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## PAPER AND METHOD OF MAKING THE SAME

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This invention relates to the manufacture of paper.

The principal object of my invention is to provide a method for incorporating into paper filled with alkaline filler certain originally and normally soluble constituents in a substantially insoluble form.

An important object of my invention is the incorporation of sodium silicate in the form of an insoluble material into paper filled with alkaline filler.

A further object of my invention is to provide a process whereby fibrous material, sodium silicate, alum, and alkaline filler are employed in the beater, and wherein a restorative material is added to the paper mix at the wet end of the paper machine.

Other objects of my invention will become apparent in the course of the following description.

It is desirable at times in the papermaking operation to incorporate soluble material into a fibrous mix and subsequently add an agent which serves mutually to react with the soluble material to form a substantially insoluble compound, which compound remains associated to a substantial degree with the papermaking ingredients, and thus becomes incorporated in the resulting paper.

Such a soluble material is sodium silicate precipitated as by alum. This has been used for a long time in papermaking for a number of purposes, particularly for imparting snap and stiffness to a sheet of paper, reducing the fuzz and the like. There are a number of other desirable characteristics that the alum-sodium silicate precipitate imparts to the stock and the sheet into which the stock is made, a good summary of these being given on page 114 of Th. E. Blasweiler's book on "The Use of Sodium Silicate for the Sizing of Paper", translated by C. F. Cross, published by Constable & Co., Ltd., London, 1926.

The ordinary method of incorporating sodium silicate into paper is by the addition of sodium silicate in the beater, followed by the addition of alum in the beater, which serves to precipitate the alum-sodium silicate reaction product, which may be referred to as aluminum silicate without thereby being limited to any definite formula for this compound. Of course the order of addition of these materials may be reversed, and sometimes the precipitation may be caused to take place in the presence of starch or other colloidal material to give a more finely dispersed precipitate. These and other variations are well known in the art.

The above method is entirely satisfactory when filler of the type of clay, talc, or the like are used, but I have found in attempting to incorporate sodium silicate in this manner in paper in which alkaline filler was employed, that the stock and the paper made from such stock possessed in only a minor degree or not at all the characteristics desired to be imparted to the stock and the paper by the addition of the sodium silicate.

Upon investigation I discovered that this was due to the fact that the effect of the alum-sodium silicate reaction product i. e. precipitate, was deteriorated even up to the point of destruction by the action of the alkaline filler, so that the characteristics desired to be obtained from the alum-sodium silicate precipitate were present only to a lessened extent, if at all, in the stock going on to the paper machine, and in the finished paper.

As result of careful experiment I have discovered that a mix made from fibrous material, soluble material such as sodium silicate, a precipitant such as alum, and alkaline filler, such as calcium carbonate magnesium hydroxide, which would produce paper stock and paper in which the characteristics imparted by the alum-sodium silicate precipitate would be present in a lesser degree than ordinarily, if indeed they were not altogether absent, would have the effect of this precipitate restored therein and thus produce stock and paper in which the desirable characteristics imparted by this precipitate were present, providing certain material such as alum was added to the mix later in the papermaking operation, at or subsequent to the point where the mix is largely diluted prior to its delivery to the web-forming device of the paper machine. Thus the material constituting the precipitate, the effect of which has

been deteriorated or destroyed, acts as a potential reaction product which is made effectual through the addition of a restoring agent.

I have also discovered that this restoring action is relatively sensitive and of relatively brief duration, and if the attempt be made to 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 papermaking, that the restorative action is again destroyed. I have further discovered that if after applying the restorative action the mix is subjected to a minimum degree of intimate contact and a minimum of time of contact, such for instance as is the case when the mix is in dilute form prior to its delivery to the web-forming end of the paper machine, the restorative action is practically not affected or only slightly affected according as the intimacy and/or time of contact may be lesser or greater. I have found also 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 practical method whereby the effect of the alum-sodium silicate precipitate may be restored in a fibrous mix containing alkaline filler, in which its effect has been deteriorated even to the point of destruction. The method of carrying out my invention is illustrated by the following description of my preferred practice.

Into a beater or similar machine I add all the fibrous material,—excepting that falling within the definition of alkaline filler hereinafter set forth, such as "broke" or the like, and such fibrous material as is present in the stock recovered from the white water in the papermaking process,—and then add sodium silicate and then alum. After the alum-sodium silicate compound has been formed on the fibre, I may then add the fibrous materials coming under the definition of alkaline filler hereinafter set forth and the alkaline filler itself. It is possible to add all the fibrous constituents and/or the alkaline filler itself in the beater prior to the addition of the alum to the sodium silicate in the beater, but my experiments have indicated that better results are obtainable when the alum-sodium silicate compound is formed on the fibre in the absence of any alkaline filler.

Moreover in furnishing the beater I prefer to employ fresh water or white water which has been clarified so that the alum-sodium silicate precipitate may be completely formed on the fibre before the addition of the alkaline filler in any form to the mix. In regard to the mixing of ingredients of fibre (free from alkaline filler), alum and sodium silicate in the beater, I do not restrict myself to any given order of addition, and also include the premixing of the alum and sodium silicate outside the beater, although I have found this practice is not so satisfactory as effecting the precipitation directly in the presence of the fibre. Also the ingredients may be added in one or more parts or steps in the beater if desired, preferably at any point prior to the addition of the alkaline filler. There may be added in the beater other substances which may normally be added in the paper making process, for example, material which will impart sizing to the paper, such as rosin size. In this connection the process of the present invention may be used in conjunction with my copending applications Serial No. 304,168, filed September 5th, 1928, Serial No. 304,170, filed September 5th, 1928, and Serial No. 304,176, filed September 5th, 1928. 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 alum-sodium silicate compound in the beater may be either fresh or white water as desired. The mix still in relatively concentrated form is now at the point where it 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 fibrous mix be assured. I have found in practice that it is also satisfactory to add the alum at a subsequent point in the process, for example, prior to the passage of the diluted mix to the screens, the screens effecting very thorough mixing in this case. In fact, the addition of the alum at any point at the wet end of the paper machine is suitable.

In regard to the amount of sodium silicate used, this will be regulated by the intensity of the effect desired to be produced. The range from one-half of one per cent. to four per cent. of 60° Bé. sodium silicate calculated on the total air dry weight of the material in the beater will be found to satisfy most requirements.

In regard to the amount of alum employed, it is desirable to use an amount equal to that which would give a slight acid reaction were the alum mixed alone with the sodium silicate. Owing to the fact that various samples of sodium silicate differ so widely in alkaline content, it is best to determine in a preliminary test, by titrating a sample of sodium silicate with alum, how much alum it would take to bring the sodium silicate to this slightly acid reaction. In regard to the amount of alum required to be used in the capacity of a restoring agent, it is desirable to use

approximately the same amount or a little more than was originally employed for precipitating the sodium silicate. If material other than alum is used, either originally or as restoring agent, a suitable amount is somewhat more than that which will effect a maximum preciptation of the sodium silicate, as determined by titration of a sample.

An illustrative furnish which may advantageously be used in practicing my invention is:

*Materials added in beater*

| | Pounds |
|---|---|
| Fibrous furnish, (air dry basis) e. g. sulphite and soda pulps, | 1700 |
| Inorganic alkali metal salt, e. g. 60° Bé. sodium silicate, | 30 |
| Precipitant, e. g. alum, | 30 |
| Alkaline filler, (bone dry basis), e. g. calcium carbonate magnesium hydroxide, | 300 |

*Material added to mix proportionally and continuously on dilution*

| | Pounds |
|---|---|
| Restoring agent, e. g. alum, | 30 |

Another illustrative furnish is as follows:

*Materials added in beater*

| | Pounds |
|---|---|
| Fibrous furnish, (air dry basis), e. g. equal parts of sulphite pulp, soda pulp and old paper stock, | 1700 |
| Inorganic alkali metal salt, e. g. 60° Bé. sodium silicate, | 40 |
| Precipitant, e. g. alum, | 40 |
| Alkaline filler, (bone dry basis), e. g. calcium carbonate magnesium hydroxide, | 300 |

*Material added to mix proportionately and continuously on dilution*

| | Pounds |
|---|---|
| Restoring agent, e. g. alum, | 40 |

However, I do not by any means restrict my invention to the above formulæ which are intended as illustrative only and not limiting, nor to any definite quantities of sodium silicate or ratio of sodium silicate to alum, when the alum is used either as the original precipitating agent or as restoring agent, as I have found that my invention may be satisfactorily employed with varying amounts of sodium silicate with a wide variation both of the ratio of sodium silicate to alum, and the ratio of alum used as originally precipitating agent to the alum used as restoring agent, but of course from the standpoint of economy, I prefer to use the least amounts of sodium silicate and alum which experience indicates under given conditions will produce the desired result.

I have found that sodium silicate is merely a representative of a class of substances which may be incorporated into paper in substantially the same manner. This class of substances consists of those inorganic alkali metal salts with a pH value greater than 7.0, which are precipitable by material which depresses their hydroxyl ion concentration. Sodium silicate has already been cited as one example of such a class of substances. Another example is sodium stannate.

As a precipitant and/or restoring agent for the sodium silicate or equivalent substance, I may use any material which depresses the hydroxyl ion concentration thereof in the place of alum, for example, acidic material such as sulphuric acid, or sodium bisulphate ($NaHSO_4$), or salt of a trivalent metal such as ferric iron, or the other salts of aluminum. I may also employ ammonium salts such as ammonium chloride or sulphate. However, from the standpoints of cost and efficiency I prefer to use the ordinary aluminum sulphate commonly known as alum.

In addition to my copending applications mentioned above, this invention may be suitably employed in connection with other of my copending applications, e. g., Serial Nos. 304,171 and 304,175, both filed September 5th, 1928.

Where I use the expression "alkali metal" I mean to include the hypothetical alkali metal ammonium ($NH_4$).

By the term "alkaline filler" I mean substantially water insoluble filler which when agitated in contact with freshly boiled distilled water, say for an hour, will impart a pH value to such water greater than 7.0, that is, which will be on the alkaline side of the neutral point. Among fillers included in this group may be mentioned 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, issued August 10, 1926; calcium carbonate magnesium hydroxide disclosed in my U. S. Patent No. 1,415,391, issued May 9, 1922; and other substantially water insoluble normal or basic carbonates of alkaline earth metals, (which expression is herein intended to include magnesium), or compounds, double salts, or physically associated mixtures of these with one or more other acid soluble materials of a substantially water insoluble nature.

By the term "alkaline filler" I also intend to include fibrous material and/or other material such as paper coating constituents or the like containing one or more compounds of the character referred to, such as "old papers" or similar papers, "broke", or the like.

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 pre-

pared fibre and which are capable of being produced on a Fourdrinier, cylinder, or other forming, felting, shaping or molding machine.

By the term "wet end of the paper machine", I intend to include those instrumentalities employed in paper manufacture by which and/or in which a relatively concentrated paper mix is diluted, and treated, conveyed or fed up to the point of web-formation, such as the mixing box, regulating and proportioning devices, rifflers, troughs, screens, head boxes, inlets, and the like, including also instrumentalities used in the white water cycle.

While I have described in detail the preferred embodiment of my invention, it is to be understood that the details of procedure, the proportions of ingredients, and the arrangement of steps may be widely varied without departing from the spirit of my invention or the scope of the subjoined claims.

I claim:

1. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and a precipitant therefor, and alkaline filler, and adding to the resulting mix a 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 incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and a precipitant therefor, and alkaline filler, and adding to the resulting mix a 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.

3. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and a precipitant therefor, and alkaline filler, and adding to the resulting mix a restoring material at the wet end of the paper machine, and thereafter making paper therefrom.

4. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and acidic material, and alkaline filler, and adding to the resulting mix a restoring material at the wet end of the paper machine, and thereafter making paper therefrom.

5. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and a salt of a trivalent metal, and alkaline filler, and adding to the resulting mix a restoring material at the wet end of the paper machine, and thereafter making paper therefrom.

6. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and a salt of aluminum, and alkaline filler, and adding to the resulting mix a restoring material at the wet end of the paper machine, and thereafter making paper therefrom.

7. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and alum, and alkaline filler, and adding to the resulting mix a restoring material at the wet end of the paper machine, and thereafter making paper therefrom.

8. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and alum, and alkaline filler, and adding to the resulting mix acidic material at the wet end of the paper machine, and thereafter making paper therefrom.

9. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and alum, and alkaline filler, and adding to the resulting mix a salt of a trivalent metal at the wet end of the paper machine, and thereafter making paper therefrom.

10. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and alum, and alkaline

filler, and adding to the resulting mix a salt of aluminum at the wet end of the paper machine, and thereafter making paper therefrom.

11. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and alum, and alkaline filler, and adding to the resulting mix alum at the wet end of the paper machine, and thereafter making paper therefrom.

12. The method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt and alum, and alkaline filler, and adding to the resulting mix a subsequent quantity of alum at the wet end of the paper machine, and thereafter making paper therefrom.

13. The method of incorporating sodium silicate into paper filled with alkaline filler, comprising mixing fibrous material, the reaction product of sodium silicate and a precipitant, and alkaline filler, and adding to the resulting mix a restoring agent at the wet end of the paper machine, and thereafter making paper therefrom.

14. The method of incorporating sodium silicate into paper filled with alkaline filler, comprising mixing fibrous material, the reaction product of sodium silicate and alum, and alkaline filler, and adding to the resulting mix alum at the wet end of the paper machine, and thereafter making paper therefrom.

15. The method of incorporating sodium silicate into paper filled with alkaline filler, comprising adding to a paper mix containing fibrous material, alkaline filler, and the reaction product of sodium silicate and alum which has been deteriorated by said alkaline filler, alum at the wet end of the paper machine, and thereafter making paper therefrom.

16. The method of incorporating sodium silicate into paper filled with alkaline filler comprising mixing fibrous material, sodium silicate, alum, and alkaline filler, then adding a subsequent quantity of alum at the wet end of the paper machine, and thereafter making paper therefrom.

17. The method of incorporating sodium silicate into paper filled with alkaline filler comprising mixing fibrous material, sodium silicate, alum, and alkaline filler in the beater, then adding a subsequent quantity of alum at the wet end of the paper machine, and thereafter making paper therefrom.

18. The method of incorporating sodium silicate into paper filled with alkaline filler consisting of alkaline earth metal compound comprising mixing fibrous material, sodium silicate, alum, and alkaline earth metal compound, then adding a subsequent quantity of alum at the wet end of the paper machine, and thereafter making paper therefrom.

19. The method of incorporating sodium silicate into paper filled with alkaline filler consisting of calcium carbonate comprising mixing fibrous material, sodium silicate, alum, and calcium carbonate, then adding a subsequent quantity of alum at the wet end of the paper machine, and thereafter making paper therefrom.

20. The method of incorporating sodium silicate into paper filled with alkaline filler consisting of calcium carbonate and magnesium compound comprising mixing fibrous material, sodium silicate, alum, and calcium carbonate and magnesium compound, then adding a subsequent quantity of alum at the wet end of the paper machine, and thereafter making paper therefrom.

21. The method of incorporating sodium silicate into paper filled with alkaline filler consisting of calcium carbonate magnesium hydroxide comprising mixing fibrous material, sodium silicate, alum, and calcium carbonate magnesium hydroxide, then adding a subsequent quantity of alum at the wet end of the paper machine, and thereafter making paper therefrom.

22. That step in a method of incorporating into paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising adding a restoring agent at the wet end of the paper machine to a potential reaction product of said alkali metal salt and said precipitant.

23. As a new composition of matter, a paper mix ready for delivery to a web-forming device comprising fibrous material, alkaline filler, and the substantially undeteriorated reaction product of an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, and a precipitant therefor.

24. As a new composition of matter, a paper mix ready for delivery to a web-forming device comprising fibrous material, alkaline filler, and the substantially undeteriorated reaction product of sodium silicate and a precipitant.

25. As a new composition of matter, a paper mix ready for delivery to a web-forming device comprising fibrous material, alkaline filler, and the substantially undeteriorated reaction product of sodium silicate and alum.

26. As a new composition of matter, a pa-

per mix ready for delivery to a web-forming device comprising fibrous material, alkaline filler, and precipitated aluminum silicate.

27. A paper comprising fibrous material, alkaline filler and the substantially undeteriorated reaction product of an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, and an hydroxyl ion concentration depressing precipitant therefor.

28. A paper comprising fibrous material, alkaline filler, and the substantially undeteriorated reaction product of sodium silicate and an hydroxyl ion concentration depressing precipitant therefor.

29. A paper comprising fibrous material consisting of sulphite and soda pulp, alkaline filler, and the substantially undeteriorated reaction product of sodium silicate and an hydroxyl ion concentration depressing precipitant therefor.

30. A paper comprising fibrous material consisting of sulphite and soda pulp, alkaline filler and precipitated aluminum silicate.

31. A paper comprising fibrous material consisting of sulphite and soda pulps and old paper stock, alkaline filler, and the substantially undeteriorated reaction product of sodium silicate and an hydroxyl ion concentration depressing precipitant therefor.

32. A paper comprising fibrous material consisting of sulphite and soda pulps and old paper stock, alkaline filler and precipitated aluminum silicate.

33. A paper comprising fibrous material, alkaline filler, and the substantially undeteriorated reaction product of sodium silicate and alum.

34. A paper comprising fibrous material, alkaline filler, and precipitated aluminum silicate.

35. A sized paper comprising fibrous material, alkaline filler, and the substantially undeteriorated reaction product of sodium silicate and alum, and sizing.

36. A sized paper comprising fibrous material, alkaline filler, the substantially undeteriorated reaction product of sodium silicate and alum, and rosin sizing.

37. A sized paper comprising fibrous material, alkaline filler, precipitated aluminum silicate and the reaction product of rosin size and alum.

38. The method of incorporating into sized paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt, sizing material, material which depresses the hydroxyl ion concentration of said alkali metal salt, and alkaline filler, and then adding to the resulting mix hydroxyl ion concentration depressing material at the wet end of the paper machine, and thereafter making paper therefrom.

39. The method of incorporating into sized paper filled with alkaline filler an inorganic alkali metal salt with a pH value greater than 7.0, which is precipitable by material which depresses its hydroxyl ion concentration, comprising mixing fibrous material, said alkali metal salt, rosin size, material which depresses the hydroxyl ion concentration of said alkali metal salt, and alkaline filler, and then adding to the resulting mix hydroxyl ion concentration depressing material at the wet end of the paper machine, and thereafter making paper therefrom.

40. The method of incorporating sodium silicate into paper filled with alkaline filler, comprising mixing fibrous material, sodium silicate, a precipitant therefor, and alkaline filler, and adding to the resulting mix a restoring agent at the wet end of the paper machine, and thereafter making paper therefrom.

41. The method of incorporating sodium silicate into paper filled with alkaline filler comprising mixing fibrous material, sodium silicate, alum, and alkaline filler, and adding to the resulting mix a restoring agent at the wet end of the paper machine, and thereafter making paper therefrom.

In testimony whereof I affix my signature.

HAROLD ROBERT RAFTON.