faster the reaction). Also of major consideration in the high density system is the matter of floor space; since less water is handled, the size of the bleacher can be smaller. Considerable agitation is necessary in the high density system. (2)

Since bleaching solubilizes some of the coloring matter without completely reacting with it, there will be an excessive bleach consumption if the dissolved coloring matter is left in contact with the liquor allowing further oxidation to ensue. To counteract this, the bleaching is divided into different steps by applying the bleach liquor in smaller doses with a through washing between each dose to wash out the solubilized coloring matter. This multistage bleaching enables one to make a savings in the amount of bleach consumed and also to obtain a less degradated pulp since the bleach concentrations are smaller.

Cross and Bevan discovered that the encrusting matter could be removed from fibers by direct chlorination but because the pulp becomes darker than the original material in some cases after the chlorination, it wasn't until later that anyone realized that this darkened pulp could be easily whitened by adding $Ca(OCl)_2$. Upon discovery of this fact the bleaching was broken up into two stages chlorination and hypochlorite with through washing between the stages. This made it possible to make a great saving in total Cl_2 consumed. For best removal of the color when chlorine is used, alkali is added since the chlorine reacts

to form hydrochloric acid and substitution compounds which are very soluble in alkaline solutions. If the pulp is first washed on an acid proof washer to remove the hydrochloric acid, and then the alkali is added, a 90% savings in alkali can be realized over the amount required without washing (2). By continuing these chlorination and alkaline extraction stages with a hypochlorite treatment the three stage bleach is developed. Nadelman (7) states that the chlorination-hypochlorite treatment removes the lignin portion giving higher brightness but also a greater shrinkage than from a single stage treatment.

Forni (1), in some research with hypochlorite bleached spruce sulfite pulp, discovered that with from 0-20% bleach liquor based on bleach demand there is a sharp increase in opacity; from 20-80% the change is downward; and from 80-110% the opacity againrises but never to the opacity of the original pulp.

Bleach Demand (%)	TAPPI Opacity
0	59.0
20	60.5
25	56.0
50	49.0
80	48.5
90	51.0
110	55.0

In regard to opacity there are many factors to be considered which will be dealt with soon after a small discussion on the measuring of opacity. Circa 1912-1915, Priest, Tillyer, Keuffel and others of the Bureau of Standards utilized the Martens photometer and the concept of contrast ratio was developed. The Bureau of Standards "Aminco" meter is based on Priest's instrument. Utilizing the same principle M.N. Davis later developed the meter which has come to be known as the Bausch and Lomb opacimeter (3).

Since the Bausch and Lomb opacimeter will be used exclusively in the evaluation of the results obtained in this experimental study a brief description of the operation and construction will be necessary. The Bausch and Lomb opacimeter works on the contrast ratio method. A light source is fixed on a sample backed by $MgCO_3$ and the meter is then adjusted to give the highest reading of 10. The $MgCO_3$ is replaced by a black surface consisting of a black felt lined enclosed tube and the resulting meter reading is multiplied by a factor of 10 to give the opacity reading in percent. The meter is constructed so the light passes thru a tube and is directed out of an opening over which the sample to be tested is placed. The light which is reflected then passes

thru an integrating tube containing a photoelectric cell which activates the meter. A constant voltage transformer is used to maintain a constant light intensity. (8)

Wicker (10) states that the light scattering characteristics is the most important property in regards to transparency and consequently since transparency and opacity are the opposite of each other, it should be of primary importance for opacity. Judd (5) utilized the Kubelka-Munk formula to obtain two families of curves on a single set of co-ordinates which enables one to quickly obtain the quantity "S". For a given shade the opacity depends on the product "SX" where "X" is the thickness of the paper. Stated differently, having fixed upon a value of R_∞ (reflectance of a layer thick enough so that further increase shows no change), R_o (reflectance with a black backing) becomes fixed when "SX" assumes a definite value. Technically "S" is the fraction of diffuse incident light which is reflected or scattered back by an extremely thin substance, divided by the thickness of that substance.

The ability of a material to scatter light "S", depends upon the number of light scattering points in the material per unit volume and according to the Institute of Paper Chemistry (4), in filler free paper, "S" is due to fibers, ray cells and other particles. By use of the scattering coefficient, "S", which depends only on the material and not on the basis weight or dyestuff added, Steele (9) maintains that the weight of sheet required to yield a given opacity at a fixed reflectivity is inversely proportional to the "S" value. He obtained the following "S" value for different fibers:

Pulp	"S"
Bleached sulfite (8 types)	0.106-0.133
Unbleached sulfite (5 types)	0.086-0.111
Esparto	0.161
Soda	0.174
Alpha fiber	0.161
Soft alpha fiber	0.186
Bleached kraft	0.186

Steele believes that the higher "S" values of the bleached pulps in regard to the unbleached are due to the differences existing before the bleaching.

The Institute of Paper Chemistry (4) and Steele (9) believe that the scattering power of an individual particle depends on the shape of the particle, the size, and the differences between the indices of refraction of the particle and the surrounding medium. With pigments this is true to a certain limit of

surface at which the "S" value decreases. In filled sheets the "S" value is the additive effect of the fiber and the pigment, each exerting its effect in proportion to the amount present. "S" increases rapidly with the difference between the indices of refraction of the scattering medium and the surrounding material provided that the two media are in intimate enough contact to be described as "optical contact". Since the index of refraction of the fibers and fillers in a sheet is quite different from that of air, the more air in a sheet, the more opaque it becomes.

In discussing transparency, Wicker (11) presumes that transparency depends on the size and number of surface irregularities, decreasing directly as the latter increase. He also believes transparency is directly proportional to the glossy qualities of a sheet and that it varies directly with specular reflectance (the capacity for reflecting rays of light in the same perpendicular plane as that of incidence, and with the same angles of incidence and reflection between the rays and a line normal to the sheet surface). Due to the fact that Wicker also found that transparency increases with a decrease in ash content, mineral constituents left in the paper from the cooking liquor, such as calcium, aluminum and silicon having optical properties quite different from those of cellulose, are believed to cause an "S" value which is detrimental to transparency. By going on the theory that anything harmful to transparency is desirable for opacity, it is assumed by the author that these factors are also reponsible for an improved opacity.

Since the reflectance of a colored object varies with the wavelength of the light and the color of the object, the light source is important. A fundamental property of every color is to absorb certain wavelengths of light while reflecting others. This makes it obvious that every dyestuff will reflect light differently. Any dye will exert its maximum opacifying influence when measurements are made with light of the particular wavelength absorbed to the greatest extent by the dye. According to Laughlin (6), in low concentrations of dyestuffs the pulp and dye absorb the light and scatter it independently of one another, and also at these concentrations the ratio of the absorption coefficient to the scattering coefficient for the dye alone is approximately proportional to the concentration of the dye. His experiments conclude that reddish blues, violets and black exert the greatest opacifying power; yellows, oranges, reds and greenish blues the least. The Institute of Paper Chemistry (4) states that the addition of a dyestuff to the furnish lowers the R_∞ while scarcely affecting the scattering coefficient.

From this it is seen that the factors influencing opacity are: 1) scattering coefficient (condition of filler, fiber and

pigment, degradation of cellulose chain and density); 2) color of the sheet and of the light used; 3) smoothness; 4) glossy qualities of the sheet; and 5) basis weight.

For the purpose of this investigation it was decided that number one colored ledger, a high ground-wood content coated magazine and a mixture of 50 per cent of the ledger and 50 per cent of the magazine would be the stocks to be deinked and bleached. The latter was chosen to more nearly approximate actual mill stock. These stock were all deinked before any bleaching was performed to make sure that each bleach would be carried out on pulp of constant composition.

These deinkings were identical regardless of the waste paper used and the conditions were as follows:

Consistency - - - - - - - - - - - 5 per cent
Sodium hydroxide based on
a.d. (air dry) pulp - - - - - 4 per cent
Temperature - - - - - - - - - - - 175 degrees Fahrenheit
Time - - - - - - - - - - - - - - 20 minutes

The paper was put into a stainless steel beaker, 8 inches high and 6-1/2 inches in diameter, which contained the required amount of water. It was then disintegrated by means of a 3-15/16 inches diameter agitator mounted on a drill press which was operating at a speed of 600 R.P.M. During this disintegration period live steam was injected to obtain the temperature desired and occasional injections were then given when necessary to maintain this temperature. After the temperature was reached, the caustic soda, in solution, was added and the agitator was submerged to a depth of three inches (total liquid depth - four inches). At this time the drill press was speeded up to 2133-1/3 R.P.M. and kept at this speed for 20 minutes when the deinking was completed. Twenty minutes was chosen for the length of cook by visual comparison of the deinked stock at various times, and after twenty minutes there was no appreciable gain in deinking.

After deinking the pulp was washed with tap water on an 80 mesh screen until the effluent became clear, as were all subsequent washings, and then the stocks were stored in crocks until they were bleached. A commercial preservative was added to the stock at this time.

The characteristics of these deinked pulps were determined and the results tabulated in Tables 1,2,3, 4 and 5.

Table 1. Permanganate Number of Deinked Stock (TAPPI Standard T214 m-50)

Pulp	Permanganate Number
High ground-wood content coated magazine	21.0
Number one colored ledger	9.4
50-50 mixture	16.4

Fifty grams of b.d. (bone dry) stock were used for each bleach run and the bleaches were run in duplicate. It was decided to maintain the per cent chlorine based on b.d. pulp constant for each different type of pulp regardless of the number of stages involved and also to consider caustic soda exactly equivalent in action to chlorine. On this basis the magazine stock was bleached with 7.0 per cent total chlorine, the ledger with 3.5 per cent total chlorine and the 50-50 mixture with 5.25 per cent total chlorine. All these bleach runs were performed in one liter stainless steel beakers with slow agitation by a drill press for initial mixing. All subsequent mixings were done by hand. Distilled water was used for all bleachings. The conditions for each bleach were as follows:

Single Stage Bleach

Consistency - - - - - - - - - - - - - 5 per cent
Chlorine (from Ca $(OCl)_2$)
Magazine - - - - - - - - - - - - - 7.0 per cent
Ledger - - - - - - - - - - - - - 3.5 per cent
50-50 mixture- - - - - - - - - - 5.25 per cent
Temperature - - - - - - - - - - - - - 100 degrees Fahrenheit
Time - - - - - - - - - - - - - - - 2.5 hours
pH (phenylphthalein) - - - - - - 8.5-9.5

Two Stage Bleach

Chlorination stage:
Consistency - - - - - - - - - - - - - 5 per cent
Chlorine (from Cl_2 water)
Magazine - - - - - - - - - - - - - 4.5 per cent
Ledger - - - - - - - - - - - - - - 2.25 per cent
50-50 mixture - - - - - - - - - - 3.375 per cent
Temperature - - - - - - - - - - - - - 75 degrees Fahrenheit
Time
Magazine - - - - - - - - - - - - - 2 hours
Ledger - - - - - - - - - - - - - - 1.5 hours
50-50 mixture - - - - - - - - - - 1.75 hours

Hypochlorite stage:

The same as for single stage bleach except that the per cent chlorine was changed as follows:
Magazine - - - - - - - - - - - - - 2.5 per cent
Ledger - - - - - - - - - - - - - - 1.25 per cent
50-50 mixture - - - - - - - - - - 1.875 per cent

Three Stage Bleach

Chlorination stage:

Same as chlorination stage of two stage bleach.

Alkaline extraction stage:

Consistency	12 per cent
Caustic soda (based on b.d. pulp)	
Magazine	1.0 per cent
Ledger	0.5 per cent
50-50 mixture	0.75 per cent
Temperature	162 degrees Fahrenheit
Time	1 hour

Hypochlorite stage:

The same as for single stage bleach except that the per cent chlorine was changed as follows:

Magazine	1.5 per cent
Ledger	0.75 per cent
50-50 mixture	1.125 per cent

Because the tap water used for washing had a high iron content the pulp was given a dilute acetic acid rinse before the handsheets were formed for the optical tests. The handsheets were then made up according to TAPPI Standard T214 m-50 "Forming Handsheets for Optical Tests of Pulp".

The various tests which were run have been tabulated in Tables 2,3, 4 and 5.

Table 2. Freeness of Pulp (TAPPI Standard T227 m-50) Determined by Canadian Freeness Tester

Pulp	Freeness (cc)
High ground-wood content coated magazine	
Deinked	550
Single stage bleach	560
Two stage bleach	560
Three stage bleach	560
Number one colored ledger	
Deinked	690
Single stage bleach	690
Two stage bleach	690
Three stage bleach	700
50-50 mixture	
Deinked	610
Single stage bleach	610
Two stage bleach	620
Three stage bleach	620

Table 3. Percentage Ash in Pulp (TAPPI Standard T211 m-44)

	Deinked	Single Stage	Two Stage	Three Stage
Magazine	2.7	1.7	1.55	1.3
Ledger	1.4	1.3	1.1	0.95
50-50 mixture	2.1	1.4	1.2	1.1

Table 4. Brightness of Handsheets (TAPPI Standard T217 m-48)
Hunter Multipurpose Reflectometer

	Deinked	Single Stage	Two Stage	Three Stage
Magazine	53.1	55.0	56.3	57.6
Ledger	51.7	70.1	69.6	69.7
50-50 mixture	52.3	60.2	61.2	64.3

Table 5. Opacity of Handsheets (TAPPI Standard T218-M48)
Bausch and Lomb Opacimeter

	Deinked	Single Stage	Two Stage	Three Stage
Magazine	99.0	96.6	95.0	96.4
Ledger	97.2	93.6	92.6	93.5
50-50 mixture	99.0	94.5	95.4	96.2

In every case a residual chlorine analysis was run on the bleached stock liquor and also on a blank. From the results obtained it became obvious that every run was under-bleached since there was no residual chlorine. This of course, could have been predicted by the high permanganate numbers of the pulps. This under-bleaching consequently lowered the brightness but it did allow a more justifiable comparison of the opacity since every type of stock had had exactly the same amount of chlorination

It was decided that due to the high iron content of the tap water which was used to wash the pulp and also because the handsheets could not be tested until a week after they were made, brightness results were misleading and therefore are to be regarded as inconclusive.

Opacity readings made on the handsheets show that for the number one colored ledger and the coated magazine stocks the opacity of a single stage bleach deinked pulp is lower then the unbleached deinked stock, the two stage stock opacity decreases still further, while the three stage bleached stock shows an increase in opacity over the two stage bleach but does not reach as high a value as the single stage bleach. However, in the case of the 50-50 mixture this was not true since after the original decrease for the single stage bleach there was a gradual increase in the opacities of the two and three stage bleaches with the three stage bleach having the highest opacity.

Ash determination results in all cases seem to indicate that adequate washing was given to every pulp and therefore there should be very little filler and pigment present to influence the opacity readings and the values should therefore reflect the true opacities of the fibers themselves.

Literature Citation

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