

1

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**POLYVINYLSULFONATES WITH ALUM AS
PRECIPITANTS IN THE PROTEIN SIZING
OF PAPER**

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This invention is a continuation-in-part of our copending application Serial No. 231,822, filed October 19, 1962, now abandoned.

The invention relates to the sizing of paper using polyvinylsulfonic acids and/or water-soluble copolymers of at least 10% by weight of vinylsulfonic acid and up to 90% by weight of other comonomers and/or salts of these polymers. The said polymers act as precipitants in addition to aluminum sulfate in the stock sizing of paper with animal glues, such as gelatin, bone glue and hide glue.

Surface sizing of paper with products of animal origin, such as gelatin, bone glue or hide glue, originates from the infancy of paper manufacture. It is still carried out at the present time for first quality bank-note and security paper. Glue sizing is however very often combined with rosin sizing and carried out as a stock sizing, the glue solution being introduced into the fibrous stock. Paper thus obtainable exhibits a high degree of sizing, i.e. the writing properties of the paper are not affected by abrasion, for example by the making of erasures. The paper also acquires hardness, rattle and good feel.

Although the proteins of animal glue, as high molecular weight hydrocolloids, have a certain affinity for the hydrated fiber surface, the glue is adsorbed by the paper fibers only to a slight extent if precipitants are not employed. Hence, in animal sizing, as in the case of rosin sizing, the glue must be precipitated on the paper fibers by means of precipitants. Aluminum sulfate, which is the conventional precipitant for rosin sizing, has no effect by itself in the case of animal glue. In the search for precipitants for animal glue and other proteins, certain natural polysaccharides, such as Iceland moss or carrageen have been found to be useful. Animal glue is precipitated by these polysaccharides in the presence of aluminum sulfate.

Owing to difficulties in application, particularly owing to impurities often contained in Iceland moss which must be screened off from the viscous solution prepared hot, Iceland moss has not been generally adopted as a precipitant. Condensation products of phenol or naphthalene sulfonic acids and formaldehyde, which are cheap and easy to handle, have been introduced as substitutes. Animal glue can also be precipitated by these products in the presence of aluminum sulfate.

The said condensation products, in spite of many advantages, have the disadvantage that they are not fast to light; therefore paper prepared therewith gradually becomes yellow when exposed to light. Furthermore when such paper comes into contact with substances containing iron, dark-colored iron salts may be formed. However, since animal sizing is used for the production of high grade paper from bleached pulp, particular value must be placed on an undiminished degree of whiteness and on the highest possible fastness to light. It is desirable that the degree of whiteness of the bleached pulp used as raw material be not impaired either during manufacture or during use of the finished paper.

It is an object of the invention to improve the stock sizing process of high-grade paper to be sized with protein

2

substances by making the process more economical, and to improve the quality of high-grade paper. Another object of the invention is to prepare pure with high-grade paper which is very fast to light and stable to yellowing, such as bank-note paper and security paper, and to co-employ in the sizing of such paper a precipitant which rapidly and quantitatively precipitates on the paper fiber the protein of the sizing agent in the presence of aluminum sulfate, and which produces no deleterious secondary effects in the finished paper.

I have found that polyvinylsulfonic acids and/or copolymers of at least 10% by weight of vinylsulfonic acid which are water-soluble at the usual temperatures, and up to 90% by weight of other comonomers and/or salts of these polymers are particularly advantageous precipitants in the sizing of paper with gelatin or animal glues and meet the requirements in accordance with the above-mentioned objects.

These polymeric substances, herein briefly called "VS-polymers," containing as building units in polymerized form at least 10% by weight of a monomer of the formula $\text{CH}_2=\text{CH}-\text{SO}_3-\text{X}$ in which X denotes hydrogen, alkali metal cations or ammonium cations, are by themselves just as poor precipitants for animal glue as the substances already mentioned. In the presence of aluminum sulfate, however, protein is rapidly and completely precipitated by VS-polymers in extremely fine flakes. These flakes are retained very well in the paper stock so that the added animal glue is completely utilized.

The presence of rosin size does not impair the action of the VS-polymers; on the contrary, the best results are achieved when animal glue and rosin size are used together. Although the advantages of this invention are particularly noticeable when VS-polymers and/or their salts are used instead of carrageen or the said formaldehyde condensation product, the additional use of conventional precipitants is also within the scope of this invention.

Suitable VS-polymers are not only polyvinylsulfonic acids themselves, which are the most important of such polymers, but also copolymers of at least 10% by weight of vinylsulfonic acid and one or more other water-soluble comonomers, such as acrylic acid, acrylamide, acrylonitrile and vinyl methyl ether.

The VS-polymers are more advantageously used in the form of their alkali metal salts, particularly their sodium salts, because these dissolve well in cold water.

Low molecular weight polymers and high molecular weight polymers may be used equally well; no dependence of usefulness on K-value can be established.

The VS-polymers and their salts together with aluminum sulfate exert a precipitant effect on all kinds of gelatin, hide glue and bone glue. Partly degraded and modified animal glues of anionic and cationic character are also precipitated by the precipitants according to this invention. The precipitates, which at the moment of formation are finely divided colloids, are stable in this condition for a long period so that uniform dispersion in the fiber suspension is greatly promoted. The colloid does not flocculate out quantitatively until shaken vigorously and then the water becomes clear. The completeness of the precipitation is associated with a certain minimum concentration of aluminum sulfate which as a rule is added last. Under the conditions conventional in papermaking it has been found that it is necessary to use such an amount of aluminum sulfate that the pH value is about in the range 5 to 4.5. The pH value may be further lowered without deleterious consequences for the paper sizing.

The amount of the VS-polymers or their salts required is very small. Presupposing that the pH value has been

3

adjusted to at least 5.0 with aluminum sulfate, complete precipitation of animal glue or gelatin is achieved for example with only 1% by weight of VS-polymer with reference to the amount of the said proteins. If the protein has been partly degraded, possibly by prolonged standing in the acid solution, somewhat more VS-polymer must be used. When using copolymers, the amount required as precipitant increases at about the same rate as the proportion of comonomers increases. Generally speaking, good sizing is achieved in the range of 1 to 20% by weight of VS-polymers or their salts with reference to the amount of protein.

The ratio of animal glue to rosin size may vary within the range of 0.5:1 to 3:1. When paper having a particularly hard rattle is required, however, the protein component may be further increased. The total amount of glue and rosin depends in known manner on the desired degree of sizing.

In papermaking the procedure is that the protein glue and the VS-polymer, with or without other paper sizing agents, are added to the paper stock and then aluminum sulfate is added. The stock is then further stirred as usual for some time and then supplied to the paper machine. When using VS-polymers as precipitants in stock sizing with animal glue, the normal course of papermaking need not be disturbed or interrupted and no additional expenditure or the maintenance of special working conditions is necessary. The concentration of the paper fibers in the aqueous pulp may vary between about 0.1 and 10% by weight.

Sized paper prepared from any paper raw material by the use of precipitants according to this invention is distinguished by high resistance to ink and erasure. Operation is simpler and more trouble-free than with Iceland moss; the paper retains its whiteness and is therefore more valuable than paper prepared with phenol or naphthalenesulfonic acid-formaldehyde condensation products.

The invention is illustrated by but not limited to the following examples in which parts and percentages are by weight.

Example 1

1500 parts of a 1% animal glue solution is introduced into and uniformly mixed with a fibrous stock of 9700 parts of water and 300 parts of bleached sulfite cellulose beaten to a freeness of 35° S-R (Schopper-Riegler). 3 parts of a sodium polyvinyl-sulfonate (K-value=10) is mixed with this fiber suspension. The pH value is then adjusted to 4.8 by adding 3 parts of aluminum sulfate. Paper is prepared from the fiber suspension thus prepared by dehydration on a metal wire screen and by subsequent drying in the usual way. The degree of sizing of the paper, measured by the ink flotation test at 20° C., is five times that of a paper prepared under otherwise identical conditions using 3 parts of carrageen instead of the sodium polyvinylsulfonate.

Example 2

A 1% fiber suspension of bleached sulfite cellulose beaten to 40° S-R is mixed successively with 2% of gelatin (nitrogen content 14.8%) and 0.02% of sodium polyvinylsulfonate (K-value=15). The suspension is then divided into three parts and amounts of aluminum sulfate as set out in the following table are added; different pH values are thereby set up and these are also given in the table. The yields, i.e. the percentage of protein precipitated on the paper fibers, are calculated on the basis of the nitrogen content of the paper.

Percent of aluminum sulfate added	pH-value	Percent of nitrogen in the paper	Percent yield of gelatin
0.3	5.45	0.10	33.8
0.6	4.85	0.28	94.5
0.9	4.60	0.27	91.5

4

Example 3

Paper is made from bleached sulfite cellulose (40° S-R) with an addition of 5% of animal glue, 1% of sodium polyvinylsulfonate (K-value=50) or 1% of a formaldehyde - naphthalenesulfonic acid condensation product and 1% of aluminum sulfate at pH 4.85. A comparison paper is made without additions under otherwise the same conditions. Upon exposure to light, the following degrees of whiteness were determined by means of a Zeiss Elrepho at 457 millimicrons:

Duration of exposure to light in days	Whiteness without addition	Value of the paper with polyvinyl sulfonic acid	Prepared with formaldehyde condensation product
0	87.9	87.5	81.5
10	87.8	87.3	79.2
20	87.5	86.9	76.7
30	87.1	86.5	75.2
50	86.2	85.8	74.2

Paper prepared with an addition according to this invention exhibits only a slight deviation as compared with the unsized paper in the degree of whiteness, whereas the degree of whiteness of the paper prepared with the formaldehyde-naphthalenesulfonic acid condensation product has declined considerably.

Example 4

A paper prepared from bleached sulfite cellulose, 1% of animal glue, 0.1% of sodium polyvinylsulfonate (K-value=30), 1% of rosin size and 2% of aluminum sulfate (pH value 4.7) is compared as regards the degree of sizing with a paper prepared from bleached sulfite cellulose, 2% of rosin and 2% of aluminum sulfate, the comparison being made at 20° C. by means of the ink flotation test. Whereas the comparison paper exhibits complete penetration of ink after fifteen minutes, there is no penetration of ink at any point after forty-five minutes with the paper prepared by the use of the addition according to this invention.

Example 5

A fibrous stock of 60 parts of groundwood and 40 parts of unbleached sulfite cellulose is sized with 2% of animal glue, 0.2% of sodium polyvinylsulfonate (K-value=34), 2% of rosin size and 3% of aluminum sulfate at pH value 4.5. A comparison paper merely has an addition of 2% of rosin and 3% of aluminum sulfate. The paper sized with the precipitant according to this invention does not show any detectable penetration of ink after a flotation period of 120 minutes, whereas penetration is visible after only 40 minutes with the comparison paper.

Example 6

Paper is made from 85 parts of bleached sulfite cellulose (35° S-R) and 15 parts of kaolin with an addition of 3% of animal glue, 0.1% of a copolymer of 85 parts of acrylic acid, 15 parts of sodium vinylsulfonate and 1% of rosin. The pH was adjusted to 4.8 with aluminum sulfate. The percentages are related to the solids content of the paper stock.

The paper thus obtained does not show any detectable penetration of ink after a flotation period of 55 minutes, whereas penetration is visible after only 19 minutes with a comparison paper which has been sized with rosin alone in the common manner.

Example 7

By using the method described in Example 6, but substituting 0.15% of a copolymer of 90 parts of acrylic acid and 10 parts of sodium vinylsulfonate for the copolymer used in the said example, a paper is obtained which shows an ink penetration period of 61 minutes.

5

I claim:

1. In a process for the internal sizing of paper with a protein sizing substance of animal origin wherein a precipitant is added to a slurry of cellulose fibers containing said sizing substance, the improvement of adding 1 to 20% by weight, with reference to the protein sizing agent, of a water-soluble addition polymer made up from at least 10% by weight of a monomer selected from the group consisting of vinylsulfonic acid and its alkali metal and ammonium salts, together with aluminum sulfate as said precipitant.

2. In a process for the internal sizing of paper with a protein sizing substance of animal origin wherein a precipitant is added to a slurry of cellulose fibers containing said sizing substance, the improvement of adding 1 to 20% by weight, with reference to the protein sizing agent, of a water-soluble addition polymer made up from 10 to 100% by weight of a monomer selected from the group consisting of vinylsulfonic acid and its alkali metal and ammonium salts and up to 90% of a comonomer selected from the group consisting of acrylic acid, acrylamide, acrylonitrile and vinyl methyl ether, together with aluminum sulfate as said precipitant.

3. In a process for the internal sizing of paper with

6

a protein sizing substance of animal origin wherein a precipitant is added to a slurry of cellulose fibers containing said sizing substance, the improvement of adding 1 to 20% by weight, with reference to the protein sizing agent, of polyvinylsulfonic acid, together with aluminum sulfate as said precipitant.

4. In a process for the internal sizing of paper with a protein sizing substance of animal origin wherein a precipitant is added to a slurry of cellulose fibers containing said sizing substance, the improvement of adding 1 to 20% by weight, with reference to the protein sizing agent, of sodium polyvinylsulfonate, together with aluminum sulfate as said precipitant.

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