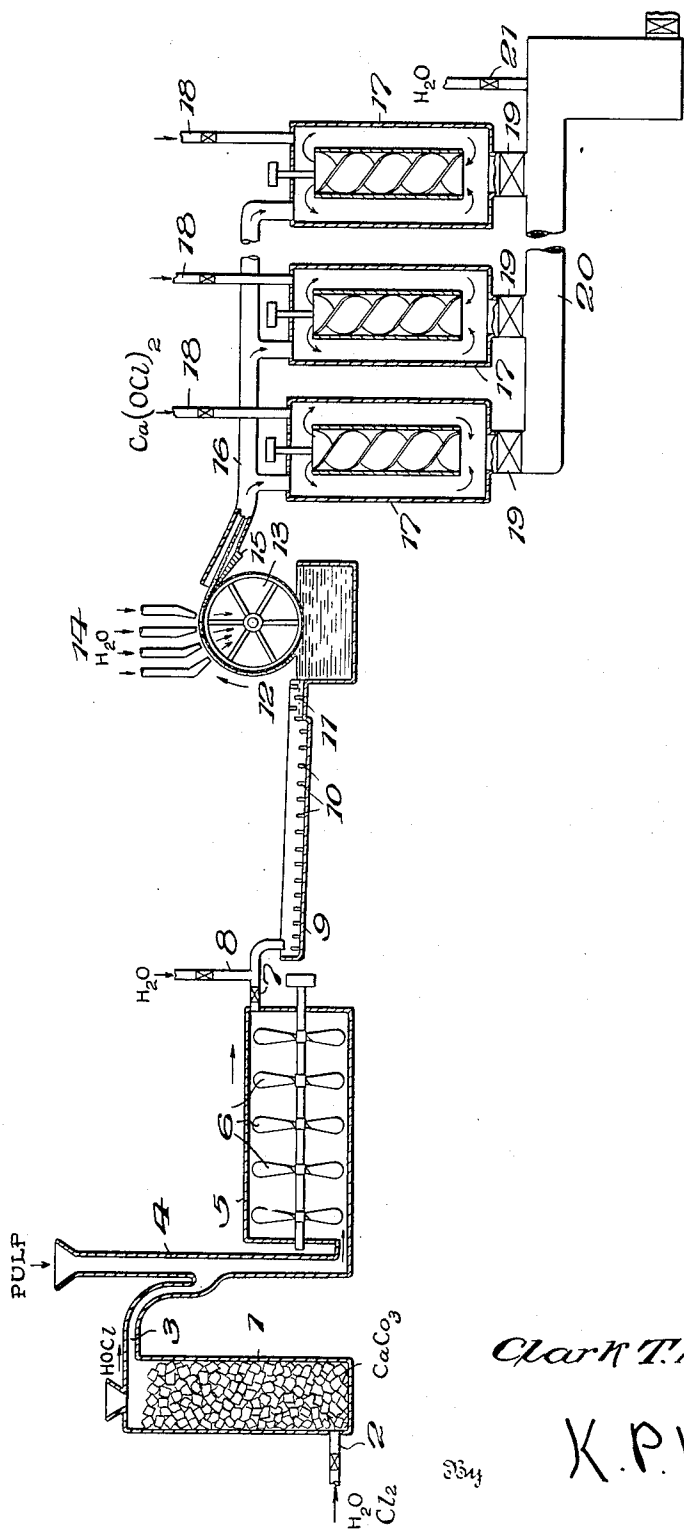


Feb. 12, 1935.

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PROCESS OF BLEACHING PULP
Filed Sept. 26, 1933

1,990,942



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UNITED STATES PATENT OFFICE

1,990,942

PROCESS OF BLEACHING PULP

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Application September 26, 1933, Serial No. 691,075

8 Claims. (Cl. 8—2)

This invention relates to processes of bleaching pulp; and it comprises a method wherein wood pulp and similar cellulose materials are submitted to a preliminary purification by the action of an aqueous liquid containing HOCl and made by passing chlorin and water into contact with calcium carbonate, the amount of this liquid, being such as to produce a dark liquor by reaction with the coloring matter of the pulp, the pulp is then drained and washed and the washed pulp is finally bleached with alkaline hypochlorite solution in an ordinary manner; all as more fully hereinafter set forth and as claimed.

The primary object attained in this invention is providing a process of bleaching pulp in which the total time and the chlorin requirements for complete bleaching and the fiber loss due to bleaching are all reduced; loss of strength in the fiber being also obviated.

Another result is the provision of a process of bleaching pulp or similar cellulose material wherein the pulp is first subjected to the chemical action of a particular aqueous liquid containing HOCl which can be made by bringing a solution of Cl_2 in water in contact with CaCO_3 . The pulp is then washed to remove coloring matter dissolved by the HOCl treatment and the washed pulp then is bleached with hypochlorite solution.

It has been ordinary practice to bleach pulp with directly applied hypochlorite solutions, such as the hypochlorites of sodium and of calcium; bleaching being carried on till commercially satisfactory bleached material is produced. Sometimes the whole bleaching is effected in one stage of operation and sometimes in two or more, with washing between stages.

I have discovered that pulp can be bleached with greater ease, less fiber loss and in most cases with a less total consumption of chlorin, if treated in the following manner:

The pulp is first subjected to the action of a reaction product resulting from the bringing of a solution of Cl_2 in water in intimate contact with CaCO_3 . This can be accomplished by passing the Cl_2 solution through a vessel containing subdivided CaCO_3 . Advantageously I introduce the Cl_2 solution at the bottom of the vessel and allow it to pass upwards through the CaCO_3 as this procedure reduces the tendency to pack and gives better results.

The action upon the pulp of this reaction product, which consists of a solution containing HOCl and CO_2 together with calcium chlorid and calcium bicarbonate, effects a dissolving of color.

The pulp remains in contact with the solution

until substantially all the "available chlorin" of the solution has disappeared. The contact between pulp and treating solution is made as intimate as possible by the use of agitating or stirring devices. When the available chlorin has disappeared the pulp is drained and washed. The liquors drawn off in the draining and washing are dark colored and carry much of the original coloring matter in the pulp.

The washing may be effected with either fresh water or with a solution of calcium hydroxide, $\text{Ca}(\text{OH})_2$, in water.

After the washing operation, the pulp is now bleached in the usual manner with a bleaching liquor containing sodium or calcium hypochlorite. It has been found that the time and total amount of available chlorin required to fully bleach the pulp is greatly reduced, the total time and total available chlorin requirements, including the chlorin required to make the HOCl solution for the preliminary treatment, being less than would be required if the bleaching were done with sodium or calcium hypochlorite alone, that is, without the preliminary HOCl treatment. It has also been found that pulp containing greater percentages of lignin and similar incrusting materials, and therefore being harder to bleach can be readily bleached because these incrusting materials are made soluble in the first step of the treatment and washed out prior to the bleaching.

The described treatment of the pulp may be considered as a purification preliminary to the actual bleaching. The chemistry involved is still obscure; but on treating the pulp with the proper quantity of a liquor made by passing chlorin water upwardly through a tower full of limestone chips, the treatment being continued until disappearance from the liquor of "available chlorin" (HOCl), non-cellulose constituents of the pulp are brought into solution to form a dark liquid; the color ranging from an amber to that of a dark beer. The pulp itself is not bleached and after washing, is usually somewhat darker than it was before the treatment. The actions involved were at first thought to be oxidation, but both oxidation and chlorination of lignin are precluded, since both involve the production of HCl. HCl is not produced from the HOCl in the present operation in substantial amount. Not more than about 15 per cent of the chlorin of the HOCl reappears as chlorin ion; that is, as hydrochloric acid or as a chlorid. The bulk of the HOCl disappears as such; it apparently goes into organic combination, forming bodies soluble in water, and perhaps of a chlorhydrin nature, which pass away with the

wash water. Whatever the chemistry involved, the HOCl, in this particular liquid and under these particular conditions, acts to solubilize non-cellulose constituents of the pulp, rather than to oxidize or chlorinate them.

The liquid delivered from the top of the tower contains hypochlorous acid, calcium chlorid and carbon dioxid (carbonic acid), as well as some calcium carbonate held in solution as bicarbonate. It contains no free HCl and the acidity of the hypochlorous acid is negligible, but the liquid has CO₂ acidity; it has the acidity due to the presence of calcium bicarbonate and free CO₂. It is, however, actually basic in the sense that the contained calcium bicarbonate will react with HCl. The amount of calcium bicarbonate in this tower liquor varies somewhat with circumstances, but the amount present has significance. The liquid as it enters the pulp treater has CO₂ acidity only and is not corrosive to apparatus. This enables the use of cheap structural materials and cheapens the cost of installation. The amount of HCl developed in the operation is very small and the dilution, great. Insofar as calcium bicarbonate is present, it takes care of this HCl. I have found that it is often desirable to supplement the calcium carbonate in the tower by additions of calcium carbonate to the tower liquor as it passes through the pulp treater. This takes care of the minimal amount of HCl developed and also preserves the initial CO₂ acidity.

The amount of tower liquor used varies with the pulp; with the amount of non-cellulose (lignin) in the pulp. I do not use sufficient of it in any case to produce any considerable bleaching of the pulp. The best results are obtained by using such an amount that the contained HOCl just disappears at a time when nearly all the non-cellulose has been rendered soluble and forms a dark liquor. This precludes any chemical attack on the fiber by the HOCl; and also the bleaching thereof.

In the present invention it is the object to treat the pulp with the described solution, HOCl, in such an amount and at such a dilution that complete exhaustion of available chlorin (HOCl) in the solution and the production of a dark liquor occur together. In this treatment the fiber itself remains unbleached; in fact, as stated, after the HOCl treatment followed by draining and washing the sheet pulp is often darker than the original raw pulp.

In the bleaching of most pulps by the present invention the total consumption of chlorin is kept below that required in prior processes generally. In many cases the total amount of chlorin used ranges between 80 and 85 pounds of chlorin per ton pulp on an air dried basis. Of this amount usually between 50 and 70 per cent is applied in the first stage as the available chlorin of hypochlorous acid and the remainder is applied in the bleaching with calcium hypochlorite. With a pulp consistency around 3 to 4 per cent, the hypochlorous acid solution added in the first stage is or may be in a concentration between 10 and 15 grams of available chlorin per liter. This concentration of available chlorin is substantially greater than that applied in most prior chlorination processes. Nevertheless the acidity of the pulp magma remains substantially less.

In the final or bleaching stage of the process a relatively small quantity of chlorin as hypochlorite bleach liquor is required and the bleaching action is rapid. The preliminary treatment with HOCl of the lignin and similar incrusting

and coloring matter and their removal when the pulp is washed lightens the load on the bleaching step. In this step the pulp may be in a substantially higher consistency than that in the first step. A consistency about 15 to 20 per cent is in most cases practicable and advantageous. In bleaching, either sodium hypochlorite or calcium hypochlorite may be used; bleaching being in the usual manner and with the usual apparatus.

The process is advantageously applied to the bleaching of most pulps in a continuous preliminary HOCl treatment and continuous draining and washing combined with a discontinuous or batch method in the final or bleaching step. This combined continuous and batch method of operation permits of adjusting the final bleaching to meet variations in the raw pulp. It has the advantage of permitting close control of the quantities of materials used in the preliminary treatment and the time of treatment so as to maintain uniform conditions.

In the accompanying drawing I have shown in more or less diagrammatic form an organization of apparatus useful in carrying on the described process.

In this showing the figure is a view in vertical section, partly in elevation, of apparatus adapted for the combined continuous and batch method of applying the process. The figure may be taken to represent a flow sheet of the process.

A tower 1 is packed with ordinary limestone in lump or chip form and chlorin and water are introduced near the bottom of the column through a valved inlet 2. From the top of the tower, through an outlet 3, a solution containing free hypochlorous acid, HOCl, together with calcium chlorid, calcium bicarbonate and CO₂ in solution is led to a conduit 4 through which a pulp magma of the desired consistency is introduced into the bottom of a treatment tank 5 provided with stirring or agitating means of usual form and designated 6. The treatment tank is of suitable horizontal length and cross sectional area to permit a desired rate of progression of the magma through the tank so as to adjust the time of the preliminary HOCl treatment; the pulp magma being, as shown, introduced near the bottom of the tank at one end and withdrawn from near the top of the tank at the other end through a valved outlet 7. As shown, the outlet 7 is provided with a valved inlet 8 for introducing water into the effluent magma. The outlet delivers into a riffle-box 9 with an open top and provided with a series of horizontal riffles 10 over which the magma trickles in order to maintain its consistency uniform and to settle out particles of dirt. From the riffle-box the magma runs through a baffled inlet 11 into a screen filter of a usual type shown at 12. In the filter, pulp is separated from the liquor and collected in a sheet upon the screen cylinder 13 within which a vacuum is maintained by applying suction thereto. A series of water jets 14 are shown and the sheet of pulp is washed with water as the cylinder 13 revolves. A doctor 15 scrapes the sheet of pulp from the cylinder and the sheet pulp is conveyed as by a suitable belt conveyor 16 to be introduced into bleaching tanks 17 in separate batches. The bleaching tanks may be of the usual type. Hypochlorite bleaching solution is introduced into the several bleaching tanks through valved inlets 18. From the bleaching tanks the magma of bleached pulp and spent bleaching liquor is removed through outlets 19 and run through conduit 20 to a place for further disposal. In the conduit water may

be added to the pulp magma through a valved inlet pipe 21.

In continuous operation of the preliminary HOCl treatment, pulp of desired consistency is fed to the treatment tank 5 through conduit 4 with addition of the treating solution in a desired proportion from tower 1; the tower being so designed that the liquid flow through the tower gives a time of contact with the limestone sufficient to dissolve a substantial amount of the lime as bicarbonate. However, finely divided calcium carbonate may be added, if desired, to the pulp in conduit 4.

In the treatment tank the mixture of pulp magma and tower effluent is slowly stirred and the rate of feed of pulp and admixed tower effluent controls the time of treatment; 20 to 30 minutes being usually sufficient. The pulp magma runs continuously from the treatment tank and over the riffles 10 where dirt may settle out. Thence the pulp runs to the filter where it is continuously collected in sheets, washed and conveyed to one of the several bleachers 17. These are used in succession. Bleaching in separate batches permits variation of the bleaching time and uniform control of the bleaching operation.

While the described process is applicable to bleaching of wood pulps and paper pulps and cellulosic materials generally, particularly advantageous results have been obtained in bleaching pulps of the type known as "hard bleaching" such as hard bleaching sulfite and kraft wood pulps. Hard bleaching pulps have a strong fiber, but the strength of fiber is apt to be lessened by the drastic bleaching required. In the present process, the preliminary treatment with hypochlorous acid in a weakly acid solution may be said to convert a hard bleaching pulp into an easy bleaching pulp, with a reduction of the amount of bleach liquor used in the bleaching proper more than sufficient to compensate for the chlorin used in the preparation of the hypochlorous acid solution. It has been found that the strength of the fiber remains substantially higher than when the pulp is bleached to the same commercial grade in ordinary bleaching methods using hypochlorite alone. In one case, the bleached pulp produced by the present process when compared with that produced by ordinary hypochlorite bleaching showed an increase of 10 points in the Mullen test, an increase of 60 per cent in fold test and of 40 per cent in tear test. The alpha cellulose content was increased from 81.30 per cent to 85.15 per cent and the copper number was lower, being 4.41 instead of 4.88. The chlorin consumption was lowered about one-third. In other words, there was a better product and a less consumption of chlorin. The operation was also quicker. The apparatus required is simple and inexpensive.

In preparing the hypochlorous acid solution, instead of limestone I can use marble chips, chalk or any other form of calcium carbonate. Dolomite chips are also applicable, the magnesium carbonate therein being attacked by the chlorin water with CO₂ evolution and formation of another alkaline earth bicarbonate in addition to the calcium bicarbonate. It being a matter of neutralizing HCl without also neutralizing HOCl, any carbonate of a normally alkaline base

is applicable, which is converted by chlorin water into a soluble bicarbonate. The alkaline earth carbonates such as calcium and magnesium carbonates react readily with chlorin water to give a solution containing free hypochlorous acid together with the corresponding chlorids and bicarbonates and with CO₂ acidity due to the bicarbonate and to dissolve CO₂ formed from the original carbonate.

This application is a continuation-in-part of 10 application Serial No. 390,376, filed Sept. 4, 1929.

What I claim is:—

1. In the bleaching of wood pulp and similar cellulose materials, the process which comprises passing chlorin and water into contact with fragmental limestone, treating wood pulp with the effluent liquor in such amount that all available chlorin therein can be exhausted without bleaching the pulp, draining and washing the pulp and thereafter bleaching the pulp with a hypochlorite bleaching solution.

2. In the process of claim 1, adding solid calcium carbonate to the pulp during treatment with said effluent liquor.

3. In bleaching wood pulp with a solution of an hypochlorite of an alkaline or alkaline earth metal, an improvement which comprises the preliminary steps of treating the pulp with a solution of free hypochlorous acid containing also calcium chlorid, calcium bicarbonate and dissolved CO₂, said solution being limited in amount to that sufficient to produce a dark liquor and insufficient to bleach the pulp, and of draining and washing the pulp prior to the bleaching.

4. A method of bleaching wood pulp and similar cellulose materials which comprises a preliminary step of treating pulp in a continuous flow with an aqueous solution containing HOCl together with chlorid and bicarbonate of an alkaline earth metal and dissolved CO₂ in amounts required to give a dark liquor and unbleached pulp, an intermediate step of continuously draining and washing the treated pulp and a subsequent step of bleaching the washed pulp in batches with a hypochlorite bleaching solution.

5. In the bleaching of wood pulp, the process which comprises preparing a solution containing free HOCl together with an alkaline earth chlorid and bicarbonate and dissolved CO₂, treating pulp with said solution in merely the amount required to give a dark liquor and an unbleached fiber, washing out the dark liquor and thereafter bleaching the fiber.

6. In the process of claim 5, maintaining a CO₂ acidity throughout the HOCl treatment.

7. In the bleaching of wood pulp and similar cellulose materials, the process which comprises passing chlorin and water into contact with fragments of an alkaline earth carbonate to make a liquid effluent containing HOCl, alkaline earth chlorid and bicarbonate and dissolved CO₂, treating the pulp with said effluent in an amount insufficient to bleach the pulp, draining and washing the pulp and thereafter bleaching the pulp with a hypochlorite bleaching solution.

8. In the process of claim 7, adding solid alkaline earth carbonate to the pulp during said HOCl treatment.

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