

UNITED STATES PATENT OFFICE

HAROLD ROBERT RAFTON, OF LAWRENCE, MASSACHUSETTS, ASSIGNOR TO RAFFOLD PROCESS CORPORATION, A CORPORATION OF MASSACHUSETTS

PAPER PRODUCT AND METHOD OF MAKING THE SAME

No Drawing.

Application filed September 5, 1928. Serial No. 304,168.

This invention relates to the manufacture of paper and more particularly to an improved sized paper containing a carbonate filler and to a method of making the same.

5 The principal object of this invention is to provide a sized paper made with a carbonate filler in such manner that the sizing effect of the sizing agent or agents employed which has been wholly or in part deteriorated
10 due to the effect of the carbonate filler is substantially completely restored.

An important object of this invention is to provide a simple and efficient process of making an improved sized paper wherein rosin size and alum are employed in the beater for
15 sizing the paper mix and wherein a carbonate filler is added to the mix in the beater, and wherein an additional amount of alum is added to the paper mix at a later point
20 in the process.

Another object of this invention is to provide a process of making sized paper wherein a sizing restoring agent is added to a previously sized paper mix containing a carbonate filler at such a point in the process
25 that the time and intimacy of contact between the sizing restoring agent and the constituents of the mix is materially limited.

A further object of this invention is to provide a process of making sized paper which differs from present paper making procedure wherein rosin size, alum, and a filler are added
30 to fibrous material in the beater only in the addition of a subsequent quantity of alum to the previously prepared mix at a point to be later indicated subsequent to the primary beating step but prior to the passing of the mix onto a web-forming device of a paper machine.

40 Other objects and advantages of this invention will become apparent during the course of the following description.

As will be apparent to those skilled in the art, it is customary to employ substantially
45 the following procedure in modern paper

making practice: Fibrous materials together with filler, size, such as rosin size, size precipitant, such as alum, and coloring matter if desired, are ordinarily mixed in a beater or the like at a dry solid content of approximately
5 5 per cent. or slightly higher, and are subjected to a heating treatment in the beater, the amount of such treatment depending upon the type of paper which is to be made. The paper mix is then ordinarily discharged from the
10 beater and introduced into a container commonly called a "beater chest," additional water usually being added. Thereafter the mix is pumped from the beater chest to a suitable refining engine, usually a jordan, at a dry
15 solid content of approximately 4 per cent. In common practice the mix is usually diluted somewhat by the addition of water, and the diluted mix is ordinarily conducted from the jordan to another container commonly known
20 as a "machine chest." From the machine chest the mix is pumped to a point near the web-forming end of the paper machine where it is largely diluted with water, water being added ordinarily in such an amount as to provide
25 a dry content of from approximately 1/2 to 1 per cent. or slightly higher, but practically never in excess of 1 and 1/2 per cent. The mix in such highly dilute condition is then passed through riffles or the like if desired and there-
30 after through screens and through the head box of the paper machine onto the machine wire or into the vat depending upon whether a Fourdrinier or a cylinder machine is employed, and during this passage additional
35 amounts of water are usually added in the form of sprays or otherwise. This exact procedure is not always followed but in some instances is modified in accordance with the type of paper being made. For example, in the
40 manufacture of certain types of paper, the beating process is almost or entirely dispensed with, the ingredients of the stock being merely mixed prior to jordaning. In
45 some instances the step of refining or jordan-

ing may be partially or wholly dispensed with. Moreover, the arrangement of the chests in respect to the mechanical treating apparatus is not in all cases precisely as described above.

The time consumed from the point of mixing the ingredients in relatively concentrated state up to the point where the stock is to be diluted for delivery to the web-forming end of the machine is relatively long in comparison with the time during which the stock exists in dilute condition prior to its delivery to the web-forming end of the paper machine. The length of time during which the mix remains in a relatively concentrated condition may vary, of course, according to conditions, but it may be any where from as little as 15 or more minutes, as in certain extreme cases, up to a matter of a number of hours. On the other hand, the time during which the mix exists in a dilute stage prior to its delivery to the web-forming end of the machine is in some cases a matter of only a few seconds and ordinarily not over a minute. Even under extreme conditions the time would never be in excess of 5 minutes.

In many instances the water supplied to the beater and also the water employed for dilution at the jordan as well as for the final dilution of the mix before delivering to the web-forming end of the paper machine consists in whole or in part of "white water" by which term is meant to be included all effluents from the web-forming end of the paper machine. It will be apparent therefore that this water functions cyclically in the process and that there may be reintroduced into the earlier stages of the process part of the material which was derived from the web-forming stage of the process, such material being returned through the medium of the "white water."

Moreover in modern paper making practice there is a tendency to reclaim the ingredients contained in the white water, sometimes merely from that portion of it which is in excess of that which can be or is to be used cyclically in the process, or sometimes from a portion or from all of that which is to be used cyclically, or both, by subjecting the white water to some suitable procedure, as filtration, such for instance as "deckering" or actual passage through a filtering machine, or sedimentation or the like, thereby passing out the substantially purified aqueous effluent to waste, or for further use in the pulp or paper making process, with the simultaneous return of the recovered material to the paper making process. In some installations this recovered material may be returned to the beater, while in others it may be returned to the beater chest, machine chest, or other point in the process if desired.

It will therefore be apparent that independent of the exact type of apparatus and

procedure employed, the following operations are normally employed in the paper making process; the mixing of the ingredients in relatively concentrated form; their contact in such concentrated form for a relatively long period of time; their subsequent dilution to a concentration suitable for delivery to the web-forming end of the paper machine; their remaining in such dilute condition a relatively short period of time; and the recontacting of the mixture of the ingredients prior to its delivery to the web-forming end of the paper machine with the cyclically returned white water and/or material recovered therefrom. Under these conditions, where carbonate fillers have been employed in the paper making process, it has been found in some cases that the sizing effect has been appreciably affected, or more commonly that the sizing effect has been completely destroyed.

Although the practical sizing results of the use of alum and rosin size in ordinary paper making practice have been known for a long period of time, nevertheless there is as yet no unanimity of opinion as to the exact chemistry of the sizing process. Some workers in this field assert that the sizing is due purely to the adsorption of the rosin from the sizing material by the cellulose fibre and the fixing of it thereon by the oppositely charged aluminum compound. Others maintain that a precipitate of aluminum resinate is responsible for the sizing, and still others hold that the free rosin in the size is the major or entire sizing factor. Inasmuch as there is no generally accepted view as to the chemistry of sizing, it is difficult to explain chemically the exact effect of carbonate fillers on rosin sizing. However, whatever may be the reason which theory may assign for this effect, the actual results obtained in some cases where carbonate fillers have been employed are as described in the preceding paragraph.

As a result of careful experiment, I have discovered that a mix made from fibrous material, size, such as rosin size, a size precipitant, such as alum, and carbonate filler, which under ordinary conditions would produce a paper in which the sizing was damaged if not altogether destroyed, will have its sizing effect restored and thus produced a sized paper, providing certain materials are added to the mix later in the paper making operation, at or subsequent to the point where the mix is largely diluted as described above prior to its delivery to the web-forming end of the paper machine. Thus the material constituting the sizing, the effect of which has been deteriorated or destroyed, acts as a potential sizing agent which is made effectual through the addition of a restoring agent. Thus where I use the expression "po-

tential sizing agent" I mean sizing which has been deteriorated or destroyed by the action of carbonate filler. It is to be noted that in
 5 may process the action of the precipitating agent, that is the size precipitant mentioned above, is to throw down the soluble size whereas the restoring agent subsequently added acts to restore the efficacy of the previously precipitated sizing, the effect of
 10 which has already been deteriorated or destroyed.

I have also discovered that this restoring action is relatively sensitive and of relatively brief duration and if the attempt is made to
 15 effect the restoration in the mix when it is relatively concentrated, and particularly when the relatively concentrated mix is subjected to agitation as is normal in the stock chests in paper making, that the restorative action is again destroyed. I have further discovered that if after applying the restorative
 20 action the mix is subjected to a minimum degree of intimate contact and a minimum of time of contact, such as is the case when the mix is in dilute form prior to its delivery to the web-forming end of the paper machine, then the restorative action is practically not affected or only slightly affected according
 25 as the intimacy and/or time of contact may be lesser or greater. Also I have found that agitation in the dilute state has a very much less injurious effect than in the concentrated.

Based on these discoveries, I have devised a method whereby they may be applied
 30 practically to paper mill operation and sized carbonate filled papers be reliably produced thereby. I have found in general that acidic material and/or salts of trivalent metals, as ferric iron or aluminum, act as restorative
 35 agents. For instance, I have found that it is possible to restore the sizing effect to a mix containing carbonate filler in which the sizing effect has been destroyed, by addition of an acid such as sulphuric acid (H_2SO_4).
 40 I have also found that it is possible to use acid salts such as sodium bisulphate ($NaHSO_4$). However, the best agents I have so far found are the salts of the trivalent metals, as ferric iron or aluminum, and of
 45 these aluminum has by my tests to date proven to be the better. Ferric iron may be used in papers other than white, but for white papers, aluminum is the most suitable material, and even for colored papers, its relatively greater effectiveness may render it
 50 more economical.

Of the aluminum salts available the chloride, sulphate, or the like, or the double salts which are the true alums, may be used, but
 55 because of economy, the ordinary sulphate of aluminum normally known as "alum" is most suitable. I have found that any of the ordinary types of alum are satisfactory, whether acid, neutral, or basic. I have also
 60 found that whereas the acidic materials men-

tioned in the preceding paragraph can be used and although some of them are considerably cheaper than alum, the effectiveness of alum seems to be sufficiently greater in proportion to the above mentioned materials, that it becomes economical to use alum instead of these relatively cheaper materials.

Because of the uncertainty as to the chemistry of the sizing reaction as indicated above, it is not quite clear just why this restoring
 65 action of the acidic or aluminous materials takes place. If this deteriorating effect be due to the gradual transformation of the alum-rosin compound into an alkaline earth metal resinate, then the addition of the restorative material may cause a reversal of
 70 this reaction. However, it is to be clearly understood that whatever be the theory underlying the restorative action, my invention is not limited or controlled by any theory, and is entirely independent thereof, because
 75 the facts of the case are, regardless of theory, that such materials do cause a restorative action to the sizing in carbonate filled papers, thereby producing sized carbonate filled papers, which without these restorative agents would have their sizing damaged, if not completely destroyed.

The preferred method which I employ consists substantially in adding a subsequent
 80 portion of alum, preferably continuously, in the paper making process, as near as feasible to the point of web formation on the paper machine, namely at or following the point at which the paper mix is largely diluted as
 85 indicated above.

In the preferred practice of my invention I add to the beater or other similar or mixing or compounding or disintegrating or treating machine, all the fibrous materials, excepting those falling within the definition of carbonate filler hereinafter set forth, such as "broke" or the like, and such fibrous material as is in the stock recovered from the white
 90 water in the paper making process, and then add rosin size and alum. After the rosin size-alum compound has been formed on the fibre, I may then add the fibrous materials coming under the definition of carbonate filler hereinafter set forth and the carbonate filler
 95 itself. It is possible to add all the fibrous constituents and/or the carbonate filler itself in the beater prior to the addition of the alum to the size in the beater, but my experiments have indicated that better results are obtainable when the rosin size-alum compound is formed on the fibre in the absence of any carbonate filler.

Moreover, in furnishing the beater I prefer
 100 to employ fresh water or white water which has been clarified so that the alum-rosin precipitate may be completely formed on the fibre before the addition of carbonate filler in any form to the mix.

In regard to the mixing of ingredients of fibre (free from carbonate filler), alum and rosin size in the beater, I do not restrict myself to any given order of the addition of these ingredients as I may use any order of mixing as is suitable in paper making practice. Furthermore I may add the ingredients in one or more parts or steps at any point prior to the addition of the carbonate filler. For example, as is sometimes customary in the paper making practice in the case of hard water, I may add part of the alum first to the fibre and water to render harmless to the rosin size the injurious ingredients in the hard water and then I may add the rosin size followed subsequently by the remainder of the alum.

Furthermore fillers of types other than carbonate fillers may be also added in the beater if it be desired to employ them in conjunction with the carbonate fillers in the paper, as well as coloring materials, and other substances which may normally be added in the paper making process. Moreover, if it is desired, starch may be added to the mix in the beater or other point in the process, attention being directed to my copending application Serial No. 202,453 of June 29th, 1927. The mix in the beater is then given the usual treatment, passed through the beater chest, jordan and machine chest. All waters used subsequent to the precipitation of the rosin-alum compound in the beater may be either fresh water or white water, as desired.

The mix still in relatively concentrated form is now at the point where it is ready for dilution preparatory to delivery to the web-forming end of the paper machine. Here the white water from the paper machine may be used as diluting water. At this point or subsequent thereto, alum is added preferably continuously, preferably in solution, the precaution being taken that adequate mixing of the alum, the white water and other water if used, and the relatively concentrated mix coming from the machine chest be assured. A separate mixing box may be provided if desired but under ordinary machine practice this is unnecessary as there is usually adequate provision made in paper manufacturing to insure thorough mixing of the relatively concentrated mix with the diluting water. I have found in practice that it is also satisfactory to add alum at a subsequent point in the process, for example, just prior to the passage of the diluted mix to the screens, the screens effecting very thorough mixing in this case. If, however, the alum is actually added at the head box of the machine subsequent to the screens, then care should be taken that adequate distribution and mixing of the ingredients is insured by proper baffling or the like.

An illustrative furnish which may advan-

tageously be used in practicing my invention is as follows:

Materials added in beater

| | Pounds | |
|---|--------|----|
| Fibrous furnish, e. g. sulphite and soda pulps----- | 1700 | 70 |
| Size, e. g. rosin size----- | 60 | |
| Size precipitant, e. g. alum (Al ₂ (SO ₄) ₃ ·18H ₂ O)----- | 90 | |
| Carbonate filler, e. g. calcium carbonate magnesium hydroxide----- | 300 | |

Material added to mix proportionately and continuously on dilution

| | Pounds | |
|--|--------|----|
| Restoring agent, e. g. alum (Al ₂ (SO ₄) ₃ ·18H ₂ O)----- | 75 | 75 |

Another illustrative furnish is as follows:

Materials added in the beater

| | Pounds | |
|---|--------|----|
| Fibrous furnish, e. g. sulphite and soda pulps----- | 1530 | 80 |
| Size, e. g. rosin size----- | 60 | |
| Size precipitant, e. g. alum (Al ₂ (SO ₄) ₃ ·18H ₂ O)----- | 90 | |
| "Broke" containing carbonate filler, e. g. calcium carbonate magnesium hydroxide----- | 170 | |
| Carbonate filler, e. g. calcium carbonate magnesium hydroxide----- | 300 | |

Material to be added proportionately and continuously on dilution

| | Pounds | |
|--|--------|----|
| Restoring agent, e. g. alum (Al ₂ (SO ₄) ₃ ·18H ₂ O)----- | 75 | 75 |

In the above formulæ, the weights of size and carbonate filler refer to the bone dry basis, the weights of all other ingredients being given on the air dry basis.

In either of the above furnishes starch may be used as set forth above. It may be conveniently added to the beater subsequent to the addition of the carbonate filler, or otherwise if desired. Suitable coloring matter may be added if desired.

The illustrative furnishes given above produce a satisfactorily sized paper, and as will be apparent the sizing can be increased or decreased by varying the amounts of sizing ingredients used. I do not restrict myself to any given quantities of size and alum in the beaters, nor to any given quantity of alum to be used after dilution, as I have found that these quantities may be very widely varied and still give satisfactory results.

The resultant papers made by my process may be used for such purposes as those to which sized filled papers are normally put including that as a raw stock for further conversion, as for example, for coating.

As is set forth above, the primary object of my invention is to restore the sizing in the paper mix containing carbonate filler by the addition of a restoring agent such as alum. Under conditions ordinarily obtaining in paper mixes, this restoring agent would react chemically with the carbonate filler and thus be destroyed. However, I am able to obtain the desired effect of this restoring agent in the paper mix and thus obtain sizing by adjusting conditions under which the restoring agent is added so as to substantially prevent it from reacting chemically with the carbonate filler. There is therefore substantially no conversion of the carbonate filler into a neutral compound by reaction with the restoring agent,

and the carbonate filler continues to exist in the mix. Whereas I have not limited myself to any definite amount of carbonate filler nor any definite amount of restoring agent used, the illustrative furnishes given herein indicate that normally the carbonate filler constitutes a substantial percentage of the total furnish and consequently of the paper produced, and that it is present in the furnish in an amount greatly in excess of the stoichiometrical equivalent of the restoring agent added. Thus it will be noted that even were conditions such that reaction between the restoring agent and the carbonate filler could take place and go to completion, which is substantially not the case in my invention, the final result would not be a neutralization of the mix but rather a using up of the restoring agent and the mix would remain on the alkaline side owing to the excess carbonate filler present. It is thus apparent that my process, in which a paper is produced containing a substantial quantity of carbonate filler, is wholly unrelated to any papermaking procedure wherein alum or the like is added to a paper mix for the purpose of substantially neutralizing the same so that the final paper will contain substantially no alkaline constituents.

While I have described herein the use of rosin size as a size and alum as a size precipitant to produce a sizing effect, and have shown a method for the restoration of this sizing effect after it has suffered deterioration or destruction, it is to be understood that sizes other than rosin size may be employed for sizing. Such sizes are those which have been derived by treatment with an alkaline substance or the like from material originally of acid characteristics or of a partially or completely saponifiable nature, and which are used in conjunction with a size precipitant as alum. Examples of such sizes are soaps, for instance the oleates, and partially or wholly saponified waxes, for instance saponified beeswax. A size precipitant, other than alum, which is suitable, although not as effective, is sodium bisulphate. The material constituting the sizing formed from such sizes and size precipitant as alum is affected by carbonate fillers similarly to the material constituting the sizing formed from rosin size and alum, but by my method of restoring the sizing effect, the deterioration or destruction of the sizing effect when such sizes are used is counteracted. It is to be understood, therefore, that the use of any such size and size precipitant to impart sizing to a paper in which my method is used for the restoration of the sizing falls within the scope of my invention.

Although there have been proposals for sizing paper containing carbonate filler with the use of rosin (see, for example, Losh's British Patent No. 2,664 of 1859, and Cap-paza's British Patent No. 5,776 of 1899) the

method which I employ is wholly different from those disclosed in the above referred to patents as will be apparent or from any other method which has to my knowledge yet been proposed.

By the term "carbonate filler" as employed herein is meant the substantially water insoluble normal or basic carbonates of alkaline earth metals (which expression is herein intended to include magnesium), or compounds, or double salts, or physically associated mixtures of these with one or more other acid soluble materials of a substantially water insoluble nature, these fillers whether simple or complex as above, being characterized by the fact that, when agitated in contact with freshly boiled distilled water in concentrated suspension for say an hour, they impart to the water a pH value which is on the alkaline side of the neutral point, and also by the fact that they give off carbon dioxide gas when brought into contact with an aqueous mineral acid, e. g., hydrochloric acid. Examples of such fillers are calcium carbonate, of which lime mud from the causticizing process is one form; calcium carbonate magnesium basic carbonate employed in the paper disclosed in my U. S. Patent No. 1,595,416 of August 10, 1926; and calcium carbonate magnesium hydroxide, disclosed in my U. S. Patent No. 1,415,391 of May 9, 1922. As will be apparent, these fillers are referred to not only in their chemically pure form but also in commercial form containing such impurities as may occur in such commercial products; and also when present with other material, so that they constitute only a part, either major or minor, of the whole. It should be stated that any given filler of the type referred to is not necessarily of uniform particle size; nor are the average particle sizes of the fillers necessarily alike, as some of the fillers of the type referred to have relatively coarse grain particles, whereas others are much more finely divided, and some are so finely divided that they may be said to approach or be in the colloidal condition.

Moreover, by the term "carbonate filler", I mean to include not only the case where the carbonate filler is added as such in the paper making process, but also the case where it may be added wholly or in part incorporated with fibrous material and/or other material such as paper coating constituents or the like. Such a case would be where paper made with carbonate filler, either as a filling or coating constituent, or both, is reused in the paper making process. Such papers may be those known to the trade as "old papers" or "old waste papers" or "waste papers" in any form, or returned trimmings or damaged paper or the like, or they may be the "broke", that is, the partially made, the imperfect, or the waste paper which accom-

panies the paper making, finishing, storing, packing, shipping, or the like operations in a paper mill, and which is reworked either in the same or some other mill. Such papers are sometimes reworked by themselves and added in broken down or in pulp form in the paper making process, being treated or cooked in some cases with or without chemicals and washed if desired, this reworking meaning to include the process of deinking if such is practiced or of bleaching or of both deinking and bleaching, or sometimes they are added directly in the paper making process and broken down to pulp form therein. In any event they are a source of carbonate filler in the paper to be made, and are included in the term "carbonate filler" as used herein.

When I use the word "paper" herein, I use it in the broad sense to include products of manufacture of all types and of all weights and thicknesses, which contain as an essential constituent a considerable amount of prepared fibre and which are capable of being produced on a Fourdrinier, cylinder, or other forming, felting, shaping or molding machine.

Although the expression "wet end of the paper machine" may at times be used to convey various meanings, where I use the expression in the claims I intend it to include those instrumentalities provided in paper manufacture by which and/or in which the relatively concentrated mix is diluted, and treated, conveyed or fed up to the point of web formation, such as the mixing box, regulating and proportioning devices, riffles, troughs, screens, machine head boxes, inlets, and the like, including also instrumentalities used in the white water cycle, but I do not intend to include in this definition the web-forming device itself, that is, the moving wire in the case of a Fourdrinier machine or the cylinder mold in the case of a cylinder machine.

Although I have described in detail several illustrative furnishes I do not intend to be limited thereby, as my invention may be practiced with a broad variety of formulae, using various materials customarily employed for various grades of paper in any suitable proportions. Moreover, various changes in procedure, ingredients, and arrangement of steps may be resorted to in the practice of my invention without departing from the spirit of my invention or the scope of the subjoined claims.

I claim:

1. The method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler a sizing restoring material under conditions favoring the minimizing of the time of contact of the constituents of the mix, and thereafter making paper therefrom.

2. The method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler a salt of a trivalent metal under conditions favoring the minimizing of the time of contact of the constituents of the mix, and thereafter making paper therefrom.

3. The method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler a salt of aluminum under conditions favoring the minimizing of the time of contact of the constituents of the mix, and thereafter making paper therefrom.

4. The method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler alum under conditions favoring the minimizing of the time of contact of the constituents of the mix, and thereafter making paper therefrom.

5. The method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler alum under conditions favoring the minimizing of the intimacy and time of contact of the constituents of the paper mix, and thereafter making paper therefrom.

6. The step in a method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler alum at a point in the process subsequent to that at which the paper mix exists in relatively concentrated form.

7. The step in a method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler alum at a point in the process where the concentration of the solids is not over one and one half per cent. on the dry basis.

8. The step in a method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler alum at a point in the paper making process not more than five minutes prior to web formation.

9. The step in a method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler alum at the wet end of the paper machine.

10. That step in a method of manufacturing a sized paper filled with carbonate filler comprising adding on aluminum salt at the wet end of a paper machine to a paper mix containing fibrous material, carbonate filler, and a potential sizing agent.

11. That step in a method of manufacturing a sized paper filled with carbonate filler comprising adding alum at the wet end of a

paper machine to a paper mix containing fibrous material, carbonate filler, and a potential sizing agent.

nesium compound, and adding a subsequent quantity of alum at the wet end of the paper machine.

5 12. The steps in a method of manufacturing a sized paper filled with carbonate filler comprising mixing fibre, size, size precipitant, and carbonate filler, and adding to such mix a sizing restoring material at the wet end of the paper machine.

23. The method of manufacturing a sized paper filled with carbonate filler comprising 70 calcium carbonate magnesium hydroxide consisting of mixing fibre, size, alum, and calcium carbonate magnesium hydroxide, adding a subsequent quantity of alum at the wet end of the paper machine, and making paper 75 from the resulting mix.

10 13. The steps in a method of manufacturing a sized paper filled with carbonate filler comprising mixing fibre, size, alum, and carbonate filler, and adding a subsequent quantity of alum at the wet end of the paper machine.

24. The method of manufacturing a sized paper filled with carbonate filler comprising adding to a previously sized paper mix containing carbonate filler a sizing restoring material under conditions favoring the minimizing of the intimacy and time of contact of the constituents of the mix, and thereafter making paper therefrom. 80

15 14. The steps in a method of manufacturing a sized paper filled with carbonate filler comprising mixing fibre, rosin size, alum, and carbonate filler, and adding a subsequent quantity of alum at the wet end of the paper machine.

In testimony whereof I affix my signature. 85
HAROLD ROBERT RAFTON.

20 15. The steps in a method of manufacturing a sized paper filled with carbonate filler comprising mixing fibre, rosin size, alum, and carbonate filler in the beater, and adding a subsequent quantity of alum at the wet end of the paper machine.

25 16. The steps in a method of manufacturing a sized paper filled with carbonate filler comprising precipitating a size with alum in the beater, and adding a subsequent quantity of alum at the wet end of the paper machine.

30 17. That step in a process of sizing paper containing carbonate filler comprising the restoration of sizing in a paper mix by the addition of a sizing restoring material at the wet end of the paper machine.

35 18. That step in the process of sizing paper containing carbonate filler comprising the restoration of sizing by addition of alum at the wet end of the paper machine.

40 19. The method of restoring the sizing to a previously sized paper mix containing carbonate filler whose sizing has been deteriorated by the carbonate filler, comprising the addition of alum to said mix at the wet end of the paper machine.

45 20. The steps in a method of manufacturing a sized paper filled with carbonate filler comprising an alkaline earth metal carbonate consisting of mixing fibre, size, alum, and an alkaline earth metal carbonate, and adding a subsequent quantity of alum at the wet end of the paper machine.

50 21. The steps in a method of manufacturing a sized paper filled with carbonate filler comprising calcium carbonate consisting of mixing fibre, size, alum, and calcium carbonate, and adding a subsequent quantity of alum at the wet end of the paper machine.

55 22. The steps in a method of manufacturing a sized paper filled with carbonate filler comprising calcium carbonate and magnesium compound consisting of mixing fibre, size, alum, and calcium carbonate and mag-

90

95

100

105

110

115

120

125

130