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PAPER MANUFACTURE

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This invention relates to the manufacture of paper.

The principal object of this invention is the manufacture of paper filled with alkaline filler.

An important object is the manufacture of paper filled with alkaline filler and having a layer of non-alkaline filler applied to one or both surfaces thereof.

A further object of this invention is the manufacture of paper filled with alkaline filler having a layer of filler of higher index of refraction than said alkaline filler concentrated at at least one surface thereof.

A further object of this invention is the manufacture of a multi-ply paper containing alkaline filler, having at at least one surface thereof a concentration of non-alkaline filler.

A further object is the manufacture of paper containing filler of high refractive index incorporated therein and alkaline filler concentrated at at least one surface thereof.

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

In my copending application Serial No. 534,462, filed May 1, 1931, now matured into Patent No. 1,914,526, issued June 20, 1933, I have described a method of manufacturing paper wherein an alkaline filler is applied to a forming web or to one or both sides of an already formed paper web. The web itself may contain additional alkaline filler incorporated therein. The alkaline filler may be applied to the web while it is still on the web-forming device or on the paper machine prior to the completion of the drying of said web.

Paper made by the above process has in general proved to be very satisfactory, but in certain cases difficulty has been encountered owing to adverse effect of the alkaline filler at or near the surface of the paper, either on certain inks, colors, and the like used on the paper, or in certain processes to which the paper is subjected where surface alkalinity is undesirable, for example in the lithographic process. I have found that one method of overcoming this difficulty is to apply an acidic material to the web as set forth in my copending applications Serial No. 644,909, filed November 29, 1932, now matured into Patent No. 1,976,744, issued Oct. 16, 1934, and Serial No. 646,025, filed December 6, 1932, now matured into Patent No. 1,976,745 issued Oct. 16, 1934, whereby there is produced at or near the surface of a web filled with alkaline filler a less alkaline condition, or there is formed in situ at or near the web surface a non-alkaline compound from the action of the acidic material upon the alkaline filler. In this connection cross reference is additionally made to my copending applications Serial No. 501,674, filed December 11, 1930, and Serial No. 672,901, filed May 25, 1933. I have also found another method of overcoming this difficulty, which I disclose herein, and that is to apply a non-alkaline filler to the surface or surfaces of a paper web containing alkaline filler, whereby the undesirable surface alkalinity of the web may be minimized, and in certain cases even eliminated.

Moreover, the paper containing alkaline filler, made according to the process of my copending application first above referred to, although relatively white and opaque in comparison with papers hereto manufactured, nevertheless if it were possessed of higher whiteness and/or greater opacity it would be even more satisfactory for certain purposes, especially for printing work wherein relatively thin papers are employed. This might be accomplished to a degree by using larger quantities of alkaline filler according to my first above referred to process, but such increase in filler would in some cases result in a weakening of the sheet, and in other cases involve technical difficulties in its application. I have found it possible to overcome these difficulties and yet produce the quality of paper desired by the method which I disclose herein, and that is to apply to the surface or surfaces of a paper web containing alkaline filler, a filler of higher index of refraction than said alkaline filler. Such filler is preferably non-alkaline. Where I refer to "filler" it will of course be understood that I use the word in the ordinary papermaking sense to mean white or substantially white substantially water insoluble material.

Non-alkaline fillers may be either of a relatively low index of refraction such as clay, talc, calcium sulphate, or the like, the index of refraction of which may be about the same or less than calcium carbonate (a common alkaline filler), or of a somewhat higher index of refraction as barium sulphate, or of a substantially higher index of refraction such as a non-alkaline filler containing zinc, lead, tin, antimony, or titanium compound, or the like. A filler of the first group above may be used in my invention where it is desired solely to diminish or eliminate surface alkalinity and where a lowering of the color (whiteness) may not be objectionable, but a filler of the second or third group is preferably used where better color and/or opacity is additionally

desired in the paper to be made. Other non-alkaline fillers which, however, are less common, may be those containing bismuth, vanadium or zirconium compound.

In order properly to understand the advantages of my invention, the economic situation in regard to the price of the various fillers must be appreciated. The non-alkaline fillers such as clay and talc are relatively cheap, but lack whiteness and do not impart any high degree of opacity to the papers in which they are used as a filler. Calcium sulphate, also relatively cheap, can be obtained with better whiteness characteristics but in general it has not such desirable qualities as have alkaline fillers. Alkaline fillers, however, even though of high grade, may be made very inexpensively, in some cases at a cost lower than that of any non-alkaline filler, whereas practically all the other fillers capable of imparting a similar whiteness or opacity to paper are of higher cost; and some of them such as the barium, and particularly the zinc, and titanium fillers are of a very much higher cost.

Furthermore, the fundamental difference between the two classes of fillers should be borne in mind. Alkaline fillers, having an alkaline reaction, are incompatible with acidic material, such as alum or size precipitate, and unless appropriate means are taken to prevent or circumvent this difficulty, such as by the numerous processes disclosed in a large number of my already issued patents, difficulty may be encountered in the papermaking procedure. Non-alkaline fillers are not subject to this particular disadvantage. However, alkaline fillers do impart a very satisfactory whiteness and excellent printing qualities to a sheet, and their very cheap cost, in conjunction with the recently patented methods for their utilization just referred to, is resulting in their being more and more widely used in the paper industry.

The non-alkaline fillers which may give comparable effects as to whiteness and opacity are chiefly the fillers with a high index of refraction indicated above; but in certain cases with lesser advantage calcium sulphate may be used. The inherent qualities of the fillers with a higher index of refraction makes it possible to obtain an opacity in a sheet of paper with a smaller quantity thereof than with the alkaline fillers commonly employed, but their high price makes it infeasible to use them except in a very restricted manner. In my invention I have combined the good qualities of both alkaline and non-alkaline fillers in such a way as to produce a sheet of excellent quality as well as one of moderate cost.

Briefly my invention consists in the manufacture of paper by employing alkaline filler preferably as the major filling agent of the paper, utilizing thereby its very low cost and excellent qualities to produce a low price but good quality paper web. To such web, preferably previous to the completion of its drying on the paper machine, I apply a preferably relatively lesser amount of non-alkaline filler, thus imparting to the web a layer of non-alkaline filler concentrated at or near the surface. The presence of this non-alkaline filler layer at or near the surface of the paper tends in a substantial degree to reduce if not eliminate the difficulties formerly involved in certain cases when alkaline filler was present at or near the surface of the web and thus for these purposes makes a paper which is superior in quality.

Moreover, if one of the fillers of the high refractive index type be employed, and a very thin layer of such filler be used, as such layer is concentrated at or near the surface and is backed up by the comparatively opaque alkaline filler in the sheet, it is possible thus to obtain paper of relatively high opacity but of reasonable cost owing to the relatively small amount of the more expensive higher refractive index filler which is employed.

My invention has other advantageous aspects. For example, paper with high percentage of filler made on fast running Fourdrinier machines is apt to be more or less two-sided, owing to the removal of a portion of the filler from the under side of the sheet by suction. Various means have been employed to overcome this two-sidedness such as by applying on the machine a coating of filler to the wire side of the sheet. Inasmuch as in sheets which are highly filled with alkaline filler, the felt side is ordinarily very white in color due to the alkaline filler, a relatively large amount of alkaline filler must be applied to the wire side of the sheet to bring it up to the shade and appearance of the felt side of the sheet. As will be apparent, the application of relatively large amounts of filler may in certain cases involve difficulties on the paper machine. However, by using a filler of a higher index of refraction than the alkaline filler used, I may by applying a thin layer of such higher refractive index filler to a sheet filled with alkaline filler, which sheet would otherwise be two-sided, convert such sheet into a sheet substantially uniform as to appearance on the two sides, as the effectiveness of such higher refractive index filler is relatively large and the amount required to bring the surfaces to the same appearance is very considerably less than would be required if an alkaline filler, such as calcium carbonate, were used for the purpose. As will be apparent this makes for better machine operation as comparatively little of the high refractive index filler need be applied; and although in certain cases it is useful to employ an adhesive material with it such as starch or the like, because of the small quantity of the filler necessary to apply in most cases, the use of an adhesive in many instances becomes unnecessary.

In the preferred practice of my invention I prepare a paper mix containing alkaline filler and run the same off on a paper machine, e. g. a Fourdrinier machine. To the forming or already formed web as it exists on the paper machine preferably prior to the completion of the drying thereof, I apply the desired non-alkaline filler suitably continuously and proportionately in the form of an aqueous suspension which may conveniently have a concentration of 1 to 3 lbs. per gallon. The application may take place either on the web-forming device, at any point from that of the delivery of the mix thereto up to the point where the formed web is delivered therefrom; or later on the paper machine to the already formed web preferably before the completion of the drying thereof. If I apply the non-alkaline filler on the web-forming device I prefer however to apply it to the already substantially positioned web in order that it may be concentrated at or near the surface. Known devices exist for applying pigment either to the under or upper side of the substantially positioned web as it exists on the web-forming device. Application of the non-alkaline filler suspension to the web subsequent to the web-forming device is conveniently made either at the press rolls, preferably at the third press roll, or at the so-called smooth rolls, using

any suitable device for applying the filler such as a trough or box contacting with the rolls, or by rolls contacting with other rolls; or the filler may be applied directly to the paper web, or by sprays, brushes or the like, or by passing the web through a trough. All these devices are well known in the art. In certain cases instead of a suspension of filler, a more concentrated form may be employed such as a paste, which may be applied by rolls similar to ink applying rolls on a printing press. In other cases the filler may be applied as a dry or substantially dry powder suitably distributed over the web.

As it is a feature of my invention that the layer of non-alkaline filler be combined with and penetrate substantially into the fibrous web, I prefer to apply the filler to the still wet or moist web particularly at such point of the paper machine where it will be subsequently subjected to pressure as between rolls in order to assist in bringing about the desired penetration. However, in certain instances I may apply the filler layer to an already dried web, providing the web is sufficiently moistened and then subjected to pressure prior to the completion of its subsequent drying in order to effect a substantial penetration of the non-alkaline filler into the sheet. Such a condition may obtain when an aqueous suspension or paste of non-alkaline filler is applied to the web at the calenders, in which case the aqueous filler may bring about the wetting of the web, and the calender rolls effect a penetration of the filler into said web prior to the time it is dried.

As will be apparent, the non-alkaline filler may be applied to one or both sides of the web according to the results desired. Any amount of non-alkaline filler desired may be applied, but in general, while not limiting myself in any way thereto, I find it suitable to apply from approximately one up to several percent or more based on the total weight of the sheet, for each side to which it is applied.

If a cylinder machine be employed either with the common type of cylinder where the only suction is that induced by gravity, or with a suction cylinder, the non-alkaline filler may be introduced to the web on the cylinder, or after it has left the cylinder, employing if desired devices similar to those used on a Fourdrinier machine for application of the filler. One suitable method is to use a thin transverse stream applied across the web from a wier box or the like.

The Fourdrinier machine and the cylinder machine referred to above may produce either single webs or multi-ply webs accordingly as they are equipped for one or the other purpose, and in either case may be used in practicing my invention. The expression "multi-ply paper" is used in the ordinary sense to mean a paper composed of more than one ply. Where multi-ply paper is to be made, two webs or plies, for example, may be brought together and united wire side to wire side, felt side to felt side, or wire side to felt side as desired, the non-alkaline filler being applied if desired to one or more sides of either or both plies. The alkaline filler may suitably be incorporated in the mix fed to one or more of the web-forming devices and/or applied to the web if desired.

A special type of paper which may be made by this method is one wherein the non-alkaline filler may constitute an inner layer in a multi-ply sheet, the alkaline filler being incorporated in one or more outer layers, whereby a minor proportion of high opacity non-alkaline filler may impart a high degree of opacity to the sheet and enhance the opacity imparted by the alkaline filler. In my copending application first above mentioned, descriptions of single web machines and multi-web machines, and numerous types of multi-ply papers which may be made thereon are more completely considered, and as that subject matter is equally applicable to the present invention, cross reference is hereby made thereto, and such subject matter is hereby made a part hereof.

As will be apparent, the present invention may be combined with the invention of my copending application first above mentioned suitably by applying a layer of alkaline filler on the paper machine to a fibrous web and then applying a second subsequent layer of non-alkaline filler: or this procedure may be reversed, the non-alkaline filler being applied first, but that is not my preferred procedure. Or the two fillers may be applied simultaneously, or mixed. The application of one or both may take place on the paper machine prior to the passage of the web from the web-forming device or subsequent thereto. The fillers may be applied one to one side and one to other, or both to the same or both sides. The mix fed to the web-forming device may be free or substantially free from alkaline filler, or may have alkaline filler, and if desired other filler also, incorporated therein.

As will be apparent, either substantially unsized or sized paper may be made in accordance with my invention. In the manufacture of substantially unsized paper, other material may be employed such as acidic material for example alum, size in an amount insufficient to impart a substantial degree of sizing to the resulting paper, starch, sodium silicate, sodium aluminate, fibre, and the like, and these may be applied in whole or in part either in the beater, and/or under conditions favoring the minimizing of the time and/or intimacy of contact of the constituents of the mix as for example at the dilute stage of the paper making process, and/or to the forming or already formed web, as is described in many of my already issued patents and copending applications. If sized paper is to be made, size is used sufficient in amount for the pupose, and any or all the other materials mentioned above as used in unsized paper may also be used if desired, and these alone or together with the size may be applied in whole or in part at any of the several places indicated as being suitable in the manufacture of the substantially unsized paper. Any kind of size is suitable which may be used with alkaline filled papers, such for example as those described in my various issued patents and copending applications. When in the manufacture of my paper, material in addition to filler is applied to the web, one or more such material may be mixed with the filler before or during web application, if desired.

Although not usually necessary as stated above when thin layers of filler are applied, the non-alkaline filler may, however, be applied to the web mixed with an adhesive, such as starch, casein or the like, if desired, and this in certain cases assists in avoiding a subsequent tendency toward dusting which may give trouble in certain cases where a heavier layer of non-alkaline filler is applied. The same practice of course may be used if desired with the alkaline filler if such be additionally applied to the web.

It is apparent that my invention is essentially different from what is termed "coated paper", i. e.

paper produced by applying to a previously dried paper web a surface coating of filler and adhesive, and allowing it to dry thereon without any substantial pressure being exerted upon the coating in the wet condition after it has been distributed upon the web, but which paper may after drying be subjected to calendering if desired, because in coated paper the fibrous layer of the sheet is substantially entirely covered and the surface consists substantially of an adhesive-filler layer; while in the present invention the applied filler while more concentrated at or near the surface, nevertheless combines with and penetrates into the web to a certain and substantial extent, (with a concentration decreasing however in a direction toward the center of the sheet), and this combination is enhanced when as in the preferred practice of my invention described above herein, the wet or moist web with the applied filler layer is subjected to pressure as by passing through rolls which may be press rolls, smooth rolls and the like, prior to the completion of the drying. Thus, the filler layer penetrates, is embedded in, and becomes an integral part of the fibrous web itself rather than a layer merely stuck on the surface of a web. My paper is thus distinct in physical characteristics from ordinary above described coated paper because of the penetration of the filler into the web itself, has better folding qualities, can be made relatively lighter in weight, and has the further great advantage of economy in manufacture.

The term "paper mix" as used herein is intended to mean a mix of various constituents including fibre from which paper may be made, either alone or after the addition of other ingredients.

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 of August 10, 1926; calcium carbonate magnesium hydroxide disclosed in my U. S. Patent No. 1,415,391 of 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.

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. Inasmuch as my invention relates to white or substantially white paper I exclude from the scope of the word "paper" as used in the claims any paper containing any such quantity of material such as pitch, asphalt or other substitute thermoplastic material as would produce a paper other than that which is known in the trade as white or substantially white paper.

When I use the expression "wire side", I use it in the ordinarily accepted papermaking sense of the term to mean that side of the web which has been adjacent the web-forming means, i. e., the wire cloth or other means serving the equivalent purpose.

Where in the claims I use the word "web" I mean to include not only the already formed web, after it has left the web-forming device, but also the forming web as it exists at any point on the web-forming device.

Where in the claims I use the word "adding" in reference to filler and a paper web, I mean the process of including a filler in the forming web and/or applying it to the surface or surfaces of the formed web, preferably prior to the completion of the drying of said web, in such a manner that the filler will be concentrated at or near the surface of the paper web, and be combined with and substantially penetrate into said web.

Reference is hereby additionally made to my Patent No. 1,812,832, issued June 30, 1931.

While I have described in detail the preferred embodiments 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. A paper which comprises a fibrous layer containing alkaline filler, at least one surface of which layer is provided throughout substantially the entire area of said surface with juxtaposed particulate substantially nonalkaline areas by virtue of having a surface layer comprising nonalkaline filler combined with and substantially penetrating into said fibrous layer.

2. A paper according to claim 1 in which said nonalkaline filler comprises calcium sulfate.

3. A paper according to claim 1 in which said surface layer comprises nonalkaline filler having an index of refraction higher than that of said alkaline filler.

4. A paper according to claim 1 in which said nonalkaline filler comprises a substantially white compound selected from the group consisting of substantially water insoluble nonalkaline barium, lead, tin, zinc, antimony, titanium, bismuth, vanadium and zirconium compounds.

5. A paper according to claim 1 in which said nonalkaline filler comprises a substantially white substantially water insoluble nonalkaline compound of zinc.

6. A paper according to claim 1 in which said nonalkaline filler comprises a substantially white substantially water insoluble nonalkaline compound of titanium.

7. A paper which comprises an inner fibrous layer and two outside filler layers, one on each side of said fibrous layer, said filler layers being combined with and substantially penetrating into said fibrous layer, at least one of said outside filler layers comprising nonalkaline filler which provides at least one surface of said fibrous layer with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface, the fibrous layer of said paper having alkaline filler present therein.

8. A paper which comprises an inner fibrous layer comprising fibrous material and alkaline filler incorporated therewith, and two outside filler layers, one on each side of said fibrous layer, comprising nonalkaline filler, combined with and substantially penetrating into said fibrous layer, at least one surface of said fibrous layer being provided throughout substantially the entire area of said surface with juxtaposed par-

ticulate substantially nonalkaline areas by virtue of the outside filler layer comprising nonalkaline filler present at such surface.

9. A paper containing alkaline filler, said paper comprising an inner fibrous layer, and two outside filler layers, one on each side of said fibrous layer, one comprising alkaline filler and the other comprising nonalkaline filler which provides one suface of said fibrous layer with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface, both filler layers being combined with and substantially penetrating into said fibrous layer.

10. A paper which comprises an outside fibrous layer, an inner layer comprising alkaline filler combined with and substantially penetrating into said fibrous layer, and a surface layer comprising nonalkaline filler combined with and substantially penetrating into said combined fibrous and alkaline filler layers, thereby providing a surface of said paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

11. A paper which comprises an outside fibrous layer comprising fibrous material and alkaline filler incorporated therewith, an inner layer comprising alkaline filler combined with and substantially penetrating into said fibrous layer, and a surface layer comprising nonalkaline filler combined with and substantially penetrating into said combined fibrous and alkaline filler layers, thereby providing a surface of said paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

12. A multi-ply paper containing alkaline filler which comprises two plies, at least one surface of each of said plies having a layer comprising nonalkaline filler combined with and substantially penetrating into said ply, at least one surface of said paper being provided throughout substantially the entire area of said surface with juxtaposed particulate substantially nonalkaline areas by virtue of one of said layers comprising nonalkaline filler.

13. A multi-ply paper containing alkaline filler which comprises two plies, each of said plies having a layer comprising nonalkaline filler combined with and substantially penetrating into the side opposite the wire side of said ply, said plies being united wire side to wire side, at least one surface of said paper being provided throughout substantially the entire area of said surface with juxtaposed particulate substantially nonalkaline areas by virtue of one of said layers comprising nonalkaline filler.

14. A multi-ply paper containing alkaline filler at least one surface of which is provided throughout substantially the entire area of said surface with juxtaposed particulate substantially nonalkaline areas by virtue of having a surface layer comprising nonalkaline filler combined with and substantially penetrating into one of the plies of said paper.

15. That step in the method of manufacturing paper containing alkaline filler which comprises applying nonalkaline filler to a fibrous web containing alkaline filler thereby providing at least one surface of said paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

16. The steps in a method of manufacturing paper containing alkaline filler comprising preparing a paper mix containing alkaline filler, delivering said mix to a web-forming device, forming a web, and adding nonalkaline filler thereto, thereby providing at least one surface of the paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

17. The steps in a method of manufacturing paper containing alkaline filler comprising preparing a paper mix containing alkaline filler, delivering said mix to a web-forming device, forming a web, and adding nonalkaline filler to said web prior to the passage of said web from said web-forming device, thereby providing at least one surface of said paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

18. The steps in a method of manufacturing paper containing alkaline filler comprising preparing a paper mix, delivering said mix to a web-forming device, forming a web, adding alkaline filler thereto, and adding nonalkaline filler thereto, thereby providing at least one surface of said paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

19. The steps in a method of manufacturing paper containing alkaline filler comprising preparing a paper mix, delivering said mix to a web-forming device, forming a web, and, prior to the passage of said web from said web-forming device, adding alkaline filler thereto and adding nonalkaline filler thereto, thereby providing at least one surface of said paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

20. The steps in a method of manufacturing paper containing alkaline filler comprising preparing a paper mix, delivering said mix to a web-forming device, forming a web, adding alkaline filler thereto prior to the passage of said web from said web-forming device, and subsequently adding nonalkaline filler thereto, thereby providing at least one surface of said paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

21. The steps in a method of manufacturing paper containing alkaline filler comprising preparing a fibrous mix containing alkaline filler, delivering said mix to a web-forming device, forming a web, and, prior to the passage of said web from said web-forming device, adding alkaline filler thereto and adding nonalkaline filler thereto, thereby providing at least one surface of said paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

22. The method of manufacturing paper containing alkaline filler which comprises preparing a paper mix containing alkaline filler, delivering said mix to a web-forming device, forming a web, adding alkaline filler thereto prior to the passage of said web from said web-forming device, and subsequently adding nonalkaline filler thereto, thereby providing at least one surface of said paper with juxtaposed particulate substantially nonalkaline areas throughout substantially the entire area of said surface.

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