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2,913,364

**METHOD OF MAKING PAPER AND PAPER-  
MAKING COMPOSITION**

Aaron Miller, San Diego, Calif., and Adolph L. Magnuson, Western Springs, Ill., assignors to Kelco Company, San Diego, Calif., a corporation of Delaware

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This invention relates to a new and useful method of manufacturing paper and to a new and useful paper composition.

It is an object of this invention to produce paper from paper-making fibers, said paper being characterized by improved commercial qualities. It is a further object of this invention to minimize mechanical treatment of paper-making materials by the method and use of a certain combination of materials hereinafter described. It is a still further object of this invention to provide a new and useful chemical treatment of the fibers used in paper making with a combination including a metallic alginate gel and a gum that will be substantially retained on said fibers and not lost in the white water. It is still another object of this invention to provide a method of paper making and a paper composition having improved qualities as to retention of fines and/or other pigment solids. It is a further object to produce a paper of improved mullen. It is a still further object to provide an improved commercial method of increasing the mullen of paper without interfering with the drainage of the paper stock and thereby slowing down the paper-making process.

One or more of the foregoing objects may be accomplished by our invention as will be hereinafter set forth. The amount and nature of improvement in the paper due to my method will vary, depending upon the type of fibers employed and the type of paper-making machine, for example, cylinder or Fourdrinier.

It is known to add materials such as galactomannan gums to paper-making fibers for the purpose of improving the mullen of paper produced therefrom. Gums, however, have the characteristic of slowing the stock and making drainage on the paper-making machine more difficult. This places a limitation on the speed of the machine and limits the amount of gum that can be used. An alginate appears to add little in the way of increased strength when used as a paper-making additive.

In accordance with our method, we treat paper-making fibers with a combination of a galactomannan gum, a water-soluble alginate, and a water-soluble polyvalent metallic salt. The last-mentioned salt causes formation of an insoluble metallic alginate gel which adsorbs together with said gum onto the paper-making fibers. Our method employing the combination comprising an insoluble metallic alginate gel and a gum has a surprising synergistic effect as will be hereinafter noted.

In the practice of this invention, we use galactomannan gums as aforementioned. Suitable galactomannan gums available commercially are locust bean gum and guar.

The water-soluble alginates that may be used in the practice of my method are alginates such as the alginic acid salt of ammonia, magnesium, potassium, sodium or other alkali metals, or the soluble alginates formed with organic base such as mono-, di-, or tri-ethanolamine. These soluble alginates may be prepared by well-known methods such as disclosed in the following United States patents: 1,814,981, Thornley and Walsh, July 14, 1931; 2,036,922, Clark and Green, April 7, 1936; 2,039,934, Green, April 7, 1936; and 2,128,551, Le Gloahec, August

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30, 1938. Other water-soluble alginic acid compounds may be used such as the alkylene glycol esters of alginic acid. Such esters may be prepared by means of the methods disclosed in U.S. Patent 2,426,125 issued to Arnold B. Steiner. In general, we prefer to use such water-soluble alginates as the commercially available sodium alginates.

The aforesaid gums or water-soluble alginates may be added in the form of an aqueous solution or dry to the pulp fibers. The water-soluble polyvalent metallic salts hereinafter described may also be added either dry or in solution to the pulp fibers. In general, it is preferable to add the water-soluble alginate salt and the gum to the paper-making fibers before the addition of the water-soluble polyvalent metallic salt. The aforesaid materials, i.e., water-soluble alginate, water-soluble gum, and water-soluble polyvalent metallic salt, may be added prior to the mechanical treatment of the pulp such as by beaters, Jordans or other refining equipment. It is preferable to add these materials so as to cause the insoluble metallic alginate gel and gum complex to adsorb on the fibers after the beating and/or refining has been substantially completed. Thus, for example, the said materials used to form the insoluble alginate gel and gum may be added with advantage after the Jordans. It is important, however, that the insoluble alginate gel and gum be adsorbed on the fibers prior to the formation of the cellular mat.

The water-soluble polyvalent metallic salts that we have found useful for our purpose are those salts that will ionize and react in an aqueous system to form the corresponding insoluble metallic alginates. Such salts are the commercially available barium, calcium, zinc, iron, copper, and aluminum salts. The preferred water-soluble polyvalent metallic salt is a water-soluble aluminum salt. Such a salt may be any water-soluble aluminum sulphate, aluminum chloride, aluminum nitrate, or aluminum acetate. The usual commercially available paper makers' alum provides a particularly satisfactory water-soluble aluminum salt.

The total quantity of gum and water-soluble alginate added to the paper-making fibers should be in the range of 0.2 lb. to 24 lbs. on a dry basis per ton of dry fibers. The gum should be present in a major portion, and the water-soluble alginate should be present in a minor portion. Within these quantities of said materials we have found from 1 to 4 parts of water-soluble alginate to 9 to 6 parts of a galactomannan gum to be particularly effective. The alum or other water-soluble polyvalent metallic salt is required in an amount equal to or in excess of the stoichiometric equivalent of the water-soluble alginate employed. Thus if paper makers' alum is used, this amount will be in the range of about 0.1 to 12 lbs. per ton of fibers, although larger amounts are not precluded.

The method of this invention has utility in paper prepared both with and without rosin size. In the event rosin size is used, the alum or other polyvalent metallic salt used in accordance with my invention must not only be present in the quantity required to precipitate rosin size but in addition in a further amount as aforesaid to form the insoluble metallic alginate gel.

To illustrate the effectiveness of the method of this invention, several Kraft liner board samples were prepared on Fourdrinier paper-making machines. The fiber used was an unbleached southern Kraft. The various additives were added after beating the fibers in a Hollander beater and refining through a Noble and Wood Unifiner, a No. 1 Claffin, and a Pony Jordan. The point of addition of the additives was just before the fan pump which fed the furnish to the paper-making machine. The additives were added as a 1/2% aqueous solution and in an amount and with results as hereinafter set forth in the enumerated examples. The mullen test referred to was

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conducted in accordance with the method of the Technical Association of the American Pulp and Paper Industry.

(1) A liner board sample was prepared by adding a commercial, medium viscosity, sodium alginate in an amount equivalent to 2 pounds per ton of fibers on a dry basis together with a sufficient quantity of alum to cause said alginate to form an insoluble metallic alginate gel. The board so prepared showed a mullen strength increase of 2% over a sample board prepared without the addition of said alginate.

(2) Another liner board sample was prepared by adding a commercial, medium viscosity, sodium alginate in an amount equivalent to 8 pounds per ton of fibers on a dry basis together with a sufficient quantity of alum to cause said alginate to form an insoluble metallic alginate gel. The board so prepared showed a mullen strength increase of 3% over a sample board prepared without the addition of said alginate.

(3) Another liner board sample was prepared by adding a commercial, medium viscosity, sodium alginate in an amount equivalent to 24 pounds per ton of fibers on a dry basis together with a sufficient quantity of alum to cause said alginate to form an insoluble metallic alginate gel. The board so prepared showed a mullen strength increase of 13% over a sample board prepared without the addition of said alginate.

(4) Still another liner board was prepared by adding a commercial locust bean gum in an amount equivalent to 2 pounds per ton of fibers on a dry basis. The board so prepared showed no increase in mullen strength over a sample board prepared without the addition of said locust bean gum.

(5) A further liner board was prepared by adding a commercial locust bean gum in an amount equivalent to 8 pounds per ton of fibers on a dry basis. The board so prepared showed a mullen strength increase of 5% over a sample board prepared without the addition of said locust bean gum.

(6) An effort was made to duplicate the alginate test substituting 24 pounds of locust bean gum. This amount of gum slowed the drainage of the stock to the extent that it was not practical to prepare a test board with this amount of additive.

(7) A still further liner board was prepared in which a water-soluble alginate, a locust bean gum, and a quantity of alum were added to the paper-making fibers. The total quantity of said gum and alginate was equivalent to 2 pounds per ton of fibers on a dry basis. The alginate was present in a ratio of 3 parts of alginate to 5 parts of gum. The quantity of alum added was sufficient to cause said alginate to form an insoluble metallic alginate gel. The resulting board showed a 10½% increase in mullen strength.

(8) Another liner board was prepared in which a water-soluble alginate, a locust bean gum, and a quantity of alum were added to the paper-making fibers. The total quantity of said gum and alginate was equivalent to 8 pounds per ton of fibers on a dry basis. The alginate was present in a ratio of 3 parts of alginate to 5 parts of gum. The quantity of alum added was sufficient to cause said alginate to form an insoluble metallic alginate gel. The resulting board showed a 16% increase in mullen strength.

(9) Still another liner board was prepared in which a water-soluble alginate, a locust bean gum, and a quantity of alum were added to the paper-making fibers. The total quantity of said gum and alginate was equivalent to 24 pounds per ton of fibers on a dry basis. The alginate was present in a ratio of 3 parts of alginate to 5 parts of gum. The quantity of alum added was sufficient to cause said alginate to form an insoluble metallic alginate gel. The resulting board showed a 24% increase in mullen strength.

We claim as our invention:

1. In the process of producing paper from paper-

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making fibers suspended in water, the improvement comprising admixing with said fibers, prior to the information of a cellular mat therefrom, a galactomannan gum, a water-soluble alginate and a water-soluble polyvalent metallic salt, the total quantity of said gum and alginate being in the range of 0.2 lb. to 24 lbs. per ton of said fibers on a dry basis, the major portion of said quantity being the gum and the quantity of said water-soluble polyvalent metallic salt being an amount sufficient to cause the water-soluble alginate to form an insoluble metallic alginate gel.

2. In the process of producing paper from paper-making fibers suspended in water, the improvement comprising admixing with said fibers, prior to the formation of a cellular mat therefrom, a locust bean gum, a water-soluble alginate and a water-soluble polyvalent metallic salt, the total quantity of said gum and alginate being in the range of 0.2 lb. to 24 lbs. per ton of said fibers on a dry basis, the major portion of said quantity being the gum and the quantity of said water-soluble polyvalent metallic salt being an amount sufficient to cause the water-soluble alginate to form an insoluble metallic alginate gel.

3. In the process of producing paper from paper-making fibers suspended in water, the improvement comprising admixing with said fibers, prior to the formation of a cellular mat therefrom, guar, a water-soluble alginate and a water-soluble polyvalent metallic salt, the total quantity of said guar and alginate being in the range of 0.2 lb. to 24 lbs. per ton of said fibers on a dry basis, the major portion of said quantity being the guar and the quantity of said water-soluble polyvalent metallic salt being sufficient to cause the water-soluble alginate to form an insoluble metallic alginate gel.

4. In the process of producing paper from paper-making fibers suspended in water, the improvement comprising admixing with said fibers, prior to the formation of a cellular mat therefrom, a locust bean gum, a water-soluble alginate and papermakers' alum, the total quantity of said gum and alginate being in the range of 0.2 lb. to 24 lbs. per ton of said fibers on a dry basis, the major portion of said quantity being the gum and the quantity of said papermaker's alum being an amount sufficient to cause the water-soluble alginate to form an insoluble aluminum alginate gel.

5. A product particularly suitable for use in the manufacture of paper, comprising wood fibers suspended in water and a galactomannan gum and an insoluble metallic alginate gel adsorbed on said fibers.

6. A produce particularly suitable for use in the manufacture of paper, comprising wood fibers suspended in water and locust bean gum and an insoluble aluminum alginate gel adsorbed on said fibers.

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