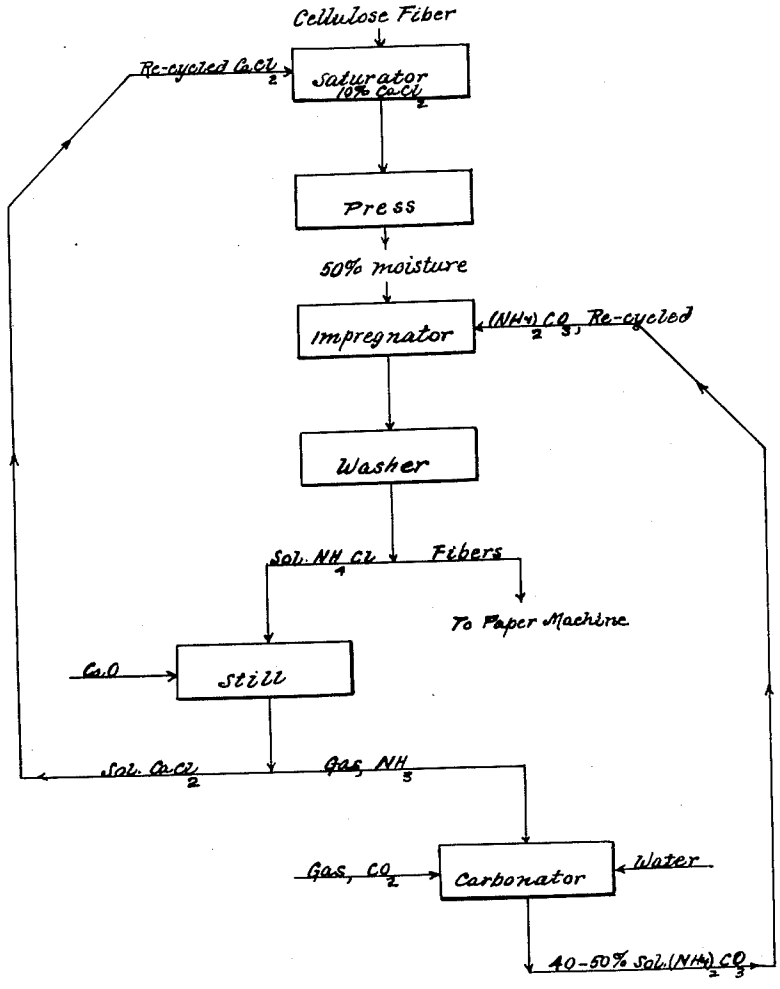
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METHOD OF INCREASING THE OPACITY OF CELLULOSE FIBERS

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METHOD OF INCREASING THE OPACITY OF CELLULOSE FIBERS

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The paper industry is confronted today with a difficulty inherent in the property of cellulose, to wit: a compromise between whiteness, of more properly "brightness" of the finished sheet, and the desire to have such a sheet of paper so opaque that any printing on the back of said sheet will be free from "show-through," in the language of the printer.

The desire for whiteness leads to ever more drastic bleaching methods, the latest being the use of chlorine dioxide. Unfortunately, the perfect removal of non-cellulose matters by such technique also results in the bleached fiber becoming somewhat transparent. This fault is, in turn, corrected by the addition of pigments, or loading material, varying from cheap clay to expensive titanium dioxide. But unless the amount of such loading material be kept quite small there will be a serious loss of strength in the finished sheet, the reason being, of course, that proper bonding of the fibers to one another is adverseiy effected by the presence of such foreign material. Every sheet of paper where both whiteness and opacity is desired is, therefore, a compromise between all these sundry factors.

To understand just how I have corrected this difficulty it is necessary first of all to consider the structure of the cellulose fiber. If the fiber, per se, as liberated in pulping and without bleaching, is examined under the microscope it presents the appearance of a hollow tube, the cell wall itself being often perforated by many tiny apertures between the outside surface and the hollow, central canal. On bleaching the cell wall itself is attacked. It is an open question just how the lignification that still exists is produced, whether it is a mere mechanical mixture or a true chemical combination. Exponents of the latter theory postulate the presence of a compound called "Lignocellulose." Be that as it may, in perfectly bleached pulp there has been a definite attack upon said cell wall and it becomes minutely "scarred" by the removal of such material. Simultaneously, the un-wanted transparency is produced, and it is obvious that a large internal area has come into existence.

It is the aim and object of my process to coat this internal area with the loading material and as much as possible to fill the internal pores as well with solid pigment of some type. Naturally, this can only be done if said pigment is precipitated in situ, any mere admixture of solids, in the beater or elsewhere, can never reach the interior of the fiber nor can it really be attached to said fibers. Contrariwise, the sheet can only be a haphazard mixture of fiber and pigment, hence, the inevitable loss of strength. It has long been known that pigment precipitated in the beater is far better than a mere mixture, thus: If calcium chloride be added to the beater and subsequently precipitated with soda ash then a better sheet results than if the same amount of dry, precipitated chalk be added to the beater.

It is well known that the "retention" of said pigment is enhanced by its method of application, but perhaps the lesson that might have been learned is not quite so simple. Obviously, owing to the great dilution in the beater, stock rarely being above 6%, the precipitate of calcium carbonate is produced essentially between said fibers and not within them, yet there is a tendency in that direction which accounts for the improvement in the finished sheet. There

is also some adhesion on the outside of said fiber which is unobtainable if a dry, finished pigment be added to the beater.

My process consists in carrying out said precipitation in partially dehydrated pulp, a substance far too stiff to be mobile in any manner. I place the limits as obtained from tests between a pressed sheet having two parts of water to one of fiber and a more strongly pressed sheet having two parts of fiber to one of water, or approximately between 30% and 70% of moisture as specified in the claims. The first is readily obtained from the presses of the conventional pulp drier, and the latter can be obtained by further pressing of said sheet in a differential screw-press, or any screw or hydraulic press. Obviously, the type requiring the least amount of labor is to be preferred.

In operation, I use a 5% to 20% solution of a salt of the base of the selected pigment, fully saturate the fiber and then press to reach the predetermined moisture content. A strong solution of the precipitating chemical is then added and enough time is given so that diffusion will produce complete reaction between the two solutions. Obviously, the amount of pigment thus added depends upon two factors: to wit, amount of solution retained in the fiber on pressing, and the percentage of the metallic salt resident in said solution. After complete reaction, the pulp is washed with water so as to obtain a well washed pulp and minimum dilution of the soluble material which must be recovered as an item of economy and that it may not accumulate in the white water from the paper machine.

As bases I employ either calcium, magnesium, or zinc. As the precipitating chemical I use always a salt of ammonium, either the carbonate, the hydroxide and/or the sulphide. The bases are used either as chlorides or as sulphates so the ultimate soluble salt removed by washing the fiber is always the chloride or the sulphate of ammonium. I will now give a specific instance in each case involved. The first of these examples is represented on the drawing attached hereto, and in conjunction with the text will be found self-explanatory.

(1) The fiber is first suspended in a 10% solution of calcium chloride, pressed to a moisture content of 50% and sprayed with a concentrated solution of ammonium carbonate in sufficient amount to precipitate all the calcium as the carbonate. Sufficient time is allowed to elapse to ensure complete precipitation and the fiber is then washed. I prefer to do this with downward displacement but that is optional. The washed fiber is ready for the paper machine and will contain approximately 10% of loading material. Continued washing, with some mechanical violence, will but remove about 2% so it is obvious that the calcium carbonate is largely retained within the structure of the fiber. The solution washed out of the pulp is essentially ammonium chloride. Slacked lime is added to this solution in the conventional ammonia still and ammonia is evolved on heating. The still liquor is a solution of calcium chloride, suitable for impregnating another batch of pulp. The evolved ammonia is commingled with gases containing carbon dioxide and absorbed in water in a convention coke-packed tower yielding a solution of approximately 40%–50% ammonium carbonate, suitable for precipitating another batch of calcium chloride-impregnated fibers. Calcium carbonate is thus made directly from slacked lime, while both chlorine and ammonia is re-cycled instead of wasted, making my process very economical, as well as very effective. The pulp on drying is very white and opaque, with little loss of strength in spite of the heavy loading.

It will be obvious that magnesium could be substituted throughout for calcium the loading material thus becoming the even whiter magnesium carbonate. Similarly,

any intermediate mixture of both could be used. Zinc could likewise be used but there would be a little change in handling the ammonia wash water. It would not be possible to use zinc oxide direct in decomposing the ammonia solution, but if lime were used, as herein, then a very low grade type of zinc oxide, such as roasted ore, could be commingled with the calcium chloride solution and carbon dioxide passed through. The result would be a very pure solution of zinc chloride, to initiate the impregnation, and if it were then precipitated with ammonium carbonate the loading material would become zinc carbonate.

(2) The pulp is suspended in a solution of magnesium sulphate of 10% strength, pressed to a moisture content of 50% and sprayed with a concentrated solution of ammonium carbonate in sufficient amount to precipitate all magnesium as the carbonate. Sufficient time must elapse to ensure complete precipitation and the fiber is then washed. Said fiber is ready for the paper machine and will contain approximately 9% of magnesium carbonate. The wash water is evaporated to dryness and fused at approximately 350° C. with evolution of one-half of the resident ammonia which is converted to carbonate in water solution as before. The fused residue is ammonium bi-sulphate which serves in place of sulphuric acid to produce the magnesium sulphate required in the impregnation step. Any source of magnesia may be used as raw material. In this way, very cheap raw material is made available and the excellence of the impregnated fiber is much enhanced. Obviously, zinc can be substituted for magnesium at will, but calcium cannot be used owing to the slight solubility of calcium sulphate.

(3) In this example the only metal involved is zinc as the object is to impregnate the fiber with zinc sulphide, the pigment which stands next to titanum dioxide in covering power. The fiber is therefore saturated with a zinc solution. Either the chloride or the sulphate may be used. After pressing to the desired moisture content precipitation is made with ammonium sulphide, best made by commingling ammonia, hydrogen sulphide, and water in a coke packed tower as described under Example 1. After washing the pulp will be ready for the paper machine. Unless particularly high opacity is wanted a weaker solution or a harder pressing than previously used will suffice, owing to the far greater covering power of the zinc sulphide. All such matters are optional. If a chloride solution is used then the wash water will be a solution of ammonium chloride. It is commingled with lime in a still, the ammonia distilled off and used to make fresh ammonium sulphide. The still liquor is a solution of calcium chloride. This is now commingled with some cheap type of zinc oxide, such as a crude roasted ore, washed chimney gas or any gas containing carbon dioxide is passed until the zinc is in solution as chloride and the resident calcium precipitated as the carbonate. If the sulphate be selected, then the wash water is evaporated to dryness, further heated to form the bi-sulphate, the evolved ammonia recovered in water and further treated with hydrogen sulphide to form new ammonium sulphide. The bi-sulphate is then dissolved in water, used to dissolve fresh zinc from roasted ore, the solution conventionally purified until it gives only a white precipitate with ammonium sulphide, and then re-cycled to precipitate another batch of fiber. It is manifestly impossible to substitute anything for zinc and a sulphide in this example.

Under some exceptional circumstances, it might be desirable to precipitate magnesium or zinc as the hydroxide by substituting ammonium hydroxide for carbonate or sulphide, said precipitated hydroxide being subsequently further treated to improve its opacity. This may be done by carbon dioxide, by hydrogen sulphide, or by a water solution of a titanium salt of which the most suitable is the fluoride. Having thus fully described my process, I claim:

1. The method of increasing the opacity of cellulose fiber which comprises; saturating said fiber with a 5% to 20% solution of a chloride selected from the group consisting of calcium and magnesium; removing such a portion of the saturating solution that the moisture content of the resulting fiber shall be between 30% and 70%; commingling with said moist fiber a sufficient amount of a solution of ammonium carbonate to precipitate all of the resident metal as the corresponding carbonate; washing the resultant fiber substantially free from ammonium chloride, thus obtaining said ammonium chloride in strong solution; commingling said ammonium chloride solution with sufficient hydroxide of the metal selected to decompose said ammonium chloride and heating to expel ammonia; re-cycling the resulting chloride solution, after adjustment to the initial strength, as a regenerated saturating solution to fresh fiber; commingling the ammonia previously obtained with water and with a gas containing carbon dioxide to produce a solution of ammonium carbonate for re-cycling to a fresh precipitation of metallic carbonate.

2. The method of increasing the opacity of cellulose fibers which comprises; saturating said fiber with a water solution of a salt of a metal selected from the group consisting of calcium, magnesium and zinc, said solution containing from 5% to 20%, by weight, of the selected salt; removing such a portion of the solution that the moisture content of the resulting fiber shall be between 30% and 70%; commingling said moist fiber with a sufficient amount of a solution of an ammonia salt suitable for precipitating the resident metallic salt in a substantially insoluble, white, form, within and upon the aforesaid fiber; washing the resultant mixture of fiber and precipitate substantially free from soluble ammonia salt, thus obtaining same in a strong solution; separating said ammonia salt into its acid and basic components by combining the acid portion with a fresh supply of the selected metal, and liberating the ammonia for re-use in forming a regenerated ammoniacal precipitating liquor; finally re-cycling both combinations to saturate and precipitate a white substance upon fresh fiber.

3. The method of increasing the opacity of cellulose fiber which comprises; saturating said fiber with a solution of zinc sulphate containing from 5% to 20% of said salt; removing such a portion of the saturating solution that the moisture content of the resulting fiber shall be between 30% and 70%; commingling with said moist fiber a sufficient amount of a solution of ammonium sulphide to precipitate all resident zinc as the sulphide; washing the resultant fiber substantially free from ammonia salt; evaporating said solution and heating the dried residue to decompose same into ammonium bi-sulphate and free ammonia; converting the latter into ammonium sulphide for a fresh precipitation and neutralizing the ammonium bi-sulphate in water solution with zinc to re-form a fresh saturating solution.

4. The method of increasing the opacity of cellulose fibers which comprises; saturating said fiber with a 5% to 20% solution of a sulphate selected from the group consisting of magnesium and zinc; removing such a portion of the saturating solution that the moisture content of the resulting fiber shall be between 30% and 70%; commingling said moist fiber with a sufficient amount of a solution of ammonium carbonate to precipitate all of the resident metal as the corresponding carbonate; washing the resultant fiber substantially free from ammonium sulphate; evaporating the resultant solution to dryness and fusing the contained solids with evolution of ammonia and formation of ammonium bi-sulphate in fused form; converting the evolved ammonia into ammonium carbonate and dissolving zinc-bearing material in a solution of the bi-suphate formed in said fusion step; purifying said zinc solution and re-cycling it to saturate fresh fiber; and re-cycling the solution of ammonium carbonate to the precipitation step of the process.

5. The method of increasing the opacity of cellulose

fiber set forth in claim 4, with the added step that the washed mixture of fiber and metallic carbonate obtained therein be further treated by commingling it with a solution of titanium fluoride before forming into a sheet.

6. The method of increasing the opacity of cellulose fiber set forth in claim 2, with the added step that the washed mixture of fiber and precipitate obtained therein be made still more opaque by commingling said mixture with a solution of titanium fluoride before it be formed into a sheet.

7. The method of increasing the opacity of cellulose fibers which comprises; saturating said fiber with a 5% to 20% solution of a sulphate selected from the group consisting of magnesium and zinc; removing such a portion of the saturating solution that the moisture content of the resulting fiber shall be between 30% and 70%; commingling said moist fiber with a solution of ammonium hydroxide to precipitate all resident metal as the corresponding hydroxide; washing the resultant fiber substantially free from ammonium sulphate; evaporating the resultant solution and fusing the contained solids with

evolution of ammonia and formation of ammonium bi-sulphate in fused form; dissolving the ammonia evolved in water to re-form the hydroxide previously specified, and neutralizing the solution of the fused bi-sulphate with suitable material to reform the saturating solution previously specified.

8. The method of increasing the opacity of cellulose fibers set forth in claim 7, with the added step that the opacity of the fiber-precipitate mixture be further increased by commingling same with a compound selected from the group consisting of carbon dioxide, hydrogen sulphide, and titanium fluoride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,006,016	Eide et al.	June 25, 1935
2,080,437	Rafton	May 18, 1937
2,583,548	Craig	Jan. 29, 1952
2,676,884	Hamburg	Apr. 27, 1954