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MANUFACTURE OF PRESSED CELLULOSE ARTICLES

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This invention relates to manufacture of pressed cellulose articles; and it comprises a fine dry, fragmental sulfur having a fineness of the order of 200 mesh, being immiscible in water, having a purity of the order of 99.5 per cent and being substantially free from insoluble, amorphous sulfur, said product being made by wet grinding sulfur in the presence of a peptizing agent, such as a colloidal tanning agent, washing to remove such agent and drying; and it also comprises, as a new article, a hot-pressed cellulose product having uniformly dispersed therethrough from 5 to 200 per cent of sulfur in water repellent form and having a fineness of the order of 200 mesh, the said product being substantially free from peptizing agents for sulfur; and it further comprises a process of making such an article wherein a dispersed paper pulp is mixed with the above described sulfur preparation, (usually before drying the same) the mixture of paper pulp and sulfur is formed into final shape and is then hot pressed; all as more fully hereinafter set forth and as claimed.

The fine sulfur of commerce usually occurs in one of two forms. The term "flowers of sulfur" is at times loosely applied to cover both types. Strictly speaking this term applies only to sulfur which has been sublimed and condensed in finely divided form. The other type of fine sulfur is merely a ground product obtained by grinding "rock", "roll" or "lump" sulfur, as the coarser particles produced by various processes are called. Both of these forms are immiscible in water and neither is much finer than about 50 mesh. There is a considerable demand for a sulfur of greater fineness. For some purposes it is desired to have such a product miscible with water while in other cases a water repellent product is desired.

An important use for fine sulfur is in the so-called dusting powders used as fungicides for fruit and other trees. The fine sulfur of commerce has not proved entirely satisfactory for this purpose since it does not readily stick to the foliage. It is usually necessary to employ a so-called "sticker" in the dusting powder to supply the necessary adhesiveness.

Fine sulfur is also used to some extent for impregnating paper and carboard. Surface impregnation is usually employed. It has been proposed to mix fine sulfur with paper pulp before making the same into paper, cardboard and the like. Here again it is found that the fine sulfur of commerce does not possess the requisite adhesiveness for best results. It does not readily stick to the cellulose fibres. This method has not been developed commercially due to the large losses caused by this lack of adhesiveness. It has been proposed to overcome this difficulty by the use of certain agents whose alleged purpose is to precipitate on and to stick to the fibre, dragging the sulfur along with them. But such agents do not form advantageous components of cellulose pulp articles.

In a prior and copending application, Serial No. 608,866, filed May 2, 1932, of which the present application is a continuation in part, I have described and claimed a fine sulfur product miscible with water; the said product being obtained by wet grinding sulfur in the presence of a peptizing agent having tanning properties. This product, as described in the acknowledged application, can be washed to remove the peptizing agent and, while still wet, will retain its miscibility with water. A dry miscible preparation can be obtained by drying the product without removing the peptizing agent.

The present application is directed more particularly to an immiscible fine sulfur product which may be obtained from the above described miscible product by removing any peptizing agent and then drying. Drying destroys the property of miscibility. I have found that such a dry product has many highly valuable properties. I have also found that the process of making cellulose pulp articles, described but not claimed in my acknowledged copending application, can be improved by removing peptizing agents from the ground sulfur pulp prior to admixture with cellulose pulp.

While the miscible sulfur of my acknowledged copending application is valuable for a large number of industrial uses, I have found that the property of miscibility of this product is not always desired. Moreover the presence of the wetting or peptizing agent in the sulfur is disadvantageous for some purposes. For example, I have found that, in making sulfur and oil emulsions for spraying fruit trees, the presence of a peptizing agent such as tannic acid or sulfite waste liquor causes the sulfur pulp to be precipitated in curds when added to the oil emulsions. If the peptizing agent is removed by washing prior to addition to the oil emulsion, in accordance with my present process, the sulfur mixes with the oil and remains suspended.

I have also found that the dry immiscible preparation of my present invention is especially valuable when used in fungicide dusting powders. The new product sticks to the leaves whereas the miscible product is easily washed off. In fact

the sticking properties of my new product are so great that the use of the "stickers" in such products may usually be dispensed with. As previously mentioned the commercial "flowers of sulfur" does not show sufficient adhesiveness without the use of stickers. A possible explanation of this phenomenon is that the particles of my product are fragmentary or granular in shape while those of flowers of sulfur are spherical.

I have also found that, in the manufacture of paper products, the presence of a peptizing agent is disadvantageous for several reasons. In the presence of such an agent the sulfur particles do not stick readily to the paper fibres. A large proportion of the sulfur is washed off and lost during the process. Moreover, the presence of such agents largely destroys the water repellent properties of the sulfur and hence impairs the final products from the standpoint of waterproofness. If tannin is used as peptizing agent it is likely to impart a slight color to the paper product, especially if the water used contains any iron.

The immiscible sulfur product of the present invention can be readily produced from that of my acknowledged application merely by washing and drying. As described in the prior application one method of making a miscible sulfur is to take a pound of tannic acid (or 4 pounds of dry sulfite waste liquor solids or 8 pounds of a commercial preparation of sulfite waste liquor containing 50 per cent solids) add 0.75 ton of water and a ton of sulfur and run the mixture through some sort of fine grinding device to form a sulfur pulp. The sulfur can then be allowed to settle out. It may be washed while wet and will still retain its miscibility with water. With the dispersing agent washed out, the wet pulp of sulfur and water is still miscible with water and with wet paper pulp.

In the present invention the sulfur pulp containing peptizing agent is washed, usually by decantation, to remove this agent down to a concentration of say 0.005 per cent. The washed sulfur pulp is then dried. Drying destroys its miscibility with water. This new product is water repellent, it has a composition usually ranging from 99.5 to 99.9 per cent sulfur, it has a fineness of the order of 200 mesh and is considerably finer than flowers of sulfur or than sulfur ground in the absence of peptizing agents. Its solubility in carbon disulfide is substantially 95 per cent showing the substantial absence of amorphous sulfur, it has a fragmental particle structure and readily adheres to foliage and other objects when dusted thereon.

In my acknowledged copending application I described the use of peptizing agents having tanning properties, such as tannic acid and sulfite waste liquor. These peptizing agents are better for producing the desired results than any others with which I am acquainted. However, for certain purposes, other peptizing or wetting agents may be employed in making the products of the present invention. These include saponin, gelatin, casein and the like. When sulfur is wet ground in the presence of these agents and the resulting sulfur pulp is washed for their removal and then dried, a highly valuable new sulfur product is produced having the descriped properties. When these peptizing agents are employed instead of tannin or sulfite waste liquor it is generally necessary to add them in somewhat greater quantities, ranging up to 120 pounds per ton of sulfur in some cases. This usually renders their use disadvantageous from an economic standpoint.

In my acknowledged copending application I have described the making of a cellulose pulp article containing immiscible sulfur uniformly distributed within the article. As there stated, sulfur in miscible form containing peptizing agent can be incorporated with wet cellulose pulp in the manufacture of paper; being simply added to the pulp and stirred. Pulp board or paper can, for example, be made by suspending sulfur in the water used for paper or pulp board making and otherwise proceeding exactly as usual. The wet sheet or board can then be washed with water. This removes the peptizing agent and restores the sulfur to its normal water-repellent condition. After the paper or board is thus manufactured and dried, the sulfur can then be fused in place. It is a convenient operation to incorporate sulfur in wet paper pulp, making dry pulp board and then hot stamp to make finished articles. The sulfur melts in stamping and sets in cooling. In this way, it is possible to make articles of waterproof nature, non-absorbent of moisture, of high insulating value and proof against mildew, bacterial action, etc. The porosity of the product is not necessarily destroyed.

A better method of producing a cellulose article impregnated with the sulfur of my invention and free from peptizing agents is to wash the mixture of sulfur pulp and wetting agent for removal of the latter prior to admixture with the paper pulp. Washing by decantation is usually satisfactory but a fine filter may be employed if desired. Special solvents may be used for removal of the peptizing agents.

One method of proceeding to make the cellulose pulp articles of the present invention is to take ordinary ground sulfur of commerce, mix it with a peptizing or wetting agent in order to make it readily wet with water, then wash out the wetting agent and add the still miscible product to paper pulp. The use of the wetting agent in this process overcomes the difficulties involved in mixing untreated sulfur with water and with paper pulp. In order to stick to wet cellulose fibres sulfur particles must be readily wet with water. But untreated ground sulfur is highly water repellent. It does not effectively stick to the fibres; hence the value of my treatment.

As long as the sulfur pulp remains wet it retains its miscibility with water. It is therefore added to the paper pulp in the wet state. The sulfur particles, freed from the peptizing agent, tend to cling to the cellulose fibres. When the peptizing agent is present this adhesiveness is greatly reduced. The adhesiveness of my present product is an important factor in overcoming the losses of sulfur usually encountered when fine sulfur is added in the paper making operation. In making pulp articles I generally add the washed sulfur pulp either to the beaters or in the Jordans where it can be thoroughly mixed with the paper pulp prior to passing to the Fourdrinier machine. The sulfur is usually added in amounts equal to from about 5 to 200 per cent by weight of the finished product.

When the pulp article is dried during the finishing steps the sulfur recovers its normal water repellent state. The article is then thoroughly waterproof. Containers made of pulp board can be employed even for carrying liquids. When a wetting agent is present in the pulp board it is only partially waterproof.

I have found that, if sheeted pulp articles are

made of laminated structure, that is of several plies, only one of these plies requires impregnation with the sulfur to produce substantial waterproofness. There is another important advantage gained by impregnating only part of a multi-ply sheet. I have found that, if one or more of the plies is free from sulfur the structure as a whole retains a considerable degree of flexibility even after hot-pressing, while if all plies are impregnated the sheet is stiff and more subject to fracture upon bending. In making a multi-ply article I therefore usually leave at least one of the plies free from sulfur. One desirable structure is an article the outer plies of which are impregnated while at least one of the interior plies or the core is free from sulfur. Another advantageous structure is a compound sheet having a corrugated core impregnated with sulfur while the outside sheets are free from sulfur. These structures are, of course, advantageous even though the sulfur is not free from peptizing agents and is not of 200 mesh fineness.

Impregnation with sulfur makes a corrugated structure of about double the strength it would otherwise have. The strength of an impregnated pulp article increases rapidly with sulfur content up to about 15 per cent and more gradually from there on up to about 50 per cent by weight. Above 50 per cent the increase in strength is practically negligible. I therefore usually employ a sulfur content ranging between 15 to 50 per cent and usually not above 25 per cent.

In all cases except those applications wherein the sulfur is used mainly as a fungicide, I hot-press the pulp articles in order to melt the sulfur in place. This can be accomplished by the use of calender rolls through which the impregnated sheet may be passed or by the use of heated molds, etc. The impregnated paper pulp may be pressed into any shape desired.

In one specific operation I prepared a sulfur pulp free from peptizing agent by grinding a one ton batch of commercial pulverulent sulfur in a so-called colloid mill. Prior to grinding there was mixed with the sulfur approximately 0.75 ton of water and 1 gallon of a 30° Bé. commercial preparation of sulfite waste liquor containing about 50 per cent of solids. This mixture was run through the colloid mill and into a large settling tank equipped with an agitator. The ground sulfur pulp was allowed to settle for 1 hour and the supernatant liquor was drawn off. About 1500 pounds of water were run into the tank, the agitator was started to thoroughly mix the material and then the mix was allowed to settle for 1 hour, after which the supernatant liquor was again decanted off. This washing process was repeated 3 times until the proportion of sulfite waste liquor remaining in the sulfur pulp was reduced to less than .01 per cent by weight of solids based on the sulfur. This sulfur pulp was then introduced into the Jordans of a paper mill in amount to give about 25 per cent by weight in the finished product. The sulfur and paper pulp mixture was then passed to the Fourdrinier machine where it was made into sheet card board. After passing the drying rolls the sheet was passed through a pair of corrugated calender rolls maintained at a temperature of about 260° F. or sufficient to melt the sulfur in situ. To the corrugated sheet thus formed there was applied on both sides sheets of non-impregnated paper in the usual manner. The resulting composite sheet was found to have a strength of about double a similar sheet without a sulfur impregnated core. The impregnated sheet was also waterproof. It was made into a carton suitable for transporting fish or other like materials.

While I have described several embodiments and in some detail, various modifications in the procedure outlined may be made without departing from the spirit and scope of my invention. In making the sulfur product of my present invention any of the peptizing agents mentioned may be utilized in the grinding step. It is also possible to employ any of these sulfur products in the production of the cellulose articles of my invention. Various proportions of sulfur may be used in making these articles. Other modifications which fall within the scope of the following claims will be immediately evident to those skilled in the art.

What I claim is:

1. As a new material, a hot-pressed cellulose product having uniformly dispersed therethrough from 5 to 200 per cent of sulfur in water repellent form and having a fineness of the order of 200 mesh, the said product being substantially free from peptizing agents for sulfur.

2. In the manufacture of cellulose pulp articles, the process which comprises wet grinding sulfur in the presence of a peptizing agent having tanning properties to an extreme degree of fineness, removing the peptizing agent from the resulting sulfur pulp, mixing the sulfur with paper pulp, forming the pulp mixture into shape and hot pressing.

3. The process of claim 2 wherein the peptizing agent is one having tanning properties.

4. The process of claim 2 wherein the peptizing agent is sulfite waste liquor.

5. The process of claim 2 wherein the sulfur is ground to a fineness of the order of 200 mesh.

6. In the manufacture of cellulose pulp articles the process which comprises mixing ground sulfur with a wetting agent, washing out the wetting agent, mixing the resulting miscible product while still wet with paper pulp, forming the pulp mixture into shape and hot pressing.

7. As a new material, a hot-pressed cellulose product having uniformly dispersed therethrough from 15 to 50 per cent of fine, water repellent sulfur, the said fine sulfur being substantially free from amorphous sulfur and having a fineness of the order of 200 mesh, the said product being substantialy free from peptizing agents for sulfur.

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