This invention relates to the production of pigmented cellulosic pulp by precipitating the pigment inserted in and on and around the fibers of the pulp in amount exceeding the weight of the fibers.

According to the present invention a highly pigmented fibrous product is produced by adding cellulosic fibers in the form of dry paper pulp to a dilute solution of calcium chloride, barium chloride or zinc chloride to form a pulp in such a manner that prolonged mechanical working or beating such pulp to effect swelling and hydration and gelatinizing of the cellulosic fibers followed by precipitation of an insoluble calcium, barium or zinc pigment, particularly calcium carbonate, barium sulfate, zinc sulfate or hydroxide, etc., in and on and around the modified fibers by the addition of a soluble salt such as sodium carbonate, sodium sulfate, etc.

I have found that ordinary commercial waste calcium chloride liquor containing about 10% calcium chloride can advantageously be used in the production of fibrous pigments or pigmented fibers of high pigment content by adding dry cellulosic fiber pulp to such liquor to form a suspension of such pulp therein and by mechanical working of the pulp with the solution in a beater or the like until the fibers are swollen and hydrated and converted into a gelatinous or gel-like form and by subsequent precipitation of an insoluble pigment, particularly calcium carbonate, within as well as on and around the thus modified fibers, particularly by the addition of a solution of sodium carbonate thereto.

Commercial calcium chloride in a dry form is commonly produced from calcium chloride solutions by concentrations of such solutions to give the dry product. Dry calcium chloride can be redissolved in water or in aqueous pulp solutions to form strong calcium chloride solutions. In my prior applications Serial Nos. 664,425 and 669,199 I have described the production of pigmented fibrous products by the treatment of cellulosic fibers in pulp form by adding the dry calcium chloride to the aqueous pulp stock at a paper or pulp mill to effect modification of the fibers followed by precipitation of an insoluble pigment in and on and around the modified fibers.

I have found that the use of strong solutions of calcium chloride is not necessary, and that the more dilute solutions of ordinary waste calcium chloride liquor can be advantageously used by adding dry cellulosic pulp fibers thereto and by prolonged mechanical working of the resulting pulp to effect swelling and hydration and modification of the fibers to convert the fibers into a modified gelatinized or gel-like state with a minimum of free water around the fibers, and that valuable pigmented fibrous products can be obtained by then treating the gelatinized fibers with a solution of a soluble salt such as sodium carbonate to precipitate an insoluble pigment such as calcium carbonate in and on and around the modified fibers, with subsequent removal of the by-product salt from the resulting pigmented product.

The dry pulp fibers which are used in the present process for making the fibrous pigment products include various paper pulp fibers and particularly cellulosic fibers, including both chemical and semi-chemical pulp and groundwood fibers such as sulfate pulp, sulfite pulp, soda pulp, semi-chemical pulp, mechanical pulp, etc. The dry pulp stock may be bleached or unbleached stock and may be stock which has been previously refined in a beater or refining engine or which may advantageously be unrefined stock, and which is converted into a refined stock by the mechanical treatment of beating or refining to which it is subjected in connection with the treatment of the dry pulp after its addition to the dilute calcium chloride solution.

The proportions of dry cellulosic stock to dilute calcium chloride solution can be varied but in general the amount of calcium chloride present in the dilute solution will advantageously be several times the weight of the stock treated therewith. I have found, for example, that an ordinary by-product waste calcium chloride solution containing about 10% of calcium chloride can be advantageously used for beating and hydrating and treating an amount of dry stock corresponding to a 2% stock (dry basis) in such solution, the amount of calcium chloride in this case being about five times the weight of the stock (dry basis) treated; and that the resulting modified and hydrated and gelatinized stock can then be treated with a sodium carbonate solution to form a fibrous pigment suspension containing a large amount of finely divided calcium carbonate pigment precipitated both within the fibers and on and around the fibers and amounting, e.g., to around 80% or more of the weight of the resulting fibrous pigment (dry basis).

The present process is well adapted for use at locations where cheap by-product waste cal-
2,583,548

cium chloride solutions are available, by ship-
ing the dry pulp from the pulp or paper mill and by adding the dry pulp to such dilute sol-
lutions and subjecting the same to prolonged mechanical treatment therein.

The mechanical treatment of the pulp is such that the solutions can be carried out in an ordi-
ary beater, with or without refining of the pulp, but advantageously with refining of the pulp
during the beating operation, or in combination with refiners through which the pulp is to a
greater or less extent circulated to effect re-
fining of the pulp fibers in such solution. The
prolonged mechanical working of the pulp is
important and should be continued until the
pulp fibers are swollen and hydrated and modi-
fied and converted into a gelatinous or gel-like
state with a minimum of free water around the
fibers and with a greater part of the water in
the form of a solution contained within the
swollen and gelatinized fibers. The refining of
the pulp in connection with such treatment
with the dilute calcium chloride solution not
only promotes the swelling and hydration and
gelatinizing of the fibers but also gives a refined
pigmented fibrous product, at the end of the
process, which can advantageously be added as
a fibrous pigment to refined paper pulp for pa-
per manufacture.

While the ordinary 10% waste solutions of
calcium chloride are advantageously used in
the present process, an even more dilute solution
of calcium chloride can be used with the dry fibrous
stock, particularly with dilute stock containing
a small percentage of fibers (dry basis) provided
that the mechanical treatment is sufficiently pro-
longed to bring about the swelling and hydrating
and modifying and gelatinizing of the fibers. For
example, with a 5% calcium chloride solution
and with an added amount of dry fibers corre-
sponding to a 1% or 2% stock (dry basis), and
with prolonged mechanical working or beating
of the stock in such solution, followed by pre-
cipitation of the insoluble pigment in and on
and around the modified fibers, a pigmented fi-
brous product can be produced containing an
amount of pigment greatly in excess of the weight
of the fibers (dry basis). With stocks of higher concentration, e.g., around 4% to 6%
fibers, made from the dry paper pulp, stronger
solutions, around 10% calcium chloride, are
advantageously used.

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

Bleached sulfite pulp was added to a waste
calcium chloride solution containing about 10%
calcium chloride in amount sufficient to form a
pulp of around 2% fibers (dry basis) and the
resulting pulp was subjected to mechanical work-
ing in a beater and with circulation of a portion
of the pulp through a refiner and back to the
beater until the fibers had been swollen and
hydrated and converted into a gelatinous con-
dition with a minimum of free water. Sodium
carbonate was subsequently added in the form of
a 10% solution and in amount sufficient to react with the calcium chlo-
ride to precipitate calcium carbonate. The reac-
tion of the sodium carbonate solution brought
about shrinking of the swollen hydrated fibers
and resulted in the production of a highly pig-
mented fibrous product which after washing to
remove by-product sodium chloride contained
on a dry basis about 80% of calcium carbonate
and about 20% of modified fiber.

The resulting fibrous pigment or pigmented
fibrous product, after washing to remove the so-
dium chloride solution, can advantageously be
used for addition to other paper pulp to pig-
ment the same, giving a fibrous pigment which
readily admixes with the untreated fibers. When
the fibrous pigment is refined during the process
of its production, the resulting fibrous pigment
is a refined product which can be added to re-
fined paper pulp shortly before its use on the
paper machine for paper manufacture.

The fibrous pigment produced by the present
process can advantageously be used to give a
dry fibrous pigment product which can be stored
and shipped and used in a paper mill by adding
it to water or to pulp to convert it into the form
of aqueous pulp. Where such fibrous pigment
is dried for storage or shipment the drying should
be carried out without excessive overheating of
the product, as by drying at moderate tempera-
tures. Such dry fibrous pigments are more par-
ticularly described and claimed in my compan-
ion application Serial No. 15,516.

While in the above example the dry pulp
was bleached sulfite pulp and the amount
used was such as to give a stock of about 2%
with the 10% calcium chloride solution, a more
concentrated stock can be used, e.g., up to 5
or 6%, the practical range being from about 2%
to around 6% or even as low as 4%, to give pig-
mented products which in a dry state would
contain more pigment than fiber and advanta-
geously several times as much pigment as fiber
up to e.g. eight or more parts of pigment to
one of fiber (dry basis).

So far, bleached sulfite fiber is more interest-
ing than bleached sulfite pulp stock can be similarly used, including unbleached stock and other chemical, semi-chemical or me-
chanical pulps which are produced at a pulp
mill and shipped in a dry state for use in the
process. Unrefined pulp or fibrous product used
as fiber can be subjected to a refining treat-
ment as part of the mechanical treatment
of the pulp in the calcium chloride solution.

The prolonged mechanical treatment to effect
swelling and hydrating and gelatinizing of the
pulp fibers in the calcium chloride solution, when
carried out with beating or refining of the pulp
will give a refined pigmented fibrous product
after the pigment has been precipitated therein.

While pigmented products can be made in
which the amount of pigment does not greatly
exceed the amount of fiber (dry basis) the process
is particularly advantageous for producing fibrous
pigments with several times as much pigment as
fiber, particularly two or three or four times as
much pigment as fiber, or even more (dry basis).
Such fibrous pigments will retain the fibrous
character of the modified fibers but will have a
large amount of finely divided precipitated pig-
ment, largely precipitated within the fibers, and
also on and around the fibers. And such fibrous
pigments have the advantage that the loss of
pigment from the paper stock is minimized when
used as pigmented with untreated fibers and used for paper manufacture.

The fibrous pigments produced by the pre-
sent process can advantageously be used in making
paper or for coating paper, such as described in
my prior applications Serial Nos. 664,428 and
668,199.

Calcium carbonate is a particularly advanta-
geous pigment in the new fibrous pigment prod-
uct. It is readily produced when sodium car-
bonate is used for reaction with the calcium
fibrous pigment or pigmented fibrous product, after washing to remove the sodium chloride solution, can advantageously be used for addition to other paper pulp to pigment the same, giving a fibrous pigment which readily admixes with the untreated fibers. When the fibrous pigment is refined during the process of its production, the resulting fibrous pigment is a refined product which can be added to refined paper pulp shortly before its use on the paper machine for paper manufacture.

The fibrous pigment produced by the present process can advantageously be used to give a dry fibrous pigment product which can be stored and shipped and used in a paper mill by adding it to water or to pulp to convert it into the form of aqueous pulp. Where such fibrous pigment is dried for storage or shipment the drying should be carried out without excessive overheating of the product, as by drying at moderate temperatures. Such dry fibrous pigments are more particularly described and claimed in my companion application Serial No. 15,516.

While in the above example the dry pulp was bleached sulfite pulp and the amount used was such as to give a stock of about 2% with the 10% calcium chloride solution, a more concentrated stock can be used, e.g., up to 5 or 6%, the practical range being from about 2% to around 6% or even as low as 4%, to give pigmented products which in a dry state would contain more pigment than fiber and advantageously several times as much pigment as fiber up to e.g. eight or more parts of pigment to one of fiber (dry basis).

So far, bleached sulfite fiber is more interest-
ing than bleached sulfite pulp stock can be similarly used, including unbleached stock and other chemical, semi-chemical or mechanical pulps which are produced at a pulp mill and shipped in a dry state for use in the process. Unrefined pulp or fibrous product used as fiber can be subjected to a refining treatment as part of the mechanical treatment of the pulp in the calcium chloride solution.

The prolonged mechanical treatment to effect swelling and hydrating and gelatinizing of the pulp fibers in the calcium chloride solution, when carried out with beating or refining of the pulp will give a refined pigmented fibrous product after the pigment has been precipitated therein.

While pigmented products can be made in which the amount of pigment does not greatly exceed the amount of fiber (dry basis) the process is particularly advantageous for producing fibrous pigments with several times as much pigment as fiber, particularly two or three or four times as much pigment as fiber, or even more (dry basis).

Such fibrous pigments will retain the fibrous character of the modified fibers but will have a large amount of finely divided precipitated pigment, largely precipitated within the fibers, and also on and around the fibers. And such fibrous pigments have the advantage that the loss of pigment from the paper stock is minimized when used as pigmented with untreated fibers and used for paper manufacture.

The fibrous pigments produced by the present process can advantageously be used in making paper or for coating paper, such as described in my prior applications Serial Nos. 664,428 and 668,199.

Calcium carbonate is a particularly advantageous pigment in the new fibrous pigment product. It is readily produced when sodium carbonate is used for reaction with the calcium
chloride to form the insoluble pigment. Other insoluble calcium pigments can similarly be produced, for example, by using sodium borate instead of sodium carbonate and precipitating insoluble calcium borate as the pigment in the fibrous pigment product.

Fibrous pigments or pigmented fibers containing precipitated barium and zinc pigments can be produced in a similar manner by the addition of dry pulp to a solution of barium chloride or zinc chloride with mechanical treatment to effect swelling and hydrating and gelatinizing of the pulp fibers in the barium chloride or zinc chloride solution followed by precipitation of the insoluble barium or zinc pigment by the addition of a soluble salt such as sodium sulfate or alum (aluminum sulfate) or other soluble sulfate, or by adding a soluble carbonate, etc., to precipitate insoluble barium or zinc sulfate or barium sulfate admixed with aluminum hydrate or barium or zinc carbonate or zinc silicate, or zinc hydroxide, etc.

The process in which barium chloride or zinc chloride is used is carried out as hereinbefore described in connection with calcium chloride by adding the dry pulp to the barium chloride or zinc chloride solution with mechanical treatment where needed to effect the hydrating and swelling and gelatinizing of the fibers so that a minimum of free water is present around the gelatinized fibers and by then precipitating the insoluble barium or zinc pigment by adding the soluble precipitating salt to the gelatinized stock.

While the process of the present invention is particularly advantageous with dilute solutions of calcium chloride, barium chloride or zinc chloride, more concentrated solutions can be used and the dry pulp can be added thereto and the swelling and hydrating and gelatinizing of the fibers accomplished with less mechanical treatment and similar highly pigmented fibers or fiber pigments can be produced containing an amount, e.g., of barium sulfate or barium sulfate and aluminum hydrate or barium carbonate or zinc sulfate or zinc carbonate or zinc silicate or zinc hydroxide in amount exceeding the weight of the fibers (dry basis) and advantageously in amount two or three or four or five times the weight of the fibers. The highly pigmented fiber thus produced can similarly be used in admixture with ordinary paper pulp to form a pigmented paper or the fibrous pigments can be treated under regulated conditions to give a dry fibrous pigment product.

I claim:

1. The method of producing pigmented cellulose pulp which comprises adding cellulose fibers to a calcium chloride solution to form a precipitated pulp containing from about 5% to 10% calcium chloride and at least about 1% of fibers, subjecting the pulp to prolonged mechanical treatment, maintaining the fibers in the calcium chloride solution until the combined effects thereof and the mechanical treatment have resulted in the fibers becoming swollen, hydrated and gelatinized, thereafter adding a soluble salt which will react with the calcium chloride to form a precipitated calcium compound pigment, the amounts of the calcium chloride and said soluble salt being such as to precipitate within, on and around the modified cellulose fibers an amount of the calcium compound pigment in excess of the weight of the modified fibers, on a dry basis.

2. The method of producing pigmented cellulose pulp which comprises adding cellulose fibers to a calcium chloride solution to form a precipitated pulp containing about 10% calcium chloride and from about 1% to 6% of fibers, subjecting the pulp to prolonged mechanical treatment, maintaining the fibers in the calcium chloride solution until the combined effects thereof and the mechanical treatment have resulted in the fibers becoming swollen, hydrated and gelatinized, thereafter adding sodium carbonate to the resultant pulp to react with the calcium chloride to precipitate a calcium carbonate pigment in finely-divided form, the amounts of the calcium chloride and the sodium carbonate being such as to precipitate within, on and around the modified cellulose fibers an amount of the finely-divided calcium carbonate greatly exceeding the weight of the modified fibers, on a dry basis.

3. The method of producing pigmented cellulose pulp which comprises adding cellulose fibers to a chloride solution selected from the group consisting of calcium chloride, barium chloride and zinc chloride to form a precipitated pulp containing from about 5% to 10% of such chloride and at least about 1% of fibers, subjecting the pulp to mechanical treatment, maintaining the fibers in such chloride solution until the combined effects thereof and the mechanical treatment have resulted in the fibers becoming swollen, hydrated and gelatinized, thereafter adding a soluble salt which will react with such chloride to form a precipitated pigment in finely-divided form, the amounts of such chloride and said soluble salt being such as to precipitate within, on and around the modified cellulose fibers an amount of the pigment in excess of the weight of the modified fibers, on a dry basis.

WILLIAM LUTTON CRAIG.

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