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The Influence of Single, Two, and Three Stage Bleaching on Fading Characteristic of Deinked Stock

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-Abstract-

A literature survey on the various bleaching methods used on deinked stock and the factors which influence the fading characteristic of deinked stock is compiled. Mention is also made of various additives which have an influence on the fading of a sheet. A description of the experimental work with caustic deinked stock of various groundwood content follows. Results indicate that the groundwood content has more effect upon fading of deinked stock than the number of stages of bleaching, although the increase in the number of stages of bleaching does reduce the amount of fading in a sheet. A greater effect by the number of stages of bleaching is obtained in the higher groundwood range.

Literature Survey

Introduction

The use of bleached deinked paper stock has increased greatly in the past years. Due to recent developments in methods of deinking, washing, and bleaching, deinked stock can now be used in all but the finest grades of writing and record paper. This development in technological knowledge has not only eased greatly the strain on our forest reserves but has also developed an economical outlet for the use of a gigantic waste material.

Various Bleaching Methods Used on Deinked Stock

Because of the non-uniformity of deinked stock and its similarity to commercial wood pulps very little has been written about the bleaching of deinked stock. The bleaching processes most used are single, two, and three stage with some peroxide and hydrosulphite bleaching being used if the groundwood content of the stock is high. These processes usually prove to be efficient to reach the required brightness of the stock and are identical with those used in commercial wood pulps.

The composition of deinked stock varies considerably in groundwood content and initial brightness depending upon the raw materials used. Therefore, a manufacturer will have to build his particular bleaching system to fit the type of raw materials used and the final brightness desired. Even from batch to batch these initial characteristics of the stock vary considerably, so that his bleaching system must be a flexible one in order to cover the range of deviation in the stock prepared.

Some of the factors which influence the type of bleaching system

used are: initial costs, space required, volume of bleaching done, and degree of brightness desired. The single stage bleaching system uses a minimum amount of space, but the chemical costs are higher and the pulp is degraded more than in ~~the~~ two or three stage bleaching. In the two and three stage bleaching the yields are lower but the final brightness is higher and the chemical costs are lower. Peroxide and hydrosulphite do not attack the cellulose, but their costs are high.

The use of sodium hypochlorite bleach has increased greatly despite the fact that its cost is higher than that of calcium hypochlorite. The reasons for this shift are listed by E. N. Poor (1) in his Nonfibrous Raw Materials Report for 1945 as follows: savings in chlorine, no sludge disposal problem, complete use of alkali, cleaner pulp, saving in space, and some advantages in the way the pulp handles on the wire.

Some experimenting has been done in the use of chlorites in the bleaching of deinked stock, but, to date, this method has not found acceptance in the deinking industry.

Fading Characteristics of Deinked Stock

Fading is defined by Webster's new International Dictionary (date?) as a gradual loss of intensity, color, distinctness, etc. In the paper industry this term is used synonymously with others such as color stability and light stability. TAPPI Routine Control Method RC-50 is the usual means of measuring the degree of fading in the paper industry. This method employs the use of an Atlas Fade-Ometer for fading the sheet and a comparison of exposed and masked portions of the sample by any suitable method.

P. Nolan, J. A. Vanden Akker, and W. A. Wink (2) state that there are at least two photochemical reactions in the discoloration of pulp. One is the so-called bleaching action produced by radiation of wavelengths longer than 385 mmu. The second is the normal dulling action caused by the action of light wavelengths shorter than 385 mmu (ultraviolet light). Thus, some pulps will gain in brightness when exposed to light while others will fade. This fact was proven in an experiment performed by J. H. Graff (3) in which he exposed different kinds of pulps to both sunlight and a sterilamp for 192 hours. The results showed that hardwood sulphite, kraft, and soda pulps gained in brightness while groundwood and softwood sulphite pulps decreased in brightness.

H. F. Lewis and D. Frommuller (4), experimenting with groundwood pulp, found that there were apparent losses in the sulfuric acid soluble lignin fraction, the Cross and Bevan cellulose fraction, and the pentosans fraction of the pulp plus partial demethylation of the lignin when the sheets were exposed in a Fade-Ometer. Upon exposure of a 45 per cent groundwood -55 per cent bl. sulphite with 15 per cent clay sheet to sunlight for 73 hours per side, Lewis and Frommuller found the same losses except that the Cross and Bevan cellulose fraction did not change, although the Copper No. and the acidity of the sheet were increased. Nolan, Vanden Akker, and Wink (2) in experimenting with the fading characteristics of groundwood found a remarkable similarity in the spectral sensitivity curves of groundwood with the spectral absorption curve of lignin derivatives.

Since the pulps with high lignin content (groundwood and unbl. s.w. sulphite) showed fading tendencies; a marked chemical change was

shown in the lignin content of faded sheets; and there ~~is~~ was a remarkable similarity in the spectral sensitivity curve of groundwood and the spectral absorption curve of lignin derivatives; it seems reasonable to assume that the major factor in the color stability of pulp is its lignin content. Deinked stock varies greatly in lignin content. Therefore, to obtain minimum fading characteristics in deinked stock, one should use no groundwood, unbleached softwood sulphite, or other highly lignified papers in his system. Three stage, and to a lesser extent, two stage bleaching, remove the lignin fraction of the pulp; therefore, it seems reasonable that these bleaching systems should produce a bleached stock which is fairly light stable.

Other factors, besides the groundwood or lignin content, which influence the color stability of bleached stock are as follows:

1. The final pH of the bleaching system dictates somewhat the fading characteristics of the bleached stock. F. Casciani and G. K. Storin (5) in experimenting with sulphite pulp found that a minimum of fading resulted when the final pH of the hypochlorite stage of a two-stage bleach was high (10 or above). In a single-stage bleach these men found that this effect was almost the reverse. The most stable color was obtained when the final pH was less than 5.75.
2. Atmospheric conditions have an effect on the color stability of bleached stock. P. Nolan, J. A. Vanden Akker, and W. A. Wink (2) state that all things being equal groundwood fades more rapidly under conditions of high temperatures and relative humidities. Of course, these conditions must be accompanied by the action of light in order to produce fading.

3. An excess of iron in the washing water may also produce color reversion as stated by E. L. Keller and F. A. Simmonds (6).
4. Aging will also cause paper to fade. This phenomenon is probably due to oxidation taking place, and has been proven by H. F. Tauner and W. K. Wilson (7).

Some attempts have been made to reduce the fading characteristics of a sheet by the addition of an inhibitor to the sheet. H. F. Tauner and W. K. Wilson (7) found that the light stability of newsprint was very materially increased by buffering the sheet at a pH of 7.2. The sample was dipped in a solution of $NaHCO_3$, and after drying was found to retain 0.12 gm. of $NaHCO_3$ at a pH of 7.2.

A study by E. A. Reineck and H. F. Lewis (8) of 130 organic compounds as inhibitors to the fading of groundwood under the influence of ultraviolet light revealed no noticeable improvement in behavior. But P. A. Nolan (9) found that the addition of Eastman Ultraviolet sensitizing solution reduced appreciably the fading of groundwood. The use of this compound is not feasible because of both high initial cost and cost of application. The results, however, support the premise that fading may be reduced or eliminated by the inclusion in a sheet of a compound which would strongly absorb the ultraviolet light which is responsible for fading. The use of fluorescent purple was found ineffective as a reducing agent for the fading of groundwood because it does not brighten the groundwood sheet as it does bleached chemical pulps.

Analyzing the material covered, ultraviolet light is responsible for the photochemical reactions which produce fading in bleached deinked stock. These reactions may be accelerated by heat and high relative

humidity. The main constituent of deinked stock which influences its color stability would appear to be its groundwood content since this fraction is almost entirely responsible for the lignin content of deinked stock. Another factor which cannot be controlled is the aging of paper which causes it to slowly lose its brightness. By eliminating these factors or the inclusion of an inhibitor in the sheet, the paper produced should show good light stability properties.

Signature?

Experimental Work

Since the lignin content has an important influence on the fading characteristic of pulp, it was decided to bleach three different stocks of approximately 10, 20, and 30 per cent groundwood. Caustic deinked stock of about 10% groundwood content, by microscopic analysis, was obtained from the Monarch Div., Allied Paper Mills, Kalamazoo, Michigan. The original furnish of this stock was as follows: 600 lbs. shavings, 2990 lbs. book, 3248 lbs. ledger, 5% caustic, 206°F, at 5% consistency. The deinked stock was divided into three parts, and laboratory caustic deinked newsprint was added to two of the samples to bring their groundwood content up to approximately 20 and 30 per cent. The three stocks were then screened on a Valley Iron Works laboratory flat screen, 0.01 inch slots, and collected on a 60 mesh screen.

Permanganate numbers were taken on each of the stocks, and the equivalent bleach consumption was determined by using the factors for sulphite pulp. The results are tabulated in Table I.

Permanganate Number and Equivalent Bleach Consumption of Deinked Stock (TAPPI standard T 214 m-50)

Pulp	Permanganate No.	Eq. Bleach Consumption
10% G.W.	6.15	2.80
20% G.W.	9.75	4.65
30% G.W.	13.25	6.50

-Table I-

Twenty five grams of b.d. (bone dry) stock from each of the three sample stocks was then bleached by the single, two, and three stage sodium hypochlorite bleaching methods. These

stocks were bleached to approximately the same brightness by use of the equivalent bleach consumption figures obtained. The results showed a range of 5 units (Photovolt) between the nine bleached stocks. The identical brightnesses were desired so that the fading results could be comparable. The conditions for each bleach were as follows:

Single Stage Bleach

Consistency---------- 6 per cent

Chlorine (from NaOCl)--------- 100% of eq. bleach consumption

Temperature---------- 100°F

Per cent completion---------- 98 per cent

pH (phenylphthalein)---------- 8.5-9.5

Two Stage Bleach

Chlorination stage:

Consistency---------- 3 per cent

Chlorine (from Cl_2 water)------ 60% of eq. bleach consumption

Temperature---------- 72°F

Per cent completion---------- 98 per cent

Hypochlorite stage:

The same as for single stage bleach except that the per cent chlorine (from NaOCl) was equal to 40% of the equivalent bleach consumption for the stock.

Three Stage Bleach

Chlorination stage:

The same as for the chlorination stage of the two stage bleach except that the per cent chlorine (from Cl_2 water) was equal to 50% of the equivalent bleach consumption for the stock.

Alkaline extraction stage:

Consistency---------- 6 per cent

Caustic soda (based on b.d. pulp) -- 2 per cent

Temperature---------- 120°F

Time---------- 2 hours

Hypochlorite stage:

The same as foe single stage bleach except that the per cent chlorine (from NaOCl) was equal to 25% of the equivalent bleach consumption for the stock.

Brightness waterleaf handsheets were then made of the bleached stocks following TAPPI standard T 218 m-48.

The handsheets were then faded in an Atlas Fade-Ometer for periods of 1, 2½, 5, 10, 20, 40, 60, 80, and 100 hours. At the end of these periods brightness readings were taken of the masked and unmasked portions on the Photovolt brightness meter and their differences calculated. All samples were faded simultaneously. The temperature in the Fade-Ometer was held between 90-95°F and the humidity was held constant.

The results obtained are illustrated in Fig. I. Certain trends which may be deduced from the graph are as follows:

1. The higher the number of stages of bleaching the less will be the fading of deinked stock.
2. The groundwood content has more influence on the fading of deinked stock than the number of stages of bleaching.
3. The higher stage bleaching has more effect on the fading of deinked stock in the higher groundwood range than in the lower groundwood range.

4. The differance in fading between two consecutive stages becomes less as the number of stages increase.

Thus, it follows that the groundwood content has the most effect upon the fading characteristics of deinked stock. The number of stages of bleaching will effect the fading characteristics of the stock to a smaller extent, but not enough to warrant its use as an economical control in the fading of bleached deinked stock. Therefore, inorder to reduce the fading of bleached deinked stock its groundwood content must first be reduced if possible. If impossible, an increase in the number of stages of bleaching will produce a small change.

Respectfully submitted by,

Phillip H. Avery

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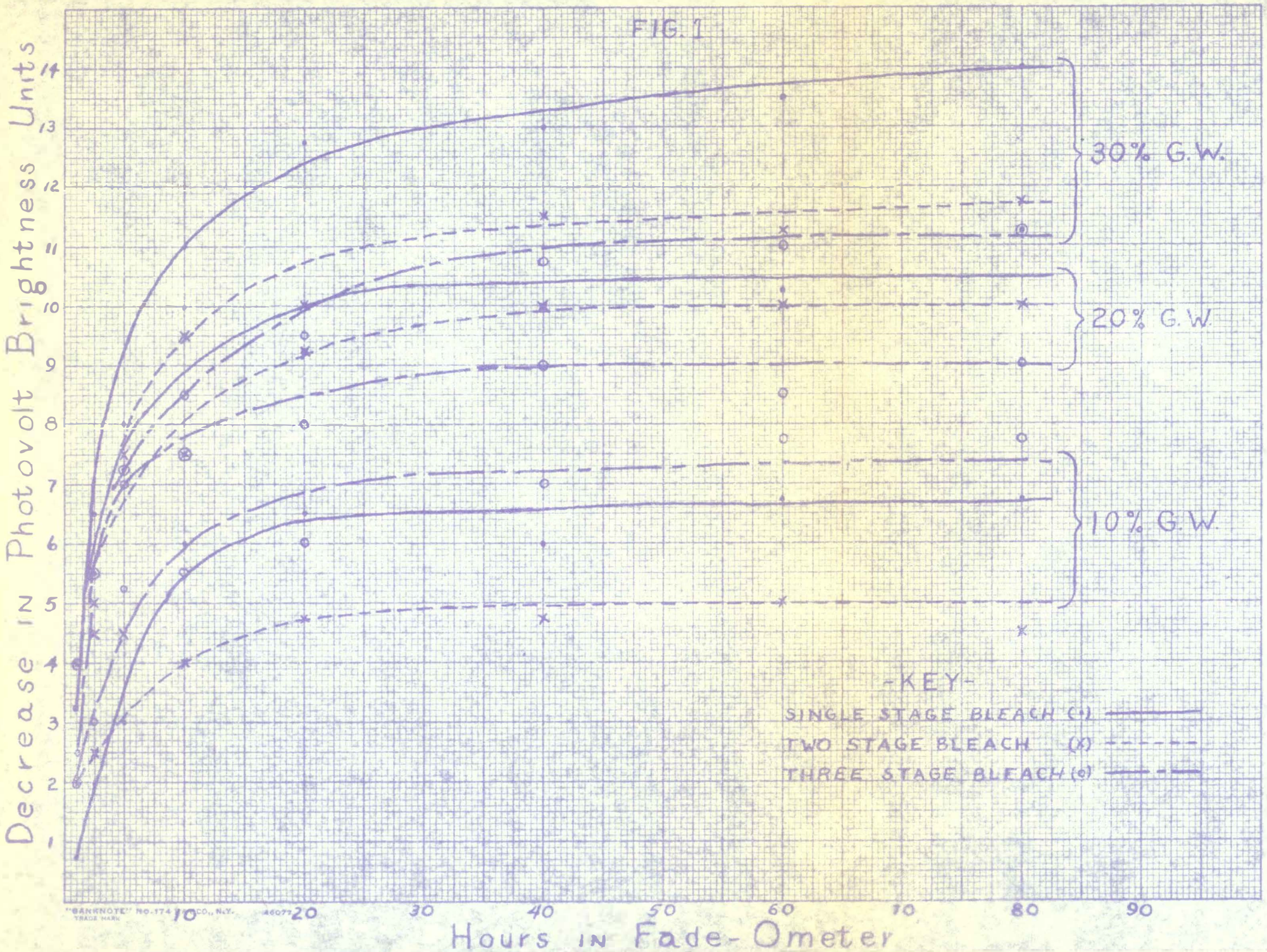
FIG. 1


Decrease IN Photovolt Brightness Units
1
2
3
4
5
6
7
8
9
10
11
12
13
14
10
20
30
40
50
60
70
80
90
Hours IN Fade-Ometer
30% G.W.
20% G.W.
10% G.W.
-KEY-
SINGLE STAGE BLEACH (•)
TWO STAGE BLEACH (X)
THREE STAGE BLEACH (o)