

UNITED STATES PATENT OFFICE

2,599,092

MULTIPLE LAYER PAPER CONTAINING PIGMENTED PULP AND METHOD OF MAKING

William Lutton Craig, Westport, Conn., assignor to R. T. Vanderbilt Company, Inc., New York, N. Y., a corporation of New York

No Drawing. Application April 30, 1946,
Serial No. 666,199

10 Claims. (Cl. 92—3)

1

This invention relates to improvements in paper manufacture, and more particularly to laminated or multilayer paper or board such as container board for making folding boxes and cartons, etc. The invention includes an improved process of making such paper or board and the improved product so produced.

The present invention enables an improved coated paper to be produced on the paper making machine, with a pigmented coating applied as a part of the paper making operation.

The manufacture of laminated or multi-layer paper or board is commonly carried out in cylinder machines having a number of cylinder vats and cylinder molds, each separately supplied with the desired stock, and each forming a layer, with the layers combined to form the final sheet of multi-ply paper or board, the number of layers depending upon the number of cylinder vats and molds in use. The outside layers of the composite or multi-ply paper or board are formed from stock from the first and last vats and molds and are called liners; and the intermediate layers are called fillers, and are commonly made of less expensive stock.

In such cylinder machines the stocks are supplied from the stuff chests to regulating boxes and from the regulating boxes to the cylinder vats, each containing a cylinder having a cylindrical screen on which a layer of partially formed wet paper is produced, which is transferred to a felt. The successive layers of partially formed wet paper from the cylinder molds form a composite or multi-ply series of layers, which are carried with the felt between rolls to squeeze out water and to compact the layers, after which the sheet passes through press rolls to drying cylinders and to calenders where a size may be applied. This method of forming laminated or multi-layer paper or board, and one form of apparatus therefor, are described, for example, in vol. V of "The Manufacture of Pulp and Paper" (2nd Edn.) section 1, pages 251-264 (McGraw-Hill Book Company). Such composite multi-layer paper or board can similarly be produced in multi-Fourdrinier and other machines.

The improved process of the present invention can advantageously be carried out in such cylinder machines to give an improved coated board or sheet without subsequent coating of the finished sheet or board in a coating machine.

According to the present invention, the composite sheet or board is provided on one side or on both sides with a surface coating layer or liner in the form of a specially prepared pigment-fiber

2

layer or fibrous pigment of highly pigmented, modified cellulosic fibers, or a layer containing such highly pigmented modified cellulosic fibers admixed with untreated fibers, which layer or liner, when sized, gives an improved coated board or sheet on a paper-making machine and without subsequent machine coating of the dried board or sheet.

The present invention is based upon the discovery that a portion of the cellulosic fiber stock (chemical, semi-chemical, or mechanical pulp) used in making paper, including cellulose fibers (chemical pulp) such as kraft, sulfite, soda pulp, etc., and particularly groundwood (ligno-cellulose) fibers (mechanical pulp), can be treated in the form of a suspension in water or pulp with calcium chloride in the form of a strong solution to modify the cellulose or the ligno-cellulose and that the so modified cellulosic fibers can then be treated with a solution of a soluble salt such as sodium carbonate to precipitate an insoluble pigment such as calcium carbonate within the modified fibers as well as on and around the modified fibers; and that the resulting modified and pigmented stock, containing the pigmented modified fibers, is particularly valuable for forming the liner or surface layer of a composite multi-layer sheet or board, or for use in admixture with untreated fibers for forming such liner or surface layer.

The cellulosic fibers which are treated to form the pigmented modified cellulosic fibers include cellulose fibers such as chemical pulp (sulfite pulp, sulfate pulp, soda pulp, etc.) as well as semi-chemical pulp and groundwood fibers (mechanical pulp), as well as mixtures of such fibers or pulps.

The cellulosic fibers are advantageously treated in the form of a relatively concentrated pulp or stock. Thus, stocks containing up to 4% or 5% or more of fibers (dry basis) are advantageously treated, and the treatment is also applicable to much more concentrated stocks at a stock consistency as high as 13% or higher, where higher concentrations are available.

The stock treated may be bleached or unbleached stock and may be stock which has been beaten in a beater, particularly in the case of long fiber chemical pulp or unbeaten disintegrated stock.

The treatment of the fibers in suspension in water is carried out with the addition of calcium chloride in sufficient amount to give a relatively strong calcium chloride solution of sufficient strength to modify the cellulose or ligno-cellu-

lose of the fibers. Solutions up to saturated solutions of calcium chloride can be used, e. g., solutions of around 15% to 20%, more or less of calcium chloride.

When solid calcium chloride is added to and dissolved in stock containing e. g. up to 4 or 5% of chemical pulp, it brings about a profound modification of the cellulose fibers after a few minutes, e. g., 5 to 10 minutes, with proper agitation. The fibers become more or less gelatinous and transparent in appearance. It may be the calcium chloride combines with the cellulose to form complex products, or it may be the calcium chloride exerts a modifying or hydrating effect upon the cellulose molecules. Whatever the theoretical explanation of the action of the calcium chloride on the cellulose may be, it brings about a profound change in the nature and appearance of the cellulose fibers. Similarly, when semi-chemical pulp or groundwood fibers are similarly treated with calcium chloride the action is to bring about a profound change in the nature and appearance of the fibers.

After this treatment with calcium chloride the stock is treated with a solution of a soluble salt, such as sodium carbonate (soda ash) or sodium borate, e. g., in the form of a 10% solution in sufficient amount to react with the calcium chloride and precipitate an insoluble pigment, e. g., calcium carbonate or calcium borate in and on the modified fibers. The amount of added soluble salt is equal to or somewhat more or less than the amount which is sufficient to react with all of the calcium chloride used. With cellulose fibers the amount of soluble salt is advantageously slightly in excess of that required to react with all of the calcium chloride; but with groundwood fibers care should in general be taken to avoid any excess of the alkali salt which would darken or otherwise affect the stock; and with such stock the calcium chloride and sodium carbonate are used in exact reacting proportions or with a slight excess of calcium chloride to avoid any excess of sodium carbonate.

The resulting treated and pigmented stock is highly hydrated and has little strength, or relatively much less strength than the untreated stock, but it carries the precipitated pigment distributed within the hydrated fibers while pigment is also precipitated on the hydrated fibers and in the water in which the fibers are suspended.

The specially treated and modified and pigmented stock is highly pigmented. An amount of pigment can be combined with the stock which is considerably in excess of the weight of the stock treated (dry basis). Thus cellulose fibers can be modified and pigmented to give a proportion of pigment to stock (dry basis) of up to around two to one or more. Groundwood stock can be pigmented to a greater extent, up to around 4 parts of pigment to 1 of fiber (dry basis) or even higher.

The resulting stock containing the modified and pigmented fibers, with the pigment precipitated in and on and around the fibers, is used in the improved process of the present invention, either alone or admixed with untreated stock, in forming the coating or liner layer of the composite multi-layer paper or board.

The stock, after treatment with the soluble sodium salt, will contain e. g. sodium chloride in solution. When this modified and pigmented stock is used without admixture of untreated stock in making the coating or lining layer, it

may not be necessary to remove the sodium chloride, as most of the sodium chloride will be removed in the cylinder machine in the white water, and most of the remainder will be squeezed out by the pressure of the squeezing and press rolls. It is sometimes advantageous, however, to remove the sodium chloride solution by washing the treated stock, or to remove the greater portion of the sodium chloride solution and replace it with fresh water, particularly where the stock is mixed with untreated stock and the mixed stock is used for forming the coating or liner layer. The washing of the treated stock can be carried out by decantation or by washing in pulp washers, with replacement of the sodium chloride solution with fresh water, care being taken that the water drawn off is clear or relatively clear water to avoid or minimize loss of finely suspended pigment during the washing operation.

The modified and pigmented stock, before use in the last cylinder vat of the cylinder machine, may be diluted to proper consistency, e. g. around 1% of cellulosic fibers (dry basis) or somewhat less. This stock, in addition to its content of modified cellulose, will contain a high percentage of precipitated pigment. Some of the pigment may escape with the white water, but an amount can be retained in the surface layer so that this layer may contain e. g. from 40 to 80% of precipitated calcium carbonate distributed in and on and around the modified fibers.

The modified and pigmented stock, without admixture of untreated fibers, can advantageously be used in forming the coating or liner layer of the composite multi-layer pulp or board. This treated and pigmented stock is highly hydrated, and the liner layer formed therefrom has little strength or relatively much less strength than a layer formed from the untreated stock, but it nevertheless forms a valuable coating layer or liner for multi-ply paper or board.

This modified and pigmented stock can also advantageously be admixed with untreated stock, and the resulting mixed stock used in making the coating or liner layer of the composite multi-layer pulp or board. Thus, varying amounts of untreated stock, particularly cellulose fibers such as chemical pulp, can be admixed with the modified and pigmented stock to form a coating layer or liner for multi-ply paper and board which will have increased strength and which will also be heavily pigmented.

Where the modified and pigmented stock is thus admixed with untreated stock, varying proportions of the treated and untreated stocks can be used. For making coated board directly on the paper machine, the proportion of pigment in the liner or coating layer should, in general, be at least 50%, and advantageously considerably above 50%. A highly pigmented coated board can thus be produced which, after sizing on the calender rolls, gives a coated board directly on the paper machine which can be readily printed.

It is sometimes desirable to form multi-ply board with less pigment coating, e. g. around 30 to 40% pigment in the coating layer, to form a multi-ply paper or board which, when sized, can also be readily printed.

For highly pigmented coated board, it is desirable and advantageous, when untreated fibers are admixed with the modified pigmented stock, to use only a relatively small proportion of untreated stock, e. g. 10% or 20% of long fiber cellulose stock or other cellulose stock. Larger

percentages of untreated stock can be used, and even when 50% of the stock is treated and pigmented and 50% is untreated, a coating layer or liner can be formed which will contain considerably in excess of 50% of pigment (as determined by ash) as compared with the weight of fiber (dry basis). Thus, where 50% of the stock in the form of groundwood is treated to form a modified pigmented stock containing 4 parts by weight of pigment to 1 part by weight of fibers (dry basis) and when this treated stock is admixed with 50% of untreated cellulose stock, the weight of the pigment in the resulting stock and in the coating layer or liner formed therefrom may approximate twice the weight of the fibers (dry basis). When 80% of the stock such as groundwood is treated and admixed with 20% of untreated long fiber chemical pulp, the pigment content of the coating layer or liner may be around 75 to 80% of the weight of the coating layer or liner.

The process can be modified by adding organic binders, such as starch or casein, etc., to the stock before it is used on the cylinder machine, e. g. an amount equal to around 10%, more or less, based on the carbonate present.

In the carrying out of the process on a multiple cylinder machine, the new stock is used in the last cylinder vat, which produces the outer layer or liner of the composite sheet or board. Various stock can be used in the other cylinder vats, such as are commonly used in making multiple layer sheets and board, such as less expensive stock made from waste paper or reclaimed kraft, etc., for the intermediate or filler layers. Except for the use of the new pigmented and modified cellulosic stock for the outer layer or liner, the process can be carried out much the same as that now used in making multi-layer sheets or board, and with use of varying numbers of cylinder vats and cylinder molds to form composite sheets of from two to six or more layers, and with the outer layer or liner formed from the specially prepared and pigmented stock.

It is one advantage of the present invention that a particularly high proportion of pigment can be incorporated in the stock used for the outer layer or liner and that the proportion of cellulosic fibers can be relatively small. A single sheet of paper made from such stock would have little strength, but when used as an outer layer or liner for a multi-layer sheet or board, sufficient strength can be given by the other layers while the outer layer or liner is a highly pigmented layer which gives an improved pigmented finish to the sheet or board.

When the specially treated stock is formed into a sheet on the screen of the cylinder mold, the pigment tends to concentrate on the screen side of the layer, giving a smoother and more finished appearance to the sheet than would the outer surface of the layer. The outer surface with a more fibrous appearance is the surface picked up by the felt so that the pigmented surface formed on the screen is the outer surface of the composite sheet or board.

With highly pigmented stock containing a higher proportion of pigment than of fiber, and particularly with two or three or four times as much pigment as fiber, the dried composite sheet may contain so much pigment that it will tend to rub off unless protected. But by applying size to this surface of the sheet in the calenders, the size will hold the excess pigment and give a highly pigmented and sized surface with a uni-

form coating that completely covers all fibers and gives a pigment face with a high proportion of finely divided calcium carbonate pigment.

Finished sheets or boards can thus be produced with a white surface which can be printed, lacquered, etc.

The danger of removal of the surface pigment by dusting can also be reduced by adding binders to the stock before it is applied to form the surface layer or liner; and a further improved result can be obtained by sizing the sheet in the calenders in accordance with the common practice of applying sizing to sheets during the calendering operation.

Where the treated and pigmented stock is admixed with untreated stock, the untreated stock may be stock which is prepared e. g. in a beater in the ordinary way and which may be sized and prepared for use before the treated stock is added. The stocks are thoroughly admixed together before the composite stock goes to the cylinder vat, and the mixing is advantageously carried out at a point close to the cylinder vat.

Rosin soap and alum are commonly added to the untreated stock for sizing. Where untreated stock is admixed with the treated and pigmented stock, if the stocks after admixture are not sufficiently acid, a further amount of alum is advantageously added at the time of mixing or before the admixed stocks go to the cylinder vat or is added to the cylinder vat. The untreated stock may thus be ordinary stock which is prepared in the beater and which may be sized and prepared before the specially treated and pigmented stock is admixed therewith to form the composite pigmented stock for use in making the coating layer or liner of the multi-ply paper or board.

Where admixed untreated stock and treated pigmented stock are used, the portion of stock treated may be either cellulose stock (chemical pulp) or semi-chemical pulp or groundwood stock. In many cases it is more advantageous to treat groundwood stock because of the increased amount of pigment which can be incorporated in it and retained by it, care being taken as above explained to avoid excess of alkali in the treatment which would tend to darken or otherwise affect the groundwood stock treated. When untreated stock is admixed with the treated stock, the untreated stock is advantageously cellulose stock such as chemical pulp, and particularly long fiber chemical pulp which will give increased strength to the coating layer or liner.

The invention will be further illustrated by the following specific examples:

Example 1.—Sulfate kraft pulp from long-fibered wood is prepared in a beater with a content of around 4 to 5% of fibers (dry basis). The stock so prepared is placed in a separate tank provided with agitators, and solid calcium chloride is added in amount sufficient to form a solution containing about 20% of calcium chloride. The stock is stirred to insure thorough distribution of the calcium chloride and to permit its action on the fibers, and this is continued for a period of 5 to 10 minutes, but may be continued for a longer period. After the calcium chloride has exerted its modifying action on the cellulose fibers, there is added a sufficient amount of 10% sodium carbonate (soda ash) solution to react with the calcium chloride. This reaction takes place in a period of about 5 to 10 minutes with continued agitation, but the action can be permitted to take place for a longer time. If the sodium chloride is to be removed more or less

completely from the stock, it is washed or decanted with the addition of fresh water to replace the salt solution.

Before use in the cylinder machine, the stock is diluted to proper consistency, e. g., around 1% of modified cellulose or a somewhat lower percentage, and is then supplied to the stuff chest regulating box and cylinder vat for use in making the outer layer or liner of the composite sheet or board. The multi-cylinder machine may be otherwise operated in the usual way to form the multi-layer sheet or board which is passed through the squeeze and pressure rolls and over the dryers and calenders, being given a sizing treatment by applying a starch solution or a waterproof size on the calenders.

Example II.—2400 parts of grounded pulp of 2.5% fiber content equivalent to 60 parts of dry fibers are pumped to a treating tank and 440 parts of calcium chloride (74% CaCl_2) are added and mixed thoroughly and dissolved and the agitation is continued for about 10 minutes to effect thorough treatment and gelling of the stock by the action of calcium chloride. A sodium carbonate solution is made by dissolving 300 pounds of soda ash in water to form a solution of about 10%. This solution is pumped into the calcium chloride treated stock and allowed to mix therewith, with continued agitation, until complete precipitation has occurred. The resulting treated stock in the form of a fibrous precipitate is pumped to storage tanks and allowed to settle without agitation. After settling, the top liquor (sodium chloride solution) is drawn off and replaced with fresh water to give a treated stock which, after dilution to proper consistency, is used in the cylinder machine for forming the outer layer or liner of the composite sheet or board as described in Example I.

Examples I and II describe the use of the modified and pigmented stock without admixture of untreated stock for making the coating layer or liner of the multi-ply paper or board.

The following examples describe the use of admixed treated and pigmented stock with untreated stock.

Example III.—The stock furnish, a portion of which is untreated and a portion of which is treated, is made if 850 parts of unbleached long fiber sulfite pulp, 350 parts of flyleaf shavings, 310 parts of hard white stock (long fiber bleached sulfite) and 1,000 parts of de-inked stock (dry basis). This stock furnish is prepared in a beater in the regular manner at 6% consistency.

A portion of this stock furnish amounting to 3,000 pounds of mixed stock at 6% consistency (180 pounds of fiber, dry basis) is placed in a washer in which it is kept in circulation and somewhat diluted to permit good circulation. To this diluted stock is added 1,000 pounds of 75% calcium chloride (750 pounds CaCl_2) which is dissolved and allowed to react for 15 minutes with continued circulation. 700 pounds of soda ash is dissolved in water to form a 10% solution, and after the reaction of the calcium chloride on the stock is completed, the soda ash solution is pumped in with continued circulation of the stock and precipitation of calcium carbonate allowed to take place, this carbonate being precipitated within as well as on and around the fibers. After the precipitation is completed, the stock is washed by drawing off the sodium chloride solution and replacing it with fresh water.

A separate portion of the same stock furnish after beating and of 6% consistency, has added

thereto talc, size, alum and starch in the proportion of 25 parts of talc, 2.5 parts of rosin size (rosin soap), 3.5 parts of high free rosin size (rosin soap containing about 46% free rosin), 6 parts of alum and 6 parts of starch for 240 parts of mixed stock (dry basis). This treated stock is passed from the beater through the Jordan, through the machine chest and head box in the screens to the sluice leading to the cylinder vat, and the treated stock is admixed with the untreated stock in the sluice, the mixed stocks being then pumped to the cylinder vat.

The proportions of stocks admixed are 75% of the stock (dry basis) which has been specially treated to modify and pigment it, and 25% of the untreated stock furnish. Alum is added to keep the stock in the cylinder vat acid and at a pH of around 6.0 to 6.2.

The mixed stock from the cylinder vat is used to form the outer layer or liner of a multi-ply paper sheet or board in a regular multi-cylinder machine, and the resulting composite paper or board is passed from the cylinder vats through the usual equipment including calender rolls.

The porous and absorptive nature of the outer layer or liner makes it desirable to use a size in sizing the board which is a non-penetrating size such as a low viscosity, high solids starch size containing addition agents which give a non-penetrating size.

Example IV.—The same treated and untreated stocks are used as in Example III, but the proportions of treated and untreated stocks are the same, that is, 50% of the fibers are modified and pigmented fibers and 50% are regular untreated fibers. The procedure is otherwise the same as that of the preceding example. Although only half of the stock used in forming the outer layer or liner is modified and pigmented stock, a high proportion of pigment is included in the composite stock, amounting to considerably more than 50% of the weight of the liner layer, while in the multi-ply paper or board of Example III, a much higher proportion of pigment is contained in the outer layer or liner of the composite sheet or board.

Example V.—Instead of using treated stock which is a cellulose stock, or largely a cellulose stock, as in Examples III and IV, groundwood can be treated to modify and pigment it, as in Example II, and the resulting modified and pigmented groundwood stock is admixed with untreated cellulose stock and the resulting mixture used to form the outer layer or liner of the composite paper or board, according to the procedure followed in Examples III or IV.

While the foregoing examples illustrate particular methods of treatment and particular proportions of admixed treated and pigmented stock and untreated stock, and the use of treated stock alone, for forming the outer layer or liner of the multi-ply paper or board, it will be evident that variations can be made in the amount of pigment incorporated in the treated and pigmented stock and also in the proportions of pigmented stock and untreated stock, where such mixtures are used. Thus, the outer layer or liner may be made entirely of the treated and pigmented stock, as illustrated in Examples I and II, and the proportion of pigment to fiber (dry basis) in the treated stock may be considerably in excess of 50% and may amount to as much as 4 times the weight of the fiber or more.

Where highly pigmented modified fibers are admixed with untreated fibers, the proportion of

untreated fibers is for many purposes advantageously only a small percentage of the total fibers, e. g., 10% of long fiber chemical pulp admixed with 90% of pigmented cellulose pulp or ground-wood stock; or the proportion of untreated stock may be higher, e. g. 20% or 25% or more of the total or in some cases as much as 50%, as illustrated in Example IV.

It is one advantage of the process of the present invention that it can be carried out at room temperature throughout and with the use of existing equipment in a multi-cylinder machine, although the tank or apparatus where the calcium chloride is added should be constructed of material which is not corroded by the calcium chloride solution.

It is another advantage of the invention that it enables a finished carbonate-coated sheet to be produced directly on the paper making machine without subsequent treatment of the sheet or board by subsequent machine coating.

While the invention has been described more particularly in connection with the use of a multi-cylinder machine, the process can be carried out in a multi-Fourdrinier machine or in other machines for making laminated or multi-ply paper where separate wet layers are formed and joined together to make the composite sheet or board.

The present invention enables a uniformly coated sheet to be cheaply produced with the coating formed as a part of the paper making operation and without subsequent coating.

The number of plies or layers of the multi-ply sheet or board can be varied. For example, in making a sheet or board weighing about 50 pounds per thousand square feet, 5 layers or plies may be used, with the outer pigmented layer or liner forming about 10 pounds of the total weight per thousand square feet, or somewhat more or less, and with the pigmented outer layer varying in calcium carbonate content from an amount equal to or somewhat less than the fiber content of this layer up to an amount 2 or 3 or 4 times as large as the fiber content or even higher. The finished board, weighing around 50 pounds per thousand square feet, may thus contain from 5 to 10 pounds of the coating layer per thousand square feet, with the highly pigmented white surface coating finally sized to give a white finished surface which can be printed, lacquered or otherwise finished when the board is used in making boxes, cartons, etc.

The new composite sheet or board is characterized and distinguished by its outer layer or liner of highly pigmented, modified cellulosic fibers containing pigment both in and on and around the fibers. Even with a large excess of calcium carbonate pigment in the surface layer or liner, the application of non-penetrating starch size in the calender will hold any otherwise loose particles of pigment firmly bound in the surface layer or liner.

Even where highly pigmented coated sheets or board are not desired, but a filled surface board of lower pigment content, such board can readily be produced by the use of admixed modified pigmented stock with untreated stock to give a surface layer or liner containing e. g. around 30 to 40% of pigment. Such a composite sheet, after sizing, gives directly on the paper machine a filled sheet which can be printed, etc.

With higher amounts of pigment, a coated sheet can be directly produced on the paper machine, so that it will have a hard surface which

can be printed, etc., without subsequent coating treatment.

It will thus be seen that the present invention provides an improved process for making multiple layer sheets of paper and board and gives a resulting product which is an improved sheet or board characterized by its distinctive outer surface layer or liner of highly pigmented modified cellulosic fibers, or containing such modified fibers admixed with untreated fibers, and with the modified fibers containing the pigment both in and on and around the fibers.

It will further be seen that when a mixture of highly pigmented modified stock and untreated stock is used, a liner layer or coating is produced of increased strength and which will contain the untreated fibers together with the modified and pigmented fibers intimately admixed and combined therewith in the outer surface layer or liner.

I claim:

1. The method of making multiple layer paper sheets and board which comprises subjecting an aqueous suspension of cellulosic fibers, at ordinary temperatures, to the action of a strong solution of calcium chloride until the calcium chloride brings about a gelatinization of the cellulosic fibers, adding a soluble salt which will react with the calcium chloride to precipitate a calcium compound pigment in and on the gelatinized fibers, the amount of calcium chloride in the solution being sufficient that the amount of precipitated calcium compound remaining in and on the fibers is in excess of the weight of the fibers, and applying the resulting stock to form the outer layer or liner in making a multiple layer sheet or board.

2. The method of making multiple layer paper sheets and board as set forth in claim 1 in which the cellulosic fibers treated are groundwood fibers.

3. The method of making multiple layer paper sheets and board as set forth in claim 1 in which the cellulosic fibers treated are chemically-treated fibers.

4. The method of making multiple layer paper sheets and board as set forth in claim 1 in which sodium carbonate is added to react with the calcium chloride to form a calcium carbonate pigment in and on the gelatinized fibers.

5. The method of making multiple layer paper sheets and board with a highly pigmented outer surface layer or coating which comprises applying, in making the outer layer or liner of the multiple layer sheet or board, a pulp of highly pigmented and gelatinized cellulosic fibers containing an amount of finely-divided precipitated calcium compound pigment in excess of the dry weight of the fibers, said pigmented fibers being produced from swollen, hydrated and gelatinized cellulosic fibers containing a soluble salt largely within the fibers by reaction of another soluble salt therewith to precipitate the calcium compound pigment largely within the fibers as well as on said fibers.

6. The method according to claim 5 in which the highly pigmented and gelatinized cellulosic fibers are groundwood and carry an amount of pigment more than twice the dry weight of the fibers.

7. The method according to claim 5 in which the highly pigmented and gelatinized cellulosic fibers are chemically-treated fibers and carry an amount of pigment more than twice the dry weight of the fibers.

8. A composite multi-layer sheet of paper hav-

ing an outer or surface coating layer formed of highly pigmented and gelatinized cellulosic fibers containing an amount of finely-divided precipitated calcium compound pigment in excess of the dry weight of the fibers, said gelatinized and pigmented fibers having been produced from swollen, hydrated and gelatinized cellulosic fibers containing a soluble salt largely within the fibers by reaction of another soluble salt therewith to form the precipitated calcium compound pigment largely within the fibers as well as on the fibers.

9. A multi-layer sheet of paper as defined in claim 8 in which the highly pigmented and gelatinized fibers carry an amount of precipitated calcium carbonate amounting to more than twice the dry weight of the fibers.

10. A multi-layer sheet of paper as defined in claim 8 in which the highly pigmented and gelatinized cellulosic fibers are admixed with a smaller amount of unpigmented fibers in the outer layer.

WILLIAM LUTTON CRAIG.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
123,747	Tieman	Feb. 13, 1872
157,198	Duemling	Nov. 24, 1874
354,477	Just et al.	Dec. 14, 1886
821,434	Sachsenroder	May 22, 1906
1,842,712	Bradley	Jan. 26, 1932
2,080,437	Rafton	May 18, 1937
2,173,167	Hovey	Sept. 19, 1939
2,315,892	Booth	Apr. 6, 1943
2,398,420	Freeman	Apr. 16, 1946
2,457,797	Craig	Jan. 4, 1949

FOREIGN PATENTS

Number	Country	Date
141,274	Germany	Apr. 22, 1903
6404	Great Britain	of 1869
2,251	Great Britain	of 1883
5,776	Great Britain	of 1899
516,162	Great Britain	Dec. 22, 1939

OTHER REFERENCES

- An Introduction to the Chemistry of Cellulose by Marsh, published by Chapman and Hall, Ltd., London (1938), page 73.
- 25 Manufacture of Pulp and Paper, 2nd ed., vol. V, sec. 1, page 252 (1929), published by McGraw-Hill, New York.