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WATERPROOFING FIBROUS AND OTHER MATERIALS

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This invention relates to the waterproofing of fibrous and other materials such as are used in the manufacture of sized or water-resistant paper, and more particularly to the rendering of the fibers and filling material thereof either neutral or alkaline.

Rosin sized paper has always been made with the fibers thereof acidified. That is, the present processes of engine sizing where the sizing ingredients are mixed with the pulp, some form of sodium resinate and sulfate of alumina are always used and unless sufficient of the sulfate of alumina (alum) is used to acidify the fiber, as well as the sodium resinate, no sizing effect is obtained. The amount of alum used varies from 1% to 5% of the dry weight of the fiber. One part of alum will coagulate five parts of sodium resinate but before any sizing effect is obtained, the sodium resinate must be completely decomposed and all soda removed from combination with the resin. In order to complete this reaction, about 1½ to 2 parts of alum are required for one part of sodium resinate which produces an acid condition represented by a pH of 4 to 5, and this acid condition must exist a sufficient length of time to complete the reaction.

This acid condition is required because sodium resinate is distinctly alkaline and when mixed with a cellulose fiber, the soda thereof is absorbed by the cellulose and held with such affinity that it is removed with difficulty. This fact explains why the proportions of alum and sodium resinate used in the known practice of paper sizing, are quite variable and the excessive amount of alum generally required is sufficient to produce an injurious effect upon the strength and permanency of the paper. Further, as the chemical reaction between sodium resinate and sulfate of alumina varies greatly under different conditions, there is very little uniformity in the sizing results obtained by the use of these ingredients. Accordingly, one object of my invention is to devise a process of paper sizing wherein neither alum nor sodium resinate is required to be used.

The amount of acidity required for sizing paper with sodium resinate is such that if any filling material is used that is of the type containing carbonates as are sometimes found in clay or talc, it is necessary to convert all of the carbonates into sulfates by treatment with alum before the paper can be sized because as long as any carbonates are present, the fibers cannot be acidified. In the presence of carbonates, the maximum acidity that can be produced is represented by a pH of 6.5 and this acidity is due to

the acid reaction resulting from the presence of carbon dioxide in solution. Even in the diluted condition of the paper stock at the wet end of a paper machine, a pH of 5 cannot be obtained with alum in the presence of a carbonate.

Yet in recent years, many large manufacturers of book paper have used calcium carbonate as a loading material to the extent of 20% of the weight of the paper. It is impossible to acidify such papers and they are always unsized when a sodium resinate size is attempted to be used thereon. Such paper may be given a waterproofing effect by the use of wax emulsions, when effect is not produced by a chemical reaction as in sizing, but by the fusibility of the wax particles. Wax is a water-resistant lubricant but as it does not function as a binding agent like rosin, it is not a proper substitute for rosin in paper making. So, regardless of all methods that have been previously proposed for making a sized paper containing an alkaline filler and a size containing sodium resinate, it is not yet possible to produce a sized paper using these ingredients because both the sodium resinate and the alkaline cellulose must be treated with an acid concentration that is impossible to obtain in the presence of a carbonate.

Therefore, another object of my invention is to devise a method of sizing whereby there can be sized, any papers that are loaded with filling materials containing carbonates such as calcium or magnesium carbonate, and also any paper making fibers that contain free lime such as are found in straw pulp. Also whereby paper can be sized in the presence of hard water containing carbonates without first having to acidify all of the water with alum.

So one feature of this invention is the discovery that if a size is made with ammonia as the base for saponification, paper can be sized therewith without being acidified, because the ammonia is volatile and can be entirely removed either by hot or cold drying, which leaves the paper neutral so far as this alkali is concerned.

Another feature of my discovery is that when an ammonia soap is used for sizing paper, it is not necessary to acidify either the paper making fibers or the soap, because the ammonia absorbed by the cellulose will be removed without chemical treatment upon drying of the paper, and all alkalinity disappears from both the size and the paper fibers. Another feature of this process is that it can be used to size any paper filling materials better than it is possible to do with any combination of sodium resinate and alum.

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Therefore, whereas the current methods of coagulating sodium resinate produces first, a precipitate containing a non-volatile alkali and requires the reaction with further alum to acidify it, by the practice of this invention, it is found that the coagulate of ammonium resinate and aluminum hydrate does not require to be acidified by alum to produce a sized paper. So this invention comprises a new chemical reaction in sizing that is distinct from prior processes which involved carrying out the sizing operation in two steps; first, by coagulating the size; and second, by acidifying the basic precipitate with alum.

The process of sizing of this invention not only overcomes the many difficulties found in sizing due to alkaline waters and fillers, but it makes possible the production of much stronger and more permanent papers than those that are acidified in the usual manner with alum to a pH of from 4 to 5.

In carrying out this process, there is first produced in the paper stock an alkaline precipitate consisting of hydrate of alumina and resin hydrate resulting from the reaction between ammonium resinate and alumina. After drying, the alkalinity disappears whereupon the paper treated therewith becomes neutral and sized. In the practice of this process, I prefer to use a resinate of ammonia, although any other ammonia soap may be compounded with this, if desired. The rosin, however, has a hardening action on the paper and is found preferable to all other materials, as the essential sizing ingredient.

The ammonia size may be made from rosin or any other saponifiable water-insoluble material, such as stearic acid, or similar product. The ammonia size may be added to the pulp fibers in any usual manner and it can be coagulated with an aluminum hydrate which may be added in the freshly precipitated form, or be produced from the reaction between alum and free ammonia or other alkali present in the paper stock.

An example of the method of operation of this process is as follows:

One thousand pounds of pulp fiber dry weight is mixed in an ordinary paper mill beater with about twenty thousand pounds of water. To this is added about three hundred pounds of alkaline filler such as CaCO_3 , 15 pounds of ammonium resinate (dry weight) is then added in the form of an aqueous solution containing 500 pounds of water. 15 pounds of alum are then added, which immediately reacts with the carbonate to form theoretically $3\frac{1}{2}$ pounds of precipitated alumina Al_2O_3 . Instead of adding this alum to the beater, the alum solution may first be neutralized with ammonia or other alkali, and the precipitated alumina added to the beater with the size. The hydrated aluminum oxide Al_2O_3 will combine in the beater with the ammonium resinate to form a compound which coats the fibers in the beater and which will size the paper when the pulp is dried.

Another method of operation is as follows:

The carbonate filler, or other filling material, is mixed with water in a tank to a concentration of about 20% solids to which mixture is added an aqueous solution containing ammonium resinate to the extent of about one pound of the dry resinate to one hundred pounds of filler. To this may be added one pound of alum to each one hundred pounds of filler along with sufficient ammonia or other alkali to neutralize it and precipitate the alumina.

This separately treated filling material con-

taining said sizing ingredients may be added to the paper stock in the beater, in the Jordan chest, in the machine chest, or at the wet end of the paper machine. This treatment produces a paper containing individually sized filler particles, that is, each particle thereof is coated individually with size. The paper stock in the beater may be sized by the use of ammonium resinate and alumina. If this is done, the result is a paper with fibers and filler particles individually sized with the same sizing materials. Or the paper stock may be first sized with any sodium resinate and sufficient alum to acidify the fibers, whereupon and later, the ammonia sized filler material is added thereto in the beater, machine chest, jordan, and so forth, whereby a paper is produced having its fibers individually sized by the use of sodium resinate while its filler particles are individually sized with ammonium resinate and alumina. Since the ammonium resinate is somewhat more expensive than sodium resinate, this latter procedure offers some saving in cost over treating both fibers and filler with ammonium resinate.

In general, in the final mixture of paper fibers and filling material, there must be no alkalinity derived from soda. There will be none in the mixture resulting from the practice of this invention because any alkalinity produced by the ammonium resinate disappears on drying of the paper. This produces a neutral and sized paper.

With the present processes using sodium resinate, it is not possible to fully size a heavily loaded paper containing from 20% to 30% filler even if the filler is not alkaline. By the use of my process, however, any kind of filling material can be sized. In order that ammonium resinate may properly function as a sizing material there should be always present enough excess ammonia or other alkali, to form sufficient alumina Al_2O_3 , when reacting with alum to form a resinate of alumina, but it is immaterial how this ammonium hydrate is produced.

I have also discovered that the chemical precipitate formed from ammonia resinate and aluminum hydrate will waterproof other alkaline materials such as Portland cement and other cements which contain free lime or carbonates, whereas sodium resinate and alum have no waterproofing effect thereon, and the use of alum thereon would be more destructive to the useful properties of such materials.

It will thus be seen that this invention discloses a practical method of actually sizing a paper containing an alkaline filler, by means of a chemical precipitate and that it also teaches how to size a straw pulp without washing the free lime therefrom. The simplicity of this process eliminates most of the difficulties in sizing heretofore due to the variable reactions that take place between sodium resinate and sulfate of alumina.

I claim:

1. A waterproofing material comprising the precipitate formed by the chemical reaction between an ammonium soap and aluminum hydrate.
2. A waterproofing material comprising resinate of alumina formed by precipitating ammonium resinate with approximately its combining weight of precipitated alumina (Al_2O_3).
3. A sized, filled paper comprising a fibrous material, alkaline filler, rosin, and alumina derived from ammonium resinate and aluminum hydrate.

- 4. A non-acid sized paper product comprising fibrous material, rosin, and alumina derived from ammonium resinate and aluminum hydrate.
- 5. An alkaline sized paper product comprising a fibrous material, free lime, rosin, and alumina derived from ammonium resinate and aluminum hydrate.
- 6. A waterproof, calcareous cement comprising cementing material, rosin, and alumina derived from ammonium resinate and aluminum hydrate.
- 7. A sized filled paper comprising fibers sized with sodium resinate and filler particles sized by the use of ammonium resinate.
- 8. A sized filled paper comprising individually sized filler particles sized with ammonium resinate.
- 9. In a method of manufacturing sized paper, the step of adding to the paper mix from which said paper is to be made, ammonium resinate and hydrate of alumina.
- 10. In a method of manufacturing sized paper filled with alkaline filler, the step of adding to the mixture of paper stock and filler from which the paper is to be made, an ammonia soap and hydrate of alumina.
- 11. In a method of manufacturing sized paper filled with alkaline filler, the addition to the paper stock from which the paper is to be made, of ammonium resinate and hydrate of alumina.
- 12. In a method of manufacturing a sized filled paper, the steps of adding to the paper stock from which the paper is to be made, an ammonia soap, and coagulating said soap with the product of the reaction between said carbonate and sulfate of alumina.
- 13. The method of manufacturing a sized paper which includes the addition to the paper stock from which the paper is to be made, of ammonium resinate, a carbonate filler, and sulfate of alumina.
- 14. The method of making a non-acidified sized paper, which includes the addition to the paper stock from which the paper is to be made, of ammonium resinate, and sufficient hydrate of alumina to form aluminum resinate.
- 15. The method of waterproofing a filling material containing carbonates, which comprises incorporating into the wet mix a solution of an ammonia soap, and coagulating this soap with a colloidal precipitate of hydrate of alumina.
- 16. The method of paper making which comprises separately sizing the particles of the filler with a precipitate formed from ammonium resinate, sizing the paper fibers, mixing the fibers and filler, and forming into paper.
- 17. The method of paper making which includes the steps of producing in the paper stock an alkaline precipitate comprising hydrate of alumina and resin hydrate, and then drying the so treated paper stock to produce a sized neutral paper.
- 18. The method of making a filled paper which comprises the step of incorporating into the filler before adding it to the paper stock, an ammonia soap and later bringing about coagulation thereof in a beater.
- 19. The method of waterproofing a calcareous cementing material which comprises the addition to the wet mass, a solution of an ammonia soap, and coagulating the soap with hydrate of alumina.
- 20. The method of waterproofing a calcareous cementing material which comprises the steps of adding to the wet cement, a solution of resinate of ammonia, and precipitating rosin therefrom by the addition thereto of hydrate of alumina.

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