

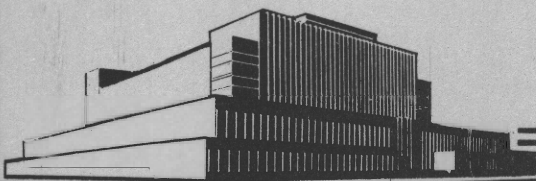
SOME OBSERVATIONS ON THE PROBLEM OF IRON IN BLEACHING WOOD PULP

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In Cooperation with the University of Wisconsin

SOME OBSERVATIONS ON THE PROBLEM OF

IRON IN BLEACHING WOOD PULP¹

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Abstract

In bleaching, both the chlorination and hypochlorite stages, particularly the former, tend to remove iron from pulp, but if iron-containing water is used for washing, the pulp will reabsorb iron. Indications are, however, that iron contents up to 0.15 p.p.m. are tolerable in the washing water. In general, iron content of bleached pulp has an influence on pulp color.

Introduction

It is commonly recognized that the presence of even small amounts of iron in the process water used in bleaching will impair the brightness of the bleached pulp. Also, adverse effects on pulp strength and chemical properties, increased bleach demand and increased rate of bleach consumption have been attributed to the presence of iron in the process water. There are several instances in the literature wherein the maximum tolerable concentration of iron is set at 0.1 or 0.15 p.p.m. There are, however, no attendant accurate definitions of the corresponding loss in pulp quality when these amounts are exceeded.

The effect of the presence of iron in paper in accelerating its deterioration has been determined quantitatively by Richter (10) who found adsorbed iron salts to be definite catalysts of folding strength degradation. In the field

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²Maintained in Madison, Wis., in cooperation with the University of Wisconsin.

of rayon pulps, Essenlen and Gurley's (4) specifications indicate that the rayon industry prefers not over 7 p.p.m. of iron in such pulps.

The present report deals with the adsorption of iron from aqueous solution, and effect of iron in the process water that is used in bleaching on the color of the bleached pulp.

Iron in Process Water

Iron occurs in natural waters chiefly as ferrous bicarbonate. Less common forms are ferrous carbonate, ferrous and ferric sulfate, ferric gallotannate, and other soluble or insoluble organic combinations. The solubility of ferric iron in alkaline waters is quite low (0.1 p.p.m. at pH 8.5). Hence most of the iron in a freshly-filtered alkaline water probably would be in the ferrous form when first used in pulp and papermaking operations.

The ferrous ion, however, oxidizes very readily. In fact, one established means of lowering the iron content of water consists of a simple spraying to get the water in contact with air, followed by filtration. It thus appears that an unpredictable amount of the ferrous iron in fresh mill waters may be oxidized to the less soluble form, either accelerated by mechanical action such as the whipping of the beater roll; chemically, as in the oxidizing bleaching processes; or simply by exposure of the surface to air. Oman (8) has stated that paper will take up iron from ferric compounds but very little from the ferrous forms.

It is evident that the iron content of a pulp may increase not only through pure adsorption, but also by filtering out iron which has been precipitated as a result of oxidation. Such loosely-held iron is, of course, more susceptible to removal by turbulent washing than iron which has been truly adsorbed.

An experiment was made to obtain a quantitative indication of the oxidation effect on the dissolved iron in Madison city well water. Three bottles were filled completely with water directly from Well No. 6 for the stability test and these samples were stored at a temperature of approximately 4° C. The iron content of each was then determined according to the schedule shown in table 1. It is apparent that when air was excluded from contact with this water there was no change in the amount of iron in solution for at least 2 days. When the water was allowed to come in contact with the air, an appreciable decrease in dissolved iron occurred within 5 days and at the end of 12 days about 60 percent had precipitated. The latter point is established by the fact that the iron content values after agitation of the water at the end of the 12-day period were much higher than before agitation.

It should be noted that the decrease in the iron content of the supernatant water may not be a true measure of the rate of oxidation of the dissolved iron because the rate of settling of the oxidized material is unknown.

Adsorption of Iron from Solution

The concept of an exchange mechanism in the adsorption of cations by cellulosic materials was, according to McLean and Wooten (6), first advanced by Michaelis and Rona in 1919 (7). It has since been confirmed by several investigators that the cation-holding constituents behave in a manner similar to that of a zeolite. For example, iron may be taken up by pulps from aqueous solutions of its salts with the simultaneous release of an equivalent amount of other cation, such as calcium or magnesium, from the pulp. Treatment of the pulp with acid to lower the ash content replaces the metallic cations with hydrogen.

McLean and Wooten (6) concluded that the ash constituents exist as metal-organic compounds associated with the impurities, which include beta- and gamma-cellulose, uronic acids, oxycellulose, and reactive groups associated with the lignin. The generalization is made that the capacity for exchange adsorption decreases as the alpha-cellulose content of a pulp approaches 100 percent.

Adsorption as Related to Concentration

Preliminary to studies with natural iron-containing waters, various adsorption and bleaching data were obtained in which iron-containing suspension obtained and adsorption waters were made up with both distilled and Birmated water² and ferrous ammonium sulfate. The purpose was to insure exact control of the iron concentration and to provide a wider range of the latter than would be possible with Madison city well water.

The adsorption data reported in table 2 and figure 1 were obtained by soaking portions of a commercially bleached sulfite pulp (P-1148) in water solutions containing varying amounts of the ferrous ion and subsequently analyzing the pulp for iron content. This pulp was received in wet lap form and contained 87 percent alpha-cellulose, 0.2 percent ash, and 6 p.p.m. of iron. The color of the pulp in parts Ives was: Red, 89; green 89; blue 89.

For adsorption, 15-gram samples (moisture-free equivalent) were each alternately soaked and washed in a Büchner funnel with 5 liters of distilled water over a period of approximately 75 minutes to remove residues and impurities soluble under these conditions. The final mat was broken up in a quantity of water sufficient to give a total of 3 liters of water after the addition of the prescribed volume of iron solution. Enough ferrous ion was added from a freshly-prepared solution of ferrous ammonium sulfate to give concentrations of 0.06, 0.17, 0.33, or 0.67 mg. of iron per liter of water, and the suspension stirred vigorously to insure immediate and uniform distribution. These mixtures were allowed to stand for 18 hours at 20°-25° C.

³Madison city well water which had been passed through a filter bed of Burgess iron removal mineral.

The suspension was then poured into a sheet-machine, the pulp mat pressed between blotters at 100 pounds per square inch and allowed to dry in the air between the blotters. Convenient amounts of the dry sheets were ashed in quartz crucibles, the ash taken up in warm dilute hydrochloric acid, evaporated to dryness, and analyzed by the standard colorimetric KSCN method for the determination of iron in water (1).

Two parallel series of experiments were made. In one series distilled water was used throughout. In the second series, the quite alkaline (310 p.p.m. calculated as CaCO_3) Madison city well water was used after passage through a Birm unit.

Reference to figure 1 reveals that an increase in the initial concentration of iron in the suspension over the concentration range used resulted in an increase in the amount of iron taken up by the bleached sulfite pulp. This was true for both waters used. The curves, which are similar to adsorption isotherms, indicate that the kind of suspension water had no effect on the amount of iron adsorbed until the initial iron concentration in solution exceeded 0.2 p.p.m. Over the concentration range from 0.2 to 0.7 p.p.m., however, more iron was taken up and at an increasing rate by the pulp from the Birmated water suspensions than from the distilled water suspensions.

Two factors are recognized as possible causes of this difference. One is the difference in hydrogen-ion concentration at which adsorption occurred in the two suspension waters. The distilled water suspension had a pH value of about 6, whereas the Birmated water suspensions had a pH value of about 8.5, both values having been determined colorimetrically.

The presence of large amounts of other electrolytes in the Birmated water may have been the second factor. Krzyt (5) has pointed out that, in some cases, when two electrolytes are present, each is more strongly adsorbed than when either is present alone.

Washing of Iron-Containing Pulps

Given a pulp containing adsorbed iron the question arises if any of this iron can be removed by a thorough washing with iron-free water. To obtain information on this question, washing experiments using iron-free water were made with three pulps. Two of the pulps were in wet-lap form from the wet machine and had thus been subjected to a considerable amount of washing with water that contained about 0.06 p.p.m. of iron; one of the two pulps was an unbleached lowland white fir sulfite (Dig. No. 3687-I) containing 31 p.p.m. of iron. The third pulp was a commercial unbleached kraft pulp (P-1231) containing 33 p.p.m. of iron.

From each of these pulps four samples were taken, each containing the equivalent of 15 grams of moisture-free fiber. Each sample was washed continuously in a Büchner funnel with 1 liter of distilled water, then allowed to soak

1/2 hour in a liter of distilled water, again washed continuously with a liter of the water, soaked as before, and then given a final continuous wash with a liter of the water.

The iron contents of the samples were not lowered by this washing treatment. It is, therefore, indicated that the iron present in the pulps was held by adsorption forces sufficient to resist removal by even extensive washing with iron-free water.

The amount of iron which can be removed from a pulp by washing may vary with different pulps and different conditions of washing. Czaplá (2) found that iron could be washed readily from straw and sulfite pulps; but not from soda and mechanical pulps. Du Rietz (3) found that cations of high valence are more difficult to wash out than those of lower valence. In dealing with iron, which may be present in either the ferrous or the ferric state, this finding may be significant.

Effect of Hydrogen-Ion Concentration on Adsorption

Hydrogen-ion concentration, as previously mentioned, was probably one factor accounting for the difference in the amount of iron adsorbed from solution by a pulp suspended in, respectively, distilled and Birmated waters. The data which are deemed indicative of this are in table 3 and figures 2 and 3, those in figure 2 having been obtained using the same commercially-bleached sulfite pulp used in the water comparison.

The procedure in this experiment was to adjust the hydrogen-ion concentration of a series of suspensions in Birmated water, each containing 2.0 mg. of added ferrous iron in the same volume of solution. The desired pH was obtained by the addition of either hydrochloric acid or sodium carbonate prior to the addition of the pulp. A glass-electrode pH meter was used to measure hydrogen-ion concentration. Adsorption was allowed to proceed for 17 hours after which the suspensions were filtered on a Büchner funnel, drained with suction, but not washed. The pulps were then analyzed for iron content.

The curves in figures 2 and 3 show a marked decrease in the amount of iron adsorbed with increasing acidity of the systems, under the experimental conditions that obtained. In the pH range where alkali was added, iron was probably taken up as the hydroxide as well as adsorbed in the ionic form. Other investigators have found that the precipitation of hydrated ferrous oxide by alkali begins at pH 5.5.

An unbleached lowland white fir sulfite pulp (Dig. 3679-I) was used for the experiment shown in figure 3. This pulp was used in two forms. In the one case the pulp was extracted with 1:1 hydrochloric acid for 15 minutes and then washed until free from chlorides. This treatment reduced the original iron content from 30 to 3.4 p.p.m. In the second case the pulp was used in its original form.

Again, the amount of iron taken up increased as the acidity of the system decreased. Calculation of the amounts of iron taken up by the two pulps did not show a consistent trend of difference.

The probability of hydrolyzing some portions of the pulp by such a strong acid treatment as was used in securing the data shown in figure 3 must be recognized. Percival, Cuthbertson, and Hibbert (9) found that acid extraction lowered the alpha-cellulose content and reduced the adsorptive capacity of pulps high in alpha cellulose. Their pulp was placed in an alum solution, removed, washed, soaked in a 25 percent hydrochloric acid solution for 2 hours, washed, and again placed in an alum solution. The pulp took up only a third as much aluminum as it did in the first adsorption; and on the fourth adsorption cycle only one-seventh.

Rate of Adsorption

As might be expected the rate of adsorption of iron from solution was rapid, as illustrated by the following tabulation of typical data:

| <u>Adsorption period</u> | <u>Iron content of pulp</u> |
|--------------------------|-----------------------------|
| <u>Hours</u> | <u>P.p.m.</u> |
| 0 | 6 |
| 1/60 | 90 |
| 1/2 | 94 |
| 4 | 94 |
| 18 | 125 |

Iron Contents of Typical Pulps and an Indicated Source of Iron

Various typical pulps were analyzed to find the range of iron content likely to be encountered. They comprised both commercial pulps and experimental pulps made at the Forest Products Laboratory. Table 4 presents data on the iron contents of the unbleached pulps and of the wood chips from which four of the pulps were prepared. The data show that although the wood chips contained only 6 to 7 p.p.m. of iron, the pulps made from them contained from 30 to 200 p.p.m. of iron. Assuming a pulp yield of 50 percent and also assuming that the pulp retained all of the iron originally present in the wood, the actual amounts found in the pulps would still be from 2 to 4 times greater than thus accounted for. The adsorption data in figure 1 indicate that the source of this large increase can scarcely be attributed solely to adsorption from the water used in washing and screening, which contained only about 0.06 p.p.m. of iron. The conclusion then is that the digestion process is one of the main sources of iron contamination.

Of the pulps made at the Forest Products Laboratory, the sulfite pulps appear to be consistently lower in iron than the sulfate pulps. The sulfite digester has a stainless iron alloy lining whereas the sulfate digester is made of carbon steel. The loblolly pine sulfate pulps prepared from the same wood shipment and numbered 11 and 12 in table 4 were cooked, respectively, in the sulfate and sulfite digesters with equal amounts of liquor taken from the same source. Since the iron content of the former was 200 p.p.m. and that of the latter was 77 p.p.m., it is apparent that the difference in the iron contents observed was due to the difference in the resistance of the digester linings.

As an indication of the amount of iron in bleached pulps, it will be recalled that the bleached spruce sulfite pulp, P-1148, used in the adsorption experiments had an iron content of only 6 p.p.m.

Iron Concentration Series Using Ferrous

Ammonium Sulfate

A series of bleaches was made using ferrous ammonium sulfate as the source of iron in the process water in order to obtain a greater concentration range (0 to 0.5 p.p.m. of iron) than possible with the Madison city well water.

The equivalent of 20 grams of moisture-free pulp was bleached at 2 percent consistency in three stages. The first stage comprised direct chlorination with 5.9 percent chlorine based on the weight of pulp and the addition of enough sodium hydroxide after a reaction period of 5 minutes to raise the pH value from about 1.6 to 8.5. After exhaustion of the bleach, the pulp was washed in a Büchner funnel with 5 liters of the respective iron-containing process waters. In the second stage 0.5 percent chlorine was added in the form of calcium hypochlorite. At the end of this stage the pulp was washed as before. The third stage was a "flash" chlorination with 0.05 percent chlorine after which the pulp was washed as before. The bleached pulp was made into test sheets using the prepared process water for dilution and the sheets dried in the air between blotters.

The iron contents and colors of the sheets are presented in table 5 and illustrated in figure 4. Until the concentration of the iron in the process water was a little over 0.05 p.p.m. the bleaching procedure actually reduced the iron content of the pulp. At a concentration of 0.08 p.p.m. of iron, the bleached pulp contained 6 p.p.m. more iron than did the original pulp.

Added and Naturally Occurring Iron in Process Waters

The question inevitably arises whether phenomena observed using process waters prepared by adding iron in the form of an inorganic salt parallel those using waters with iron in its naturally occurring forms. The answer is complicated by the many forms in which the natural iron may be present, examples of which were cited early in this report. Investigation of the adsorption of all forms of natural iron is impractical due to the minute quantities involved, the extreme dilution, susceptibility to oxidation and consequent precipitation, and the action of bleaching reagents, all of which lead to difficulties

in the identification and control of the form. The locating and successful transportation of a suitable assortment of waters of about the same chemical composition, aside from iron, is in itself a major problem. Fortunately, one of the deep wells of the local municipal water supply was delivering water containing 0.28 p.p.m. natural iron, and advantage was taken of this to make several experiments using:

1. City water with the iron removed by passage through the Birm unit.
2. City water with natural iron removed, but with 0.2 p.p.m. iron added as ferrous ammonium sulfate.
3. City water direct from the Dayton Street well, containing 0.28 p.p.m. of natural iron.

A commercial spruce sulfite (P-1468) was bleached, using the same general technique as previously described. The actual bleaching conditions comprised a first stage treatment with 3.6 percent by weight of elemental chlorine, a second stage extraction with 1 percent by weight of sodium hydroxide at a temperature of 50° C., and a third stage bleach with 0.4 percent chlorine as calcium hypochlorite. The results in terms of iron content and color of bleached pulp are presented in table 6. Unfortunately, the iron content of the water made up by the addition of ferrous ammonium sulfate was 0.08 p.p.m. less than that with the naturally occurring iron.

It is indicated, however, since the effect was the same with both waters that conclusions as to tolerable iron content in the process for a given pulp may possibly be safely based on determinations made using process water to which iron has been added as ferrous ammonium sulfate. A "given pulp" is specified because the results in table 5, obtained with a different pulp indicate that the iron content-color relation varies somewhat depending on the pulp.

It should not be inferred that the comparative effect of added and natural iron is thought not to vary from one natural water to another. It is obvious that all of the data in the entire report represent only a small fraction of the amount of work required by a comprehensive study of the subject and, therefore, all indicated conclusions must be qualified by the recognition that some variation is likely to be encountered from case to case. It is true, however, that a sufficient amount of quantitative data are now available as a take-off point for a mill to determine with a comparatively small amount of work the iron tolerance for the pulps and process water with which they deal.

Adsorption of Iron from Waters with Natural and Added Iron

Preliminary experiments were made to learn whether the comparison of natural and added iron could be more quickly made by merely soaking bleached pulp in the iron-containing water for a period instead of carrying through multistage bleaches using wash waters of known iron content. A quantity of the pulp

P-1468 was bleached using distilled water throughout, and divided into three parts. Color and iron were determined on one portion and the other two were soaked respectively in water from the Dayton Street well containing 0.28 p.p.m. natural iron, and similar water containing 0.28 p.p.m. iron added as ferrous ammonium sulfate. Similar experiments were made with the unbleached pulp.

As shown by the results in table 7, about 50 percent more iron was taken up from the water containing the added ferrous salt. In the bleaching experiments the "natural" water contained about 40 percent more iron than did the "synthetic" water and the pulps adsorbed the same amount of iron from each. The two series of experiments thus roughly agree quantitatively. However, insofar as color is concerned, the relative decrease is not proportionate to the amount of iron adsorbed in the bleaching and in the soaking tests.

It is thus indicated that actual bleaching experimentation is the procedure to be recommended for determining iron tolerance.

Variation of Iron Content During Stage Bleaching

It appeared desirable to determine iron content of the pulp used in the series for sulfite pulp P-1213 after each step in the multistage bleaching, using the process water containing 0.2 p.p.m. of iron. The results obtained are recorded in table 8.

It was previously pointed out, figures 2 and 3, that (1) in the acid range an increase in the acidity of a pulp suspension containing iron tends to decrease the amount of iron a pulp will adsorb from solution and (2) extraction of an iron-containing pulp with hydrochloric acid will decrease the iron content.

The pulp used in the bleaching and washing experiment described in table 8 contained, originally, 20 p.p.m. of iron. At the end of the chlorination stage, but before washing, the iron content was reduced to 12 p.p.m. This result is in agreement with the findings cited in the foregoing paragraph. When the pulp from this stage was washed with water containing 0.2 p.p.m. of iron in the form of ferrous ammonium sulfate, the iron content of the washed pulp was 39 p.p.m. which is twice the amount present in the unbleached pulp.

After the calcium hypochlorite stage, but before washing, the iron content was reduced to the amount present in the original pulp. The subsequent washing treatment brought the iron content up again and to a new high of 62 p.p.m. The third stage "flash" chlorination with 0.05 percent chlorine, in which the pH value was the same as that contained in the previous hypochlorite stage, removed 22 p.p.m. of iron but the residual was still as high as that of the washed pulp after the first stage chlorination.

After the final washing at the end of the "flash" chlorination stage and the forming of the washed pulp into test sheets using the iron-containing water in

the sheet machine, the test sheets contained 67 p.p.m. of iron. This iron content checks with that of the bleach in table 9 in which a 0.2 p.p.m. process water was used.

The results also show the wash water to be the chief source of iron contamination.

Comparison of Three Process Waters

Several unbleached samples of monosulfite pulp S-199 were washed with different process waters and then bleached, using as process waters the corresponding ones used for the original washing. The iron content of the washed but unbleached pulps varied considerably. These pulps, with one exception, were each bleached by both a single-stage hypochlorite and a two-stage chlorination process. The details of the waters used and the color and iron contents of the bleached pulps are presented in table 9. The hard tap water contained more than the normal amount of iron when these experiments were made.

These limited data indicate that when the iron content of the unbleached pulp is high a chlorination bleach tends to remove more iron than a hypochlorite bleach. Both processes, however, remove large amounts of iron. It is also indicated that the hard tap water from which the iron was removed is as good a process water as distilled. Instances have been observed where the use of iron-free hard tap water resulted in a slightly better color than when distilled water was used.

Dependence of the Color of Bleached Pulps on Iron Content

All of the foregoing data dealing with the color and iron content of bleached pulps were plotted in figure 5 with parts blue as the dependent variable. In the sources of these data are variables such as species, digestion and bleaching process, and the amount of chlorine consumed. Nevertheless, there is an apparent general, although not precise, dependence of color on iron content.

An indicated degree of dependence was obtained when the regression coefficient of the calculated regression curve in figure 5 was found to be significant at the 5 percent level. The associated standard error of estimate was 2.45.

No inference is intended, however, that color can be predicted satisfactorily from the iron content of a pulp, nor that it would be desirable to be able to do so.

Conclusions

Papermaking pulps were observed to adsorb iron from aqueous solution, the amount increasing with increasing iron concentration. For a given concentration of iron, the amount taken up increased with decreasing acidity of the suspension. At low pH values adjusted with hydrochloric acid, the original iron content of the pulp was decreased, a fact that might well be expected.

Prolonged washing of iron-containing pulps with iron-free water did not remove all of the iron. As a matter of fact, extraction of an unbleached sulfite pulp containing 30 p.p.m. of iron with a 1:1 solution of hydrochloric acid for 15 minutes left a residual iron content of 3.4 p.p.m.

The lining of the digester in which a pulp is cooked and the water used in washing a pulp were found to be important sources of iron contamination.

Both chlorination and hypochlorite bleaching, but particularly the first, tend to decrease the iron content of a pulp. As indicated above, however, this advantage may be lost if iron-containing water is used for interstage washing. The indications are that iron contents up to 0.15 p.p.m. in process waters are tolerable.

In general, the iron content of a bleached pulp has an influence on the pulp color.

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Table 1.--Stability of dissolved iron in Madison city water during storage at 4° C.

| Bottle | Level of water | Elapsed time since filling | Iron content |
|---------------|--|----------------------------|---------------|
| <u>Number</u> | | | <u>P.p.m.</u> |
| 1 | :Full | :35 minutes | : 0.21 |
| | : | : | : .21 |
| 2 | :Full | :23 hours | : .19 |
| | : | : | : .19 |
| 3 | :Full | :46 hours | : .20 |
| | : | : | : .20 |
| 1 | :3/4 full | :5 days | : .15 |
| | : | : | : .19 |
| 2 | :3/4 full | :6 days | : .14 |
| | : | : | : .19 |
| 1 | :1/2 full | :12 days | : .09 |
| | : | : | : |
| 1 | :1/4 full, but contents : thoroughly agitated : prior to sampling. | :12 days | : .53 |
| | : | : | : |
| 3 | :3/4 full | :12 days | : .06 |
| | : | : | : |
| 3 | :3/4 full, but contents : thoroughly agitated : prior to sampling. | :12 days | : .32 |
| | : | : | : |

Table 2.--Adsorption of iron from aqueous solution
by a bleached sulfite pulp (P-1148)

| <u>P.p.m.</u> | <u>P.p.m.</u> | <u>Percent</u> | <u>P.p.m.</u> |
|---|---------------|----------------|---------------|
| <u>Distilled Water</u> | | | |
| 0.06 | 17 | 90 | 0.006 |
| .17 | 32 | 78 | .038 |
| .33 | 47 | 61 | .130 |
| .67 | 71 | 49 | .340 |
| <u>Tap Water Treated for Iron Removal²</u> | | | |
| .06 | 16 | 85 | .009 |
| .17 | 32 | 78 | .038 |
| .33 | 51 | 67 | .110 |
| .67 | 90 | 63 | .250 |

¹Calculated.

²By means of the Burgess Iron Removal Mineral.

Table 3.--Influence of H-ion concentration on iron adsorption by sulfite pulps

| Final H-ion concentration of suspension ¹ | Total iron content of pulp | Reagent used to control H-ion concentration |
|--|----------------------------|---|
| <u>pH</u> | <u>P.p.m.</u> | |
| <u>Bleached Spruce Sulfite Pulp (P-1148)</u> | | |
| Contained 6 p.p.m. Fe Prior to Adsorption | | |
| 2.74 | 19 | 5 cc. 3N HCl |
| 2.81 | 16 | 5 cc. 3N HCl |
| 5.38 | 35 | 4 cc. 3N HCl |
| 5.67 | 54 | 4 cc. 3N HCl |
| 6.35 | 105 | 3 cc. 3N HCl |
| 6.46 | 102 | 3 cc. 3N HCl |
| 6.58 | 100 | 3 cc. 3N HCl |
| 8.43 | 94 | |
| 8.68 | 100 | |
| 9.73 | 96 | 1 g. Na ₂ CO ₃ |
| 9.98 | 127 | 1 g. Na ₂ CO ₃ |
| 10.12 | 124 | 1 g. Na ₂ CO ₃ |
| <u>Lowland White Fir Sulfite (Dig. 3679-I)</u> | | |
| Contained 30 p.p.m. Fe Prior to Adsorption | | |
| 3.78 | 34 | 5 cc. 3N HCl |
| 7.65 | 137 | 1 cc. 3N HCl |
| 8.36 | 140 | |
| 9.78 | 158 | 1 g. Na ₂ CO ₃ |
| <u>HCl-Extracted Lowland White Fir Sulfite (Dig. 3679-I)</u> | | |
| Contained 3.4 p.p.m. Fe Prior to Adsorption | | |
| 2.96 | 15 | 6.5 cc. 3N HCl |
| 6.52 | 69 | 5 cc. 3N HCl |
| 7.26 | 114 | 3 cc. |
| 8.36 | 121 | |
| 9.56 | 97 | 1 g. Na ₂ CO ₃ |

¹Birmated water was used as the suspension medium to which was added, in each case, 2.0 mg. of ferrous iron, thus yielding a concentration of 0.67 p.p.m. of iron.

Table 4.--Iron contents of typical unbleached pulps

| Tabular number | | Iron content |
|-------------------------|---|-----------------|
| | | <u>P.p.m.</u> |
| <u>Commercial Pulps</u> | | |
| 1 | : Spruce sulfite (P-984) | 13 |
| 2 | : Spruce sulfite (P-1213) | 20 |
| 3 | : Eastern hemlock sulfite (P-1168) | 60 |
| 4 | : Eastern hemlock sulfite (P-1212) | 120 |
| 5 | : Southern pine sulfate (P-1231) | 33 |
| <u>Laboratory Pulps</u> | | |
| 6 | : Lowland white fir sulfite ¹ (3679-I) | 30 |
| 7 | : Lowland white fir sulfite (3687-I) | 31 |
| 8 | : White spruce sulfite (3664-I) | 76 |
| 9 | : Loblolly pine sulfite (3636-37-38-I) | 40 |
| 10 | : Longleaf pine sulfate (656-67-58) | 112 |
| 11 | : Loblolly pine sulfate ^{2,4} (2483) | 200 |
| 12 | : Loblolly pine sulfate ^{3,4} (2484) | 77 |
| 13 | : Loblolly pine sulfate ⁴ (412-13-14) | 95 |
| | : | : |

¹The iron content of the chips prior to digestion was 7 p.p.m.

²Cooked in a steel digester.

³Cooked in a digester lined with stainless iron alloy.

⁴The iron content of the chips prior to digestion was 6 p.p.m.

Table 5.--Effect of iron in the process water used in bleaching upon the color and iron content of a commercial spruce sulfite pulp (P-1213)

| Concentration of iron in -- | | Color of the bleached pulp (Parts Ives) | | | | |
|-----------------------------|----------------------------|--|--------|------|--------------------|--|
| Water used | Bleached pulp ¹ | Red | Green | Blue | Average parts blue | |
| P.p.m. | P.p.m. | | | | | |
| 0.00 | 13 | 93 | 92 | 88.5 | 88.3 | |
| .00 | 12 | 92 | 92 | 88.0 | | |
| .05 | 18 | 91 | 90-1/2 | 87.5 | 87.8 | |
| .05 | 18 | 91 | 90-1/2 | 88.0 | | |
| .08 | 25 | 90-1/2 | 90 | 87.5 | 87.8 | |
| .08 | 27 | 91 | 90-1/2 | 88.0 | | |
| .10 | 38 | 90-1/2 | 90 | 87.0 | 87.3 | |
| .10 | 36 | 91 | 90 | 87.5 | | |
| .20 | 70 | 90-1/2 | 89-1/2 | 85.0 | 84.5 | |
| .20 | 65 | 90-1/2 | 89 | 84.0 | | |
| .50 | 140 | 91-1/2 | 86-1/2 | 79.0 | 79.0 | |

¹Iron content of the unbleached pulp was 20 p.p.m.

Table 6.--Comparison of process waters containing
"natural" and "added" iron

| Description of process water used in bleaching and washing | Iron content ¹ | Color ¹ (Parts Ives) | | |
|--|------------------------------|------------------------------------|-------|------|
| | | Red | Green | Blue |
| | <u>P.p.m.</u> | | | |
| City water from which all iron had been removed | 11 | 90.3 | 89.8 | 87.6 |
| Iron-free city water to which 0.2 p.p.m. iron had been added as ferrous ammonium sulfate | 65 | 90.1 | 89.1 | 86.3 |
| City water from Dayton Street well, containing 0.28 p.p.m. "natural" iron | 68 | 90.3 | 88.5 | 86.2 |

¹Averages of four bleaches for each water.

Table 7.--Adsorption of iron from waters with natural and added iron

| | Iron content ¹ | Color ¹ (Parts Ives) | | |
|---|------------------------------|------------------------------------|-------|------|
| | | Red | Green | Blue |
| | <u>P.p.m.</u> | | | |
| <u>Pulp² Bleached with Distilled Water</u> | | | | |
| Pulp before soaking | 11 | 90.2 | 89.2 | 87.8 |
| Pulp after soaking in water containing 0.28 p.p.m. natural iron | 37 | 91.0 | 89.1 | 87.2 |
| Pulp after soaking in water containing 0.28 p.p.m added iron | 59 | 89.4 | 87.3 | 85.0 |
| <u>Unbleached Pulp²</u> | | | | |
| Pulp before soaking | 32 | 73.0 | 64.3 | 61.0 |
| Pulp after soaking in water containing 0.28 p.p.m. natural iron | 39 | 72.1 | 64.0 | 59.7 |
| Pulp after soaking in water containing 0.28 p.p.m. added iron | 56 | 69.9 | 62.2 | 58.7 |

¹Experiments were run in triplicate in the case of the natural iron; duplicate with the added iron.

²Commercial spruce sulfite, P-1468.

Table 8.--Variation in the iron content of sulfite
pulp P-1213 during bleaching

| Point in the bleaching process at which analysis was made | H-ion | Iron content of pulp | | | |
|--|---------------|----------------------|--------|--------|---------|
| | concentration | I | II | III | Average |
| | pH | P.p.m. | P.p.m. | P.p.m. | P.p.m. |
| Original pulp, unbleached | | | | | 20 |
| Stage 1, 5 minutes after addition of 5.85 percent chlorine | 1.7 | 12 | 12 | | 12 |
| Stage 1, at exhaustion after addition of NaOH, before washing | 7.0 | 11 | 14 | | 13 |
| Stage 1, after washing with iron-con- taining water ¹ | 8.4 | 36 | 45 | 36 | 39 |
| Stage 2, after exhaustion of 0.5 per- cent chlorine as Ca(OCl) ₂ | 7.8 | 18 | 20 | | 19 |
| Stage 2, after washing with iron-con- taining water | 8.4 | 66 | 57 | 62 | 62 |
| Stage 3, 20 minutes after addition of 0.05 percent chlorine | 7.9 | 38 | 40 | | 39 |
| After final washing and making up into sheets with iron-containing water | 8.4 | | | | 67 |

¹Birmated water to which had been added 0.2 p.p.m. of iron as ferrous ammonium sulfate.

Table 9.--Comparison of three process waters

| Key | Water used in washing unbleached pulp free of cooking liquor ¹ | Iron content of pulp before bleach- ing | Water used in bleaching and washing | Color (Parts Ives) | | | Iron content | | |
|-----|---|--|---|-----------------------|-------|------|-----------------|--------|--------------|
| | | | | Red | Green | Blue | I | II | Aver- age |
| | | P.p.m. | | | | | | P.p.m. | |

Bleached by a Single-Stage Hypochlorite Process

| | | | | | | | | | | | | |
|-----|--------------------------|---|-----|---|-----------------|---|--------|---|----|---|----------|-----|
| SP | :Hard tap water | : | 186 | : | Hard tap water | : | 87: 86 | : | 84 | : | 40: 30: | 35 |
| | : | : | | : | Distilled water | : | 87: 86 | : | 87 | : | 15: 24: | 20 |
| | : | : | | : | : | : | : | : | : | : | : | |
| TWP | :Hard tap water | : | 824 | : | Hard tap water | : | 86: 84 | : | 82 | : | 140:146: | 143 |
| | : | : | | : | Distilled water | : | 86: 86 | : | 86 | : | 53: 49: | 51 |
| | : | : | | : | : | : | : | : | : | : | : | |
| BWP | :Birmated hard tap water | : | 67 | : | Birmated water | : | 88: 87 | : | 86 | : | 40:... | 40 |
| | : | : | | : | Distilled water | : | 88: 87 | : | 87 | : | 40: 42: | 41 |
| | : | : | | : | : | : | : | : | : | : | : | |
| DWP | :Distilled water | : | 68 | : | Distilled water | : | 89: 89 | : | 88 | : | 18:... | 18 |
| | : | : | | : | Distilled water | : | 91: 89 | : | 88 | : | 20:... | 20 |
| | : | : | | : | : | : | : | : | : | : | : | |

Bleached ty a Two-Stage Chlorine-Hypochlorite Process

| | | | | | | | | | | | | |
|-----|--------------------------|---|-----|---|-----------------|---|--------|---|----|---|----------|-----|
| TWP | :Hard tap water | : | 824 | : | Hard tap water | : | 88: 86 | : | 84 | : | 105:120: | 112 |
| | : | : | | : | Distilled water | : | 88: 88 | : | 86 | : | 51: 54: | 53 |
| | : | : | | : | : | : | : | : | : | : | : | |
| BWP | :Birmated hard tap water | : | 67 | : | Birmated water | : | 90: 89 | : | 90 | : | 18: 20: | 19 |
| | : | : | | : | Distilled water | : | 87: 86 | : | 88 | : | 19: 24: | 22 |
| | : | : | | : | : | : | : | : | : | : | : | |
| DWP | :Distilled water | : | 68 | : | Distilled water | : | 90: 89 | : | 89 | : | 15: 17: | 16 |
| | : | : | | : | Distilled water | : | 89: 88 | : | 90 | : | 16: 21: | 19 |
| | : | : | | : | : | : | : | : | : | : | : | |

¹Sample SP was washed in a screen box; all others in a centrifuge.

FIGURE 3--EFFECT OF H-ION CONCENTRATION ON IRON ADSORPTION BY UNBLEACHED LOW-LAND WHITE FIR SULFITE PULP DIG. 3679-I

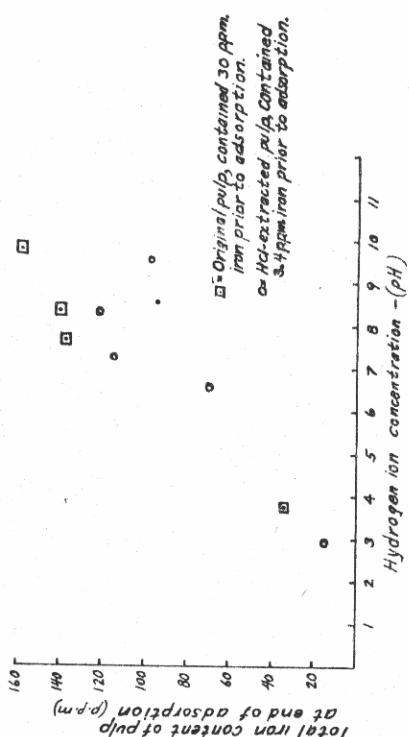


FIGURE 1. ADSORPTION OF IRON BY BLEACHED SULFITE PULP P-1148

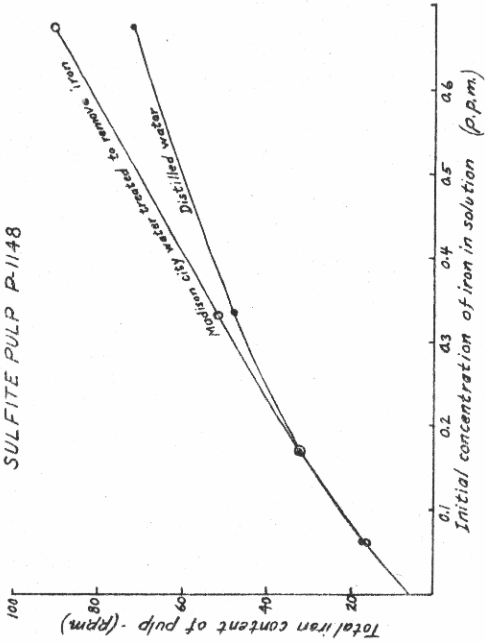


FIGURE 4. RELATION OF COLOR AND IRON CONTENT OF BLEACHED SULFITE PULP P-1213 TO IRON CONTENT OF THE WATER USED IN BLEACHING

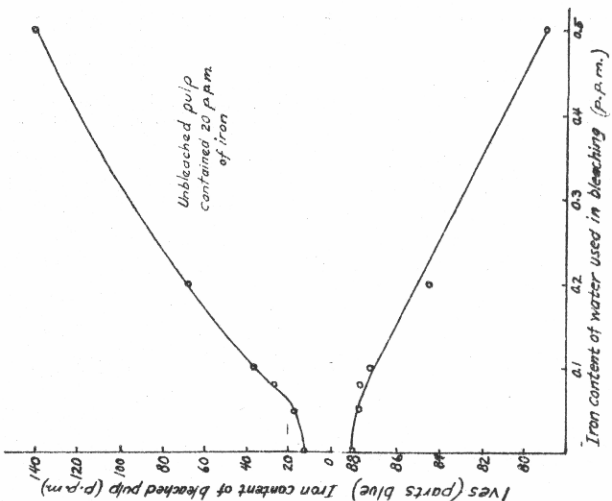


FIGURE 2. EFFECT OF H-ION CONCENTRATION ON IRON ADSORPTION BY A BLEACHED SPRUCE SULFITE PULP P-1148

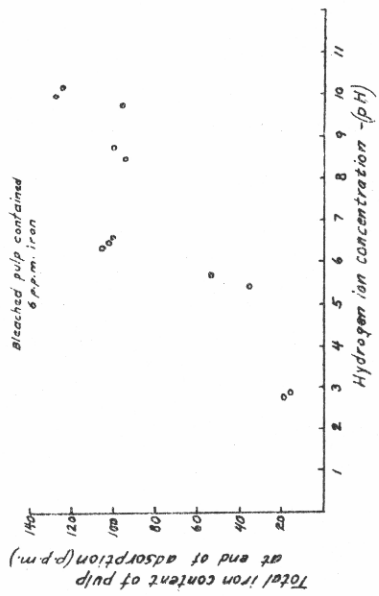
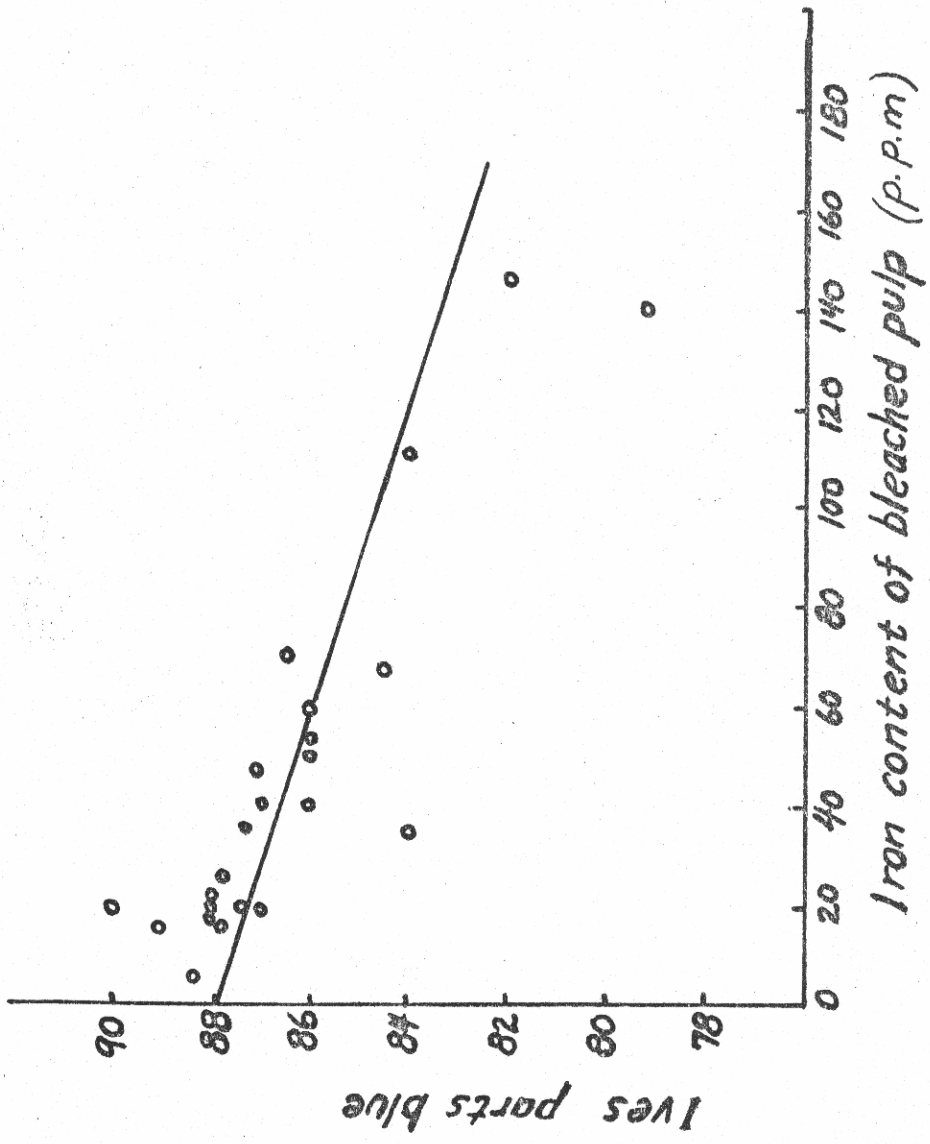


FIGURE 5. DEPENDENCE OF THE COLOR OF BLEACHED PULP ON THE IRON CONTENT.



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