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PROCESS OF TREATING BLEACHED PULP

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This invention relates to processes of treating bleached pulp; and it comprises a method wherein paper pulp bleached in any of the known ways and in an alkaline condition is made slightly acid with a dilute acid and is subsequently whitened by treatment with a minimal amount of solution containing free HOCl reacting with substances liberated by the acid; all as more fully hereinafter set forth and as claimed.

Paper pulps vary considerably among themselves; partly because of the differences in wood and partly because of differences in manufacture. Practically all pulps are bleached with the aid of chlorin in some way in order to produce whiteness or a commercially satisfactory lightening in color. The object is to do this with the least consumption of chlorin and with the least injury to the fiber.

Many methods have been proposed for bleaching paper pulp and several are in use. Originally all the bleaching was effected by hypochlorites in alkaline solution; by bleach liquors made from chlorid of lime (calcium hypochlorite) or similar aqueous liquids made with the aid of chlorin and lime or soda. This method is still in use; treatment being wholly in alkaline solution. Sometimes there are two or more successive hypochlorite bleachings. In other methods in use, there is a treatment preliminary to the alkaline hypochlorite bleach, using chlorin in aqueous solution or chlorin as HOCl; but in practically all cases there is a final treatment with an alkaline bleach liquor. In the preliminary treatment of the pulp with chlorin there is always a development of HCl acidity in substantial amount and this is neutralized in the subsequent hypochlorite bleaching. An accepted theory of action which has merit, is that lignin is separated from cellulose in alkaline solution; part of the lignin being dissolved from the wood in the digester by treatment with alkali and the rest from the pulp by the alkaline bleach liquor; the actions of chlorin in its various forms being to attack the lignin and facilitate its solution and removal. In a general way the bleaching of pulp is regarded as a removal of lignin left with the cellulose in making the pulp. It is recognized that drastic treatments in the digester and in the bleaching lead to an attack on the cellulose and a loss of strength. For making papers of great strength the alkaline treatments are sometimes limited in relative extent.

Pulps containing much lignin are regarded as hard bleaching and vice versa.

I have however found that the color in the pulp to be removed in bleaching is not wholly due to lignin; that in some pulps there are small amounts of color-giving bodies which are resistant to the action of chlorin in alkaline solution and are not necessarily removed when the stated preliminary chlorin treatment is used. These color-giving bodies, though not existing in any large amount in any pulp, are present in many in sufficient quantity to noticeably affect the whiteness of the final bleached pulp. Because of the existence of this residual color, bleaching in practice is often more drastic than is required for the sheer removal of the lignin per se. The chemical nature of these color-giving bodies is unknown but I regard them as being combinations of a color-giving material with an inorganic base, alumina or iron oxide, the color being absorbed or united to the base to form something like a lake. In any event, removal of this color-giving material or residual color, as I may call it, is, as I have found, facilitated by acid, but the residual color is set on the fiber by alkali. Observations of the behavior of these colored bodies in various pulps indicate that they exist on or in the fiber in a way analogous to a mordanted dye. In bleaching processes where acid conditions prevail in the first stage, it is possible that this color is dissolved and partially or completely removed, but if there is a residue it apparently is again set or rendered insoluble by the final alkaline treatment in the bleach liquor.

I have found that by bleaching pulp in any of the usual ways, but merely to the extent of securing a good removal of lignin, I can produce a pulp retaining the original strength and that by treating the pulp with a dilute acid, advantageously in the presence of an antichlor, the residual color is dissociated and partly solubilized. Treatment with an acid alone and unless the pulp has previously been very thoroughly washed, weakens the fiber; probably because of the development of nascent chlorin in situ in the fiber. I therefore use an antichlor; usually a sulfite which may obviate preliminary washing. With a preliminary washing less antichlor is required. The washing and the acid treatment remove the basicity of the bleached pulp. With the pulp in a slightly acid condition, it is then filtered, thus removing solubilized compounds, and while still slightly acid, a minimal addition of HOCl suffices to get rid of the objectionable colorants. The amount of HOCl used is merely enough to take care of the infinitesimal amount of color-giving bodies other than lignin left in the pulp.

While the described method of removing resid-

ual color is applicable to any pulp bleached with chlorin in any of the known ways ending with an alkaline bleach action, I regard it as mainly applicable to pulps made by alkaline digestion. The benefit obtained in treating sulfite pulp in the manner described, while substantial, is not nearly as great as in treating soda pulp, sulfate pulp, etc. No drastic treatment is used in the bleaching proper in the operation for the removal of lignin. With a special operation taking care of the resistant residual color, a light bleaching takes care of the lignin with the final result of giving a pulp of commercial whitness.

In the case of hard bleaching pulps, I find I can use a rather simple method of bleaching wherein the pulp is treated for a time with chlorin in water; in a liquor having HCl acidity. After the chlorin has acted for a time, and is partially consumed, I make the liquid alkaline with lime. Soda can be used but lime serves. Action of the chlorin is now in an alkaline solution; that is, as a hypochlorite. This double stage treatment with chlorin may be sufficient. But in many cases, I repeat the bleaching operation, adding a fresh portion of the alkaline bleach liquor to the drained, or drained and washed, pulp. At the end of this operation, the pulp may be regarded as commercially bleached. It is freed of lignin. But, because the bleaching has not been very drastic, there is still residual color, which is removed in the way hereinbefore stated.

In the present invention, after bleaching as stated, I acidulate the fiber with an acid in diluted solution. Dilute sulfuric acid is satisfactory. The acid may be added directly to the more or less exhausted bleach liquor, or the exhausted bleach liquor may be drawn off and the weak acid added. In either event I use with the acid a certain amount of an antichlor; generally sodium sulfite. SO_2, as a gas or as a solution may be used both as the acid and as the antichlor. When the pulp is well washed after the alkaline hypochlorite bleaching, but little acid is needed to break up residual color and little or no antichlor may be required to protect the fiber.

In the acid-treated fiber, the residual color is dissolved or solubilized or in some way affected so that it is made susceptible to the action of free HOCl. Following the acidification, the pulp is advantageously drained and washed, and then on addition of a small amount of HOCl, the residual color disappears. The action is not a bleaching of the fiber in the sense of the usual removal of lignin, but it is simply the destruction of a small amount of something present in hue-giving amounts. In treating a particular pulp in the way just described, the whiteness of the pulp as it left the alkaline bleach was 90 on the arbitrary color scale employed. After the acid and HOCl treatments, it was 100 or better on this same scale.

The improvement in color in the present process is, as stated, greatest with draft or other pulps, resulting from alkaline digestion; but it is substantial in the case of acid pulps, such as sulfite pulp.

The bleaching process given is merely exemplificatory. In another bleaching process which I regard as better for certain pulps, there is a triple treatment. A suspension of the pulp in water receives an addition of about enough chlorin for effectual bleaching and passes through the system as a flowing current in which the chlorin acts first as such, that is, in a solution having HCl acidity. The HCl is then neutralized with calcium carbonate, or a small amount of lime. Action is now by free HOCl. After a time, the current is made alkaline, continuing the bleaching action in a hypochlorite solution. In this method of operation, good bleaching is attained. With some pulps, it is desirable to give a further bleaching with a little alkaline bleach liquor. In either event, however, the pulp leaves the system in an alkaline condition and with some pulps there remains some of the residual non-lignin color described. There is considerably less of this residual non-lignin color than with the first described method of bleaching; but there is usually some, and in most cases, there is enough to give an undesirable hue to the bleached pulp. For this reason, the bleached pulp is advantageously treated under the present invention; it is first soured with dilute sulfuric acid and a little sulfiite and is then, preferably after filtering, treated with HOCl, as previously described.

In the HOCl treatment of the present invention, the free HOCl may be formed in situ by adding chlorin directly to the pulp in the presence of added base which neutralizes the HCl acidity of chlorin water. Or it may be formed elsewhere by contacting a chlorin solution with calcium carbonate.

In a specific embodiment of the present invention, using the first described method of bleaching, a hard bleaching kraft pulp was made into a 2.5 per cent suspension in water. To this suspension, I added six pounds of chlorin per 100 pounds of pulp (dry weight). The chlorin was allowed to act in acid solution for five minutes, and then enough milk of lime was added to make the liquid alkaline, and the reaction was continued for a further period of 20 minutes, when the chlorin was exhausted. Following this, the pulp was washed and a fresh supply of alkaline bleach liquor was added equivalent to an additional two per cent of chlorin, which was allowed to react practically to exhaustion. This gave a pulp sufficiently freed of lignin but still exhibiting an undesirable color. In this particular instance, I therefore added to the exhausted bleach liquor 100 pounds of a 0.2 per cent sulfuric acid solution, together with 0.05 pounds of sodium sulfite. The acid broke down the combination of the color with the base and the sulfite disposed of residual chlorin. The pulp was then drained and then I added HOCl equivalent to ¼ pound of chlorin, making the HOCl by sending chlorin and water through a tower containing limestone fragments and thence directly into contact with the aciduated pulp.

Instead of making the HOCl solution separately, chlorine and calcium carbonate may be added directly to the acidified pulp if so desired.

In the practice of the present invention, the amount of HOCl required in the final step is, as stated, extremely small and no special operations are required. After the acidulation and the treatment with HOCl, the pulp may be simply washed in the ordinary manner and then dried. The amount of HOCl required is, however, slightly larger in the first described process of bleaching, chlorin as such followed immediately by chlorin as hypochlorite, than in the second described method wherein chlorin is used first as such, then as HOCl, and finally, as hypochlorite. The intermediate HOCl treatment in this latter method has much the same function as the HOCl treatment in this invention; but in the bleaching operation, the HOCl is followed by an alkaline

treatment which resets on the fiber such residual color as has not been destroyed by the HOCl. For this reason, in the final treatment under the present invention, less HOCl is required than with the other method of bleaching, where alkalization follows immediately on treatment with chlorin.

What I claim is:—

1. The process of improving bleached paper pulp which comprises acidulating the bleached pulp in aqueous suspension, washing and thereafter treating the pulp with a neutral solution containing free HOCl having no acidity greater than that of HOCl and in amount sufficient to obviate residual color solubilized by the acidulation.

2. The process of improving paper pulp after bleaching by the aid of a chlorin-containing bleaching agent which comprises acidulating the bleached pulp in aqueous suspension in the presence of an antichlor, washing and thereafter treating the pulp with a neutral solution containing free HOCl having no acidity greater than that of HOCl and in amount sufficient to obviate residual color solubilized by the acid.

3. The process of claim 2 wherein the acid used for acidulation is dilute sulfuric acid.

4. The process of claim 2 wherein the antichlor used is a sulfite.

5. The process of claim 2 wherein the HOCl solution is produced in situ with the aid of chlorin and a base capable of uniting with HCl.

6. The process of claim 2 wherein the HOCl solution is made separately by contacting chlorin and water with a base capable of neutralizing HCl acidity and is thereafter added to the pulp.

7. In the manufacture of highly bleached mechanically strong paper pulps, the process which comprises bleaching a pulp with chlorin in several stages, the first treatment being in a liquid having HCl acidity and the final treatment in an alkaline solution of hypochlorite and thereafter slightly acidulating the pulp in the presence of an antichlor, washing and thereafter treating with a small amount of HOCl in a neutral solution to act on residual coloring solubilized by the acid under conditions precluding formation of HCl.

8. The process of claim 7 wherein the preliminary bleaching is first with chlorin in aqueous solution and then with chlorin in alkaline solution.

9. The process of claim 7 wherein the bleaching is first with chlorin in acid solution, second with chlorin as HOCl in the absence of HCl and, third, with chlorin as an alkaline hypochlorite.

10. A method of improving the whiteness of wood pulp bleached by an alkaline hypochlorite bleaching agent which comprises removing residual basicity from the bleached pulp and then treating the pulp with a neutral solution containing free hypochlorous acid under conditions precluding formation of hydrochloric acid.

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