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PROCESS FOR MAKING PAPER

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This invention relates to the separation and recovery of finely divided mineral matter from aqueous suspensions thereof. It is of particular value in connection with the manufacture of paper in relation to the use, retention, and recovery of the mineral filling material used therein.

In the manufacture of many grades of paper it is customary to prepare an aqueous suspension or furnish containing vegetable fibrous material such as sulfite and/or sulfate pulp, and mineral filling material or filler, such as clay, chalk, talc, calcium sulfate, and the like. This aqueous suspension is flowed over a forming device, such as a wire screen, upon which the solids (fibrous material and filler) collect in a mat while most of the liquid (water) passes through the screen. While the fibrous material is largely retained upon the screen a considerable portion of the filler usually escapes through the wire and is carried away in the effluent or white water. Generally speaking the higher the concentration of filler in the furnish going to the paper machine wire, the greater is the proportion of the filler that passes through the wire and accordingly the lower is the retention of filler in the paper web. Hence in making printing papers, in which the proportion of filler to fiber is fairly high, the question of filler retention has importance. It is not so much a question of actually losing the filler that goes into the white water because most of the filler can be recovered but there is a real operating difficulty arising from low retention. When the retention is low, i. e. when the proportion of the total filler in the furnish which is retained in the paper web is low, a quantity of filler equal to several times the amount desired in the finished paper must be present in the furnish. As a result, in making paper with high filler content it often happens that so much filler must be used in the furnish that the stock gives trouble on the wire. The operator says that the stock "lies dead" and paper of poor quality results. Aside from this serious difficulty with many furnishes a point is reached beyond which no increase in the filler content of the paper results however much the filler content of the furnish may be increased.

It will be seen therefore that in making paper of moderate filler content it is advantageous, and in making paper of high filler content it is imperative to take steps to improve filler retention. It is possible to coagulate the filler by addition of alum to the furnish just before the stock goes to the paper machine wire. In the case of pa-

pers containing inert fillers, e. g. clay, the paper is, as a result of the late alum addition, liable to be left unduly acidic with the well known disadvantages resulting therefrom. In the case of paper filled with calcium or magnesium carbonate the effects of adding alum late are even more undesirable. In such a case the alum will be present in the forming web and will react with the carbonate to liberate carbon dioxide gas which may form pits or holes in the surface of the web. Alum or other acidic material is generally considered necessary to set coloring agents or sizing agents in many papers. When such acidic material is used in furnishes containing carbonate filler the earlier the acidic material is added to the furnish the better is the result from the viewpoint of surface characteristics. In fact it is preferable to avoid entirely the use of acidic material in furnishes containing carbonate filler if avoidance is feasible.

A method in use for increasing retention in clay filled papers is to add alum to the furnish and later, just before the stock goes to the paper machine wire, to add an acidulated solution of animal glue. The action of the glue and alum together is to flocculate or coagulate the solids of the furnish so that they all settle together and are to a large extent held together on the wire. The retention of filler is of course by no means made perfect by this method but in many cases it is very appreciably improved. In the case of furnishes containing carbonate filler the use of alum and acidulated glue solution is somewhat undesirable owing to the liability of reaction with the carbonate.

I have found that retention of mineral fillers in paper webs can be greatly increased by use of karaya gum, preferably a solution or dispersion of karaya gum containing alkali. This result is contrary to what might be expected because in the past karaya gum treated with alkali has been used successfully in paper making furnishes to deflocculate the fibers and prevent coagulation thereof. The difference between previous results and those I have achieved may be due to the fact that the papers formerly made with the use of karaya gum were made without use of mineral filler or alum.

In using karaya gum as a deflocculating agent in the past it has been the preferred practice to treat the gum with ammonia. In my process for flocculating finely divided mineral matter as well as filler and fiber mixes, I may use karaya gum treated with ammonia, but I prefer to use the gum treated with an alkaline phosphate (e. g.

trisodium phosphate) because the gum, so treated, appears to be somewhat more effective, especially in furnishes which contain calcium or magnesium carbonate filler. This does not mean that karaya gum treated with other alkalis is not effective. Even a solution of gum without added alkali has a considerable effect in flocculating a suspension of mineral filler, especially alkaline filler, but karaya gum treated with an alkaline phosphate is considerably more effective.

Some flocculation is produced by introduction of the gum solution into an aqueous suspension containing only fiber and filler. A far greater effect is obtained, however, if the furnish contains a mordant such as alum or an hydroxide of a metal such as aluminum hydroxide or equivalent which is relatively insoluble in the furnish. The metallic hydroxide may be prepared separately and then added to the furnish, if desired. Usually, however, more effective flocculation is obtained if the hydroxide is precipitated in the furnish, probably because of the more uniform dispersion thus obtained. Generally speaking, the precipitation of aluminum hydroxide involves the addition of acid to the furnish, e. g. aluminum hydroxide and sulfuric acid are formed by hydrolysis of aluminum sulfate added to the furnish and some of the acid may react with the carbonate filler with undesirable evolution of carbon dioxide gas. If it is desired to avoid possibility of CO₂ evolution zinc hydroxide may be used as the mordant, and may be added dissolved in ammonia water from which it precipitates when diluted by the water of the furnish or a dispersion of aluminum hydroxide may be used.

Karaya gum, sometimes called kutira gum, is secreted by the plant *Cochlospermum gossypium* and other related species found in northern India and elsewhere. It is probable that gums from different sources vary somewhat in composition. They all swell readily in water and evolve acetic acid when treated with mineral acid. It is probable that the beneficial effect of alkali treatment according to the present invention is due to the fact that the alkali at least partially deacetylates the gum.

Karaya gum may be dispersed in water, by aid of heat if desired, to make a viscous dispersion of up to about 2% solids content. To this dispersion advantageously is added ammonia or other alkali, preferably an alkali metal phosphate. A small quantity of the gum dispersion may be added to an aqueous dispersion of mineral filler, i. e. finely divided mineral matter, or to mixtures of fiber and mineral filler, e. g. a paper making furnish. Usually such a dispersion will contain in suspension, as a mordant, a small proportion of water-insoluble metal hydroxide. The addition of the gum dispersion brings about rapid flocculation of the suspended matter which, provided it is not agitated too violently or for too long a time, will settle from its aqueous medium.

Karaya gum performs a very valuable function when used according to the invention in an actual paper making furnish where it flocculates the whole mixture, which when formed into a paper web shows a filler content much higher than the same furnish would otherwise yield.

The invention also contemplates the use of karaya gum or alkali treated karaya gum to flocculate mineral filler from aqueous suspensions which are nearly or entirely without fiber content. The solids in the white water from a paper machine making mineral filled paper normally consist chiefly of mineral filling material with

usually a small quantity of short fibers. Such solids are frequently recovered by allowing the white water to stand in settling tanks until the solids have separated in a concentrated layer which can be parted from the water layer. The concentration and separation of the solids may be greatly facilitated by addition of from 0.1 to 3% of karaya gum based on the solids present. As a result of the action of such gum the solids flocculate and settle much faster than normally, and the settling may be so complete that the supernatant liquor is left practically free from turbidity.

Another use for the flocculating effect of the karaya gum according to the invention is in flocculation of pigments which are washed by decantation. For instance the lime sludge formed in the process of recovering soda from soda pulp mill waste liquor may be flocculated by gum so that its washing may be facilitated.

A specific example of the manner in which the invention may be used follows:

A paper making furnish was prepared containing 0.61% fiber, 0.88% calcium carbonate filler, and aluminum hydrate equivalent to 0.012% of aluminum sulfate, all dispersed in water. The ingredients had been mixed in more concentrated form in a beater and put through the usual beating and refining followed by dilution. The mixture was then run out on a paper-machine to make 50 pound English Finish book paper having 21.6% of filler by analysis.

The quantity of filler in the furnish was then cut back until it was only 0.46%; the other ingredients remained the same as before. Then, just before the furnish was run out upon the paper machine, there was added a quantity of karaya gum amounting to 0.2% of the paper being made. The karaya gum was added continuously to the flowing paper stock from a dispersion containing

Karaya gum.....	pounds..	30
Trisodium phosphate.....	do.....	30
Water	gallons..	260

The paper made from this furnish was 50 pound English Finish book paper, having a filler content of 23.5% by analysis. Thus it is seen that when karaya gum was used the quantity of filler in the furnish was decreased by almost 50% while the quantity of filler retained in the paper actually increased somewhat.

Comparative tests indicate that in settling alkaline fillers, e. g. calcium carbonate, alone each of the forms of karaya gum above referred to, i. e. a simple aqueous dispersion and an aqueous dispersion containing an alkali such as an alkali metal phosphate, each with and without the presence of alum, is quite effective. Tests were made on a simple aqueous suspension containing 3% of calcium carbonate. At the end of 2 minutes the suspension without any addition settled less than 1 inch and the supernatant liquid was very cloudy whereas a sample treated with 0.1% (calculated on the weight of calcium carbonate) of a simple aqueous dispersion of the gum settled 9.7 inches, a sample treated with 0.1% of gum and an equal weight of trisodium phosphate settled 9.2 inches, a sample treated with 0.1% of gum and 1% of crystallized aluminum sulfate settled 5.6 inches and a sample treated with 0.1% of gum and an equal weight of trisodium phosphate and 1% of crystallized aluminum sulfate settled 9.3 inches in the same period.

Similar tests show that karaya gum alone and

karaya gum with alkali is less effective for the settling of neutral fillers such as clay but the presence of a mordant, e. g. the addition of alum or aluminum sulfate along with the gum alone or in the presence of alkali is quite effective. These tests show that with alkaline filler mordant is not needed whereas with inert filler mordant is needed.

The following results were obtained by comparative tests carried out on paper furnishes containing alkaline filler and inert filler respectively. The gum alone applied to a furnish containing calcium carbonate filler improved the retention very little. The gum with alkali gave somewhat better results. Untreated gum with alum gave greatly improved results and gum treated with alkali and alum gave best results. These results are not entirely consistent with the results obtained in treating a simple suspension of alkaline filler without fiber because whereas the gum without alum was practically as effective as the gum with alum on the filler alone the gum with alum was much more effective than the gum without alum on the paper furnish. Moreover whereas the untreated gum was practically as effective as the alkali treated gum on the alkaline filler alone, the alkali treated gum gave better results both with and without alum in the treatment of furnish containing alkaline filler.

Retention tests on a clay filled paper furnish gave results quite similar to those obtained with a calcium carbonate filled furnish.

Tests were carried out to determine the optimum deacetylation of the gum or the optimum quantity of alkali to be used with the gum in the treatment of furnishes to improve retention. The minimum effective quantity of trisodium phosphate was found to be about 15% of the weight of the gum. On the other hand 50% of trisodium phosphate on the weight of the gum was found to give substantially maximum effect. The use of trisodium phosphate in quantities up to several times the weight of the karaya gum has no apparent deleterious effect and in some cases such a quantity gives slightly better results than the 50% quantity previously mentioned.

I claim:

1. Process for the flocculation of finely divided mineral matter suspended in an aqueous medium which comprises dispersing a small amount, compared to the weight of mineral matter in suspension, of karaya gum in said aqueous medium.

2. Process as defined in claim 1 in which the karaya gum is at least partially deacetylated.

3. Process as defined in claim 1 in which the karaya gum is added to the suspension in the form of an aqueous dispersion.

4. Process as defined in claim 1 in which the karaya gum is added in the form of an aqueous dispersion of the reaction product of the karaya gum and an alkali.

5. Process as defined in claim 1 in which the karaya gum is added in the form of an aqueous dispersion of the reaction product of the karaya gum and an alkali metal phosphate.

6. Process as defined in claim 1 in which the mineral matter comprises an alkaline earth metal carbonate.

7. Process as defined in claim 1 in which the mineral matter is inert.

8. Process as defined in claim 1 in which the aqueous suspension of finely divided mineral matter contains a mordant.

9. Process as defined in claim 1 in which the aqueous suspension of finely divided mineral matter contains an insoluble metal hydrate.

10. Process as defined in claim 1 in which the aqueous suspension of finely divided mineral matter contains aluminum hydrate.

11. Process as defined in claim 1 in which the aqueous suspension of finely divided mineral matter contains zinc hydrate.

12. Process as defined in claim 1 in which the mineral matter is inert and in which an aqueous dispersion of partially deacetylated karaya gum together with a mordant is added to the suspension.

13. Process which comprises dispersing in an aqueous paper-making furnish comprising vegetable fibrous material and a substantial amount of mineral filler dispersed in an aqueous medium, a relatively small amount, based upon the solids content of the furnish, of karaya gum thereby flocculating the solids content of the furnish.

14. Process as defined in claim 13 in which the karaya gum is added in the form of an aqueous dispersion thereof.

15. Process as defined in claim 13 in which the karaya gum is added in the form of an aqueous dispersion of the at least partially deacetylated gum.

16. Process as defined in claim 13 in which the karaya gum is added in the form of an aqueous dispersion of the reaction product of the gum and an alkali.

17. Process as defined in claim 13 in which the karaya gum is added in the form of an aqueous dispersion of the reaction product of the gum and an alkali metal phosphate.

18. Process as defined in claim 13 in which the furnish contains a mordant.

19. Process as defined in claim 13 in which the furnish contains an insoluble metal hydrate.

20. Process as defined in claim 13 in which the furnish contains aluminum hydrate.

21. Process as defined in claim 13 in which the furnish contains zinc hydrate.

22. Process as defined in claim 13 in which the mineral filler is an alkaline earth metal carbonate.

23. Process which comprises adding to a paper-making furnish comprising vegetable fibrous material and a substantial amount of mineral filler dispersed in an aqueous medium, a mordant and an aqueous dispersion of an at least partially deacetylated karaya gum thereby flocculating the solids content of the furnish.

24. Process as defined in claim 23 in which the mineral filler is an alkaline earth metal carbonate.

25. Process as defined in claim 23 in which the mineral filler is inert.

26. Process as defined in claim 23 in which the mineral filler is an alkaline earth metal carbonate and the mordant is an insoluble metal hydrate and the partially deacetylated karaya gum is the reaction product of karaya gum and an alkali metal phosphate.

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