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[54] **PHOTOGRAPHIC AND ELECTROPHOTOGRAPHIC MEMBERS WITH GLASS FIBER CONTAINING PAPER SUBSTRATES**

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[51] **Int. Cl.** **G03g 5/00;** G03c 1/86

[58] **Field of Search** 96/1.8, 1.5, 67, 85

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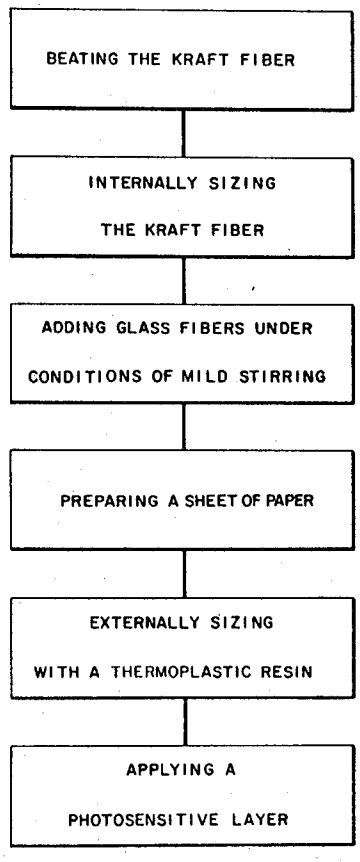
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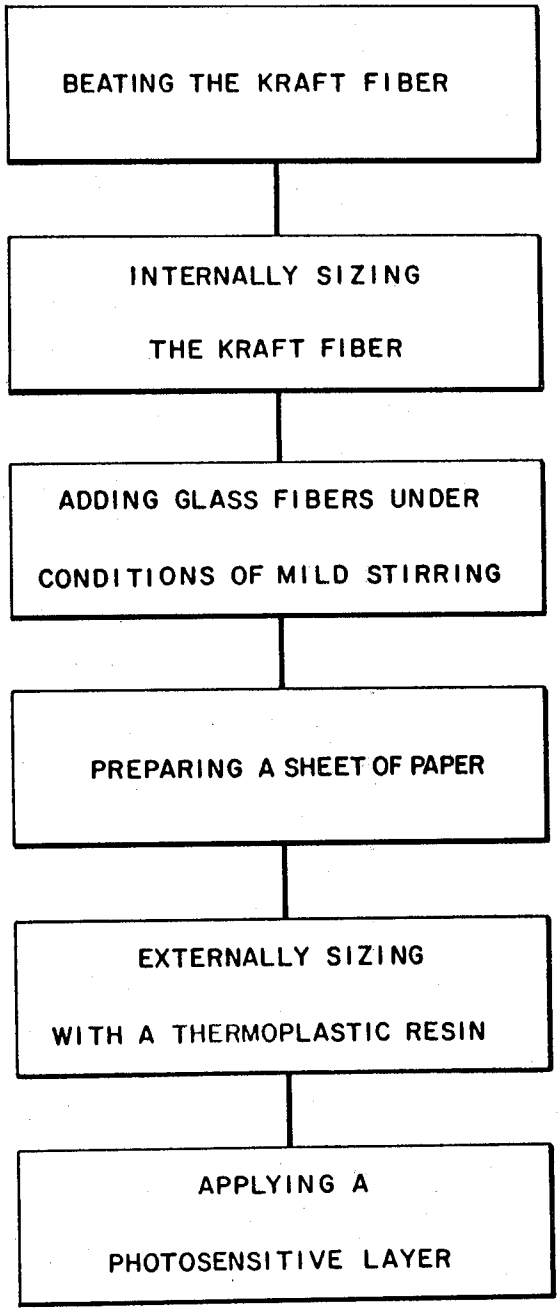
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[57] **ABSTRACT**

A dimensionally stable photographic paper is prepared by applying a photosensitive coating to a bleached softwood kraft fiber paper substrate containing from about 30 to 90 percent glass fibers. The paper base is prepared by adding from about 30 to 90 percent glass fiber to a bleached softwood kraft fiber pulp suspension just prior to passing the pulp through a paper making machine. The photographic paper of the instant invention has particular utility under conditions of high humidity.

7 Claims, 1 Drawing Figure




BEATING THE KRAFT FIBER
INTERNALLY SIZING
THE KRAFT FIBER
ADDING GLASS FIBERS UNDER
CONDITIONS OF MILD STIRRING
PREPARING A SHEET OF PAPER
EXTERNALLY SIZING
WITH A THERMOPLASTIC RESIN
APPLYING A
PHOTOSENSITIVE LAYER

PHOTOGRAPHIC AND ELECTROPHOTOGRAPHIC MEMBERS WITH GLASS FIBER CONTAINING PAPER SUBSTRATES

This is a division of application Ser. No. 857,430, filed Sept. 12, 1969, now U.S. Pat. No. 3,773,513.

BACKGROUND OF THE INVENTION

This invention relates to a dimensionally stabilized cellulose paper and to methods of preparing and stabilizing said paper. More particularly, the invention relates to the stabilization of a cellulose paper substrate of a photographic paper to render it more resistant to dimensional changes resulting from variations in humidity and to improve the strength of such a product.

It is well known that materials made up entirely or predominantly of cellulose fibers expand and contract with variations in the humidity in the ambient atmosphere. Such materials suffer an increase in their dimension upon absorption of moisture from the atmosphere and a contraction when moisture is given up to the atmosphere upon a decrease in humidity. It is also well known that in articles having fibers which are directionally oriented, such expansion and contraction usually occurs to the greatest extent in a direction perpendicular to the predominant direction of the fibers. The present invention is, therefore, particularly useful in preventing or minimizing dimensional changes which occur across the fibers of cellulose materials with changes in humidity, in addition to reducing dimensional change in the direction of the fibers.

Various expedients have been heretofore employed for the purpose of dimensionally stabilizing materials made up predominantly of cellulose fibers as, for example, plywood, wood boards, pulp products and combinations thereof, and solid paper boards. A degree of dimensional stabilization is obtained in the manufacture of plied or laminated articles by arranging the laminations with their fiber direction disposed angularly to one another rather than parallel. Although improvement in dimensional stabilization is obtained by these techniques, the operation is laborious and expensive inasmuch as it requires cutting and proper selection and assemblage of the plies.

In the area of photographic paper it has been previously recognized that it is advantageous for paper of good dimensional stability to have up to half of the hydroxyl groups of the cellulosic fibers employed in its preparation be replaced by lower fatty acid radicals. Further, an improved photographic paper was prepared in U.S. Pat. No. 3,062,679, to Herdle et al., where a partially esterified paper base was sized with a modified polyvinylacetate latex composition. While such paper has been adequate as a base of photographic paper which is used under normal conditions, the same photographic paper when used under extremely humid conditions has been found to be unsatisfactory with respect to its physical strength and dimensional stability.

The instant invention contemplates the use of glass fibers to improve the dimensional stability of photographic paper and thereby render it useful under conditions of extreme humidity. The use of attenuated fibers of glass or synthetic resin in the manufacture of dimensionally stable fiber structures confronts the difficulty of integrating or otherwise forming glass fibers into a self sufficient mass. This is due to the glass fibers being

in the form of rod-like filaments of substantial length having little, if any, crimp or curl and having perfectly smooth rounded surfaces. There is nothing on the glass fiber surfaces which might cause the fibers to cling together upon contact with one another, and, therefore it is difficult to felt the fibers onto a self sufficient mass. Because of the smooth, non-porous nature of the glass fiber surfaces, coupled with their hydrophobic characteristics, it is difficult to bond resinous materials or other adhesives to the glass fiber surfaces for the purposes of integrating the fibers one with another to increase the strength of such an element. Although these properties may be used to advantage in some applications they detract from or impair the assembly of the fibers into fiber structures having high degree of mass integrity.

By way of comparison with glass, natural fibers such as wool, cotton, and the cellulose fibers have their surfaces covered with a large number of tiny fibrils or hairy projections which apparently cause these fibers to cling to one another upon contact. This agglomerating or combining characteristic permits felting together in the dry state or from liquid suspension to form fiber structures of considerable strength. In fiber structures of this type, it is often unnecessary to make use of additional binder in the form of resinous material or the like to achieve strength sufficient for the purpose for which the structure is intended.

Because of the inability of glass fibers and other synthetic fiber structures to interfelt into a mass with sufficient strength and integrity to resist forces to which it might be exposed as an incident to normal handling, generally it is necessary to incorporate binders, such as natural fibers, or cements to gain a limited degree of bond between the fibers whether in the form of a mass, web, yarn, strand, or other pre-formed body. While the resulting mass is insensitive to humidity and can withstand normal handling, it is of a porous nature and is unsatisfactory as a holdout base for a photosensitive layer.

In accordance with the present invention, I have found that a cellulose paper product may be partially or wholly stabilized against dimensional change and yet have good holdout properties by adding glass fibers into the pulp prior to the pulp being introduced into the paper making machine. In particular, I have found that desirable dimensional stability and holdout characteristics are imparted to bleached softwood cellulose fiber paper by the addition of particular quantities of glass fibers just prior to the pulp being introduced into the paper making machine. In addition, a strong photographic paper having exceptional holdout properties and high humidity stability prepared from the dimensionally stabilized paper.

OBJECTS OF THE INVENTION

It is therefore an object of the present invention to provide a simple and inexpensive method for dimensionally stabilizing and strengthening paper made up of cellulose fiber and to produce a dimensionally stabilized cellulose paper base material.

It is yet another object of this invention to provide a dimensionally stable paper made of glass and cellulose fiber to which a photosensitive layer will adhere and be supported.

It is yet a further object of this invention to provide a photographic paper having dimensional stability, strength, and good holdout properties.

BRIEF DESCRIPTION OF THE INVENTION

These and other objects are obtained in accordance with the present invention, wherein there is provided in its broadest aspect, the incorporation of glass fibers into structural fibrous cellulose materials, whereby the usual expansion and contraction of such cellulose material by reason of change in humidity conditions and the atmosphere surrounding such materials is considerably minimized. This stabilizing effect is dependent upon the quantity of the glass fibers incorporated within the fibrous cellulose structural element. The exact quantity being incorporated within the particular cellulosic material will be dictated by the type of cellulose used as a starting material and the ultimate uses of the paper produced; that is, the quantity of glass fibers incorporated is dependent upon the amount of the usual expansion or contraction which one desires to eliminate in the particular cellulose material. In particular, effective dimensional stabilization of a cellulose fiber base for photographic paper is accomplished according to the instant invention by incorporating into a bleached softwood kraft fiber material from about 30 to 90 percent of stabilizing glass fibers based upon the weight of the dried kraft fiber.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the invention may be more clearly understood, reference is made to the accompanying drawing which illustrates one embodiment of the present invention.

FIG. 1 illustrates a flow diagram characteristic of the process of instant invention.

Referring to FIG. 1, a bleached softwood kraft fiber is first beaten to a sufficient slowness as measured by the Williams slowness test, to develop good bonding and bursting strength in the paper product. It is imperative that the kraft fiber be beaten sufficiently to effect good strength between the fibers resulting in good mullen in the final product. The slowness necessary to achieve good bonding and mullen is from about 20 to 40 seconds for a 1 gram sample. The beating may take place by any conventional technique in any suitable apparatus which will effectively beat or disperse the fibers. While any type of cellulose fiber may be used bleached softwood kraft fiber is preferred in order to achieve maximum strength in the final product. One such suitable fiber is sold under the tradename Alberta HiBrite, and is manufactured by Northwestern Pulp and Power in Hinton, Alberta.

The kraft fiber is then internally sized by rendering the stock acidic, adding a dispersing agent and a sizing composition. While any type of conventional paper sizing material can be used, the conditions of sizing would be appropriate to the particular sizing agent used. For example, if one uses melamine resin as the sizing composition the the stock solution would have to be rendered acidic to accomodate said sizing agent.

Thereafter the beating of the internally sized pulp suspension is terminated. The suspension can then either be moved to a stirring container or remain in the beater as long as no further beating takes place. At this point about 30 to 90 percent by weight glass fibers (based on the weight of the kraft fibers) are added to the pulp suspension under conditions of mild agitation, that is, stirring of moderate speed so as to prevent destruction of the glass fibers. As hereinbefore mentioned, the percentage of glass fibers added will depend upon the ultimate use of the paper to be made. Since the present invention concerns high humidity stable photographic papers, the preferred amount of glass fibers is from about 50–80 percent because percentages less than 50 percent may not yield the most satisfactory dimensional stability, while glass fibers in an amount in excess of 80 percent may not result in the maximum holdout and strength properties necessary for photographic paper. In the present context, holdout refers to the ability of the paper substrate to effectively sustain a coating of any type and, in particular, an emulsion or photographic layer on the surface of the paper. The mild agitation of the aqueous pulp-glass fiber composition is continued so as to effect complete interdispersion of pulp types of fibers without fracturing the glass fibers thereby reducing their length. While in general, gentle mixing is adequate in effecting interdispersion, the addition of acids to the solution to render the suspension acidic has been found helpful in further aiding complete inter-dispersion of the glass and cellulose fibers. Any organic or inorganic acid, including Lewis acids, may be used.

The suspension is then screened and the pulp glass fiber composition passed through a paper making machine and a sheet is prepared. Any conventional paper making apparatus, such as a Fourdrinier paper machine, can be used.

The resulting paper sheet is then externally sized with a coating of a suitable thermoplastic synthetic resin. Typical thermoplastic synthetic resins are polymers such as polyvinyl resins, i.e. polyvinyl alcohol (water or organic solvent soluble), polyvinyl chloride, copolymers of vinyl chloride, vinyl acetate, and polyvinyl alcohol, polyvinyl butyral, polystyrene, polyvinylidene chloride, acrylic resin such as polymethyl methacrylate, polyethylene, butadiene/styrene copolymers, and polyamide (nylon) resins.

After the application of the polymeric coating for external sizing there results a dimensionally stable as well as a strengthened paper. Hence when a photosensitive coating, or coatings, such as a silver halide emulsion, or any other photographic layer is applied atop the dimensionally stable paper there are adequate holdout properties and a photographic paper results which can be used under very humid conditions.

The term glass fibers, as used herein, is meant to include glass fibers of the staple or wool type, such as are attenuated from molten screens of glass by reaction with high pressure air or steam. Included also are continuous fibers mechanically drawn at high speed from streams of molten glass and which may be cut to desired lengths for manufacture of fiber structures embodying the concepts of this invention. It has been found that structures embodying the features of this invention may be prepared by using glass fibers of lengths ranging from about 1 to 10 millimeters, and that very satisfactory results are secured by the use of glass fiber having variations of a few millimeters in length. In addition, the glass fiber diameters may range from about 0.09 to 3 microns. Glass fibers of the type described may be used in the conditions in which they are delivered from the fiber forming unit, that is, with or without lubricant or sized thereon, but it is preferred to remove

any size or coating prior to use of the formation or fiber structures in accordance with this invention.

While the actual mechanism of this stabilizing action of the present invention of cellulose fibers is not fully understood, it is believed that the glass and natural fibers are orientated whereby the fibers together are able to form into a uniform mass and interlock in a manner to provide sufficient strength to resist the forces of normal handling and use as well as rendering the mass less hydrophilic. The desirable properties of the glass still remain in that the structure adopts the hydrophobic qualities of the glass fibers and hence is not detrimentally affected by humidity. The desirable properties of the natural fibers are clearly evident in that the fibers from the structure cling to each other strongly thereby indicating the necessary presence of the cellulose fibers.

The reasons why such small amount of natural fibers are able to impart desired results have not yet been fully understood. It appears, however, upon examination, that the glass fiber surfaces become covered substantially throughout with the natural fibers, said natural fibers becoming so well integrated with the glass fiber surfaces as to appear as a part thereof and impart natural fiber characteristics thereto.

The forces by which the natural pulp fibers integrate with the glass fiber surfaces appear to be greater than that which results from merely felting out the pulp fibers onto the glass fiber surfaces. In addition, the coverage of the glass fiber surfaces with what appears as a monomolecular layer of the pulp fiber substantiates the concept that the kraft pulp fibers of the instant invention carry a negative charge (anionic), while portions of the glass fiber surfaces remain positively charged (cationic). In this system a type of ionic bond forms between the cellulose and glass fibers, the like charges in the kraft fiber causing the fibers to repel each other in aqueous dispersion and to be strongly attracted to the glass fiber surfaces until the charges on the glass fibers are substantially completely satisfied by the deposition of the natural fibers. Thus physical-chemical forces are involved in the original orientation of the colloidal pulp fibers with the glass fiber surfaces to the end that the glass fibers are substantially completely covered with a small amount, compared to the weight of the glass fibers, of natural pulp fibers. The glass fibers so modified are capable of felting in the manner of the pulp fibers disposed thereon; that is, the natural cellulose pulp fibers arrange themselves all around the glass fibers and thereby enable the glass fibers so coated to felt together into a fibrous structure of high mass integrity.

For best operation, it is desirable, before addition of the glass fibers, to so thinly disperse the natural pulp fibers in the aqueous medium that they are able freely to move about and float away from each other. This is accomplished by stirring just before addition of the glass fibers. The separation of the pulp fibers is encouraged during stirring by the anionic forces which causes them to repel each other while after addition of the glass fibers complete binding is encouraged throughout by the attraction that exists between the unlike charges.

It appears that upon drying, some shrinkage occurs as the cellulose pulp fibers form into a porous intermeshed network about the glass fibers, whereby the pulp fibers retreat in part to the glass fiber intersections. Thus the dried cellulose fibers concentrate at the glass fiber intersections where they are more capable of achieving their interbonding function. It appears further that the highly dispersed networks of kraft pulp fiber lose their colloidal properties and shrink to an open but tangled mass completely interlocked with the glass fibers. At the same time, the network of glass fibers keeps the fiber structure from shrinking to a higher bulk density in the absence of compression. The pulp fiber is integrated all around the glass fiber surfaces and especially at the glass fiber intersections which operates not only to tie the glass fibers together but also to maintain a desired space relation between them. In this way desired dimensional stability, strength, and flexibility are obtained but densification resulting in increased weight is avoided.

Although mass integrity of the paper product is accomplished from the practice of the instant invention as described, a thermoplastic resin surface size of the type hereinbefore mentioned, has generally been found necessary in order to render said paper completely useful as photographic paper. The surface size effectively protects the applied photographic emulsion coating from any porosity in the paper substrate thereby effecting excellent holdout properties in the paper.

The length of the glass fiber is not controlling except for the understanding that strength generally is proportioned to length and, as previously pointed out, adequate strength results from the use of glass fibers which vary in length from very short to fairly long. However, in order to achieve maximum flexibility in the photographic paper of the instant invention glass fibers should not exceed a length of 5 millimeters. In addition, it is also beneficial to mass integrity for the natural fibers to be reduced to the smallest length possible in order to insure maximum commingling with the glass fibers. Highly pulped commercial kraft fibers contemplated for use in the present invention have lengths ranging from about 1 to 3½ millimeters.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples are illustrative of typical formulations embodying concepts of the invention so far described.

EXAMPLE I

Twenty-five pounds of Alberta HiBrite, a highly pulped kraft fiber produced by Northwestern Pulp and Power Ltd., is added to 125 quarts of water in a beater. One pound of sodium stearate and one pound of aluminum chloride is then added to the mixture and stirring initiated. Mixing takes place over a period of about 30 minutes at which time the pH was found to be about 4.5. Two pounds of melamine resin is then added to the suspension and mixing continued for another 20 minutes. At this point the speed of the beater is reduced to a point of mild agitation and thereafter enough hydrochloric acid is added to reduce the pH to about 3.0. Then under the conditions of the mild agitation, 50 pounds of "micro-fibers", which are manufactured by the John-Mansville Company and have lengths of about 1 millimeter and a diameter of 2 microns, were added to the mixture and the mild agitation continued for a period of 30 minutes. The glass-fiber pulp composition was then recovered, washed, and passed through a paper making machine where a handsheet was made.

The resulting handsheet was then tub sized by passing it through a sizing bath of polyvinyl acetate-polyvinyl alcohol copolymer for 4 seconds at 75° F and dried for

10 minutes at 120°F. The resulting paper demonstrated qualities of strength and flexibility.

A photosensitive coating is then applied to the glass cellulose fiber paper by vacuum depositing a polycrystalline layer of silver halide in accordance with the procedure outlined in U.S. Pat. No. 3,219,450 to Goldberg. It was found that the glass-cellulose fiber paper provided an excellent substrate to which the polycrystalline photographic layer readily adhered. In addition, the paper did not appear to lose any of its strength or flexibility.

EXAMPLE II

This example is carried out in order to demonstrate the dimensional stability of the paper substrate used in the photographic paper of the instant invention. Four handsheets having a composition of 75 percent glass fibers and 25 percent kraft fiber are prepared in the same manner as in Example I. Each was sized with a different thermoplastic resin manufactured by the E. J. Borden Company. The first was sized with Butadiene/Styrene copolymer, designated Butadiene/Styrene Latex (2415); the second with polymethylmethacrylate, designated Polyacrylic (2715); and the third with polyvinylacetatepolyvinyl alcohol copolymer, designated as Polyvinyl Acetate Copolymer (804).

A 5 inch strip of each paper is then taken and placed in a Neenah Expansimeter and the relative humidity regulated to 50 percent. The relative humidity is then lowered from 50 percent to 11 percent and a correction reading is taken from the micrometer. The relative humidity is then increased from a value of 11 percent to 88 percent and another correction reading taken on the micrometer. The actual expansion is then computed from the difference of the two values taken and the percentage expansion computed. The results appear in Table I.

TABLE I

	50 to 11% R.H.	11 to 88% R.H.	Actual Change 11 to 88% R.H.	% Change
75% Glass Fibers + 25% HiBrite (without sizing)	.0044	.0124	.0080	0.16
75% Glass Fibers + 25% HiBrite (sized with butadiene/styrene copolymer)	.0030	.0099	.0069	0.14
75% Glass Fibers + 25% HiBrite (sized with polymethylmethacrylate	.0043	.0156	.0113	0.25
75% Glass Fibers + 25% HiBrite (sized with polyvinyl acetate polyvinyl alcohol copolymer)	.0030	.0149	.0190	0.39

As can be observed from the Table the highest dimensional change is 0.39 percent for the polyvinyl acetatepolyvinyl alcohol sized glass-cellulose fiber paper. Since ordinary bleached softwood kraft fiber paper exhibits an expansion greater than one percent, the percentage change for all the samples, both sized and unsized, is relatively low indicating paper of good dimensional stability.

While the invention has been described in terms of a preferred embodiment, it is to be understood by those skilled in the art that various modifications of the instant invention may be made. For example, the present invention has utility in the area of electrophotography wherein a layer of photoconductive insulating material, such as zinc oxide in a binder, may be applied to the dimensionally stabilized paper substrate. In addition, many modifications may be made to adapt a particular situation or material to the teaching of the invention without departing from its essential teachings.

What is claimed is:

1. A photosensitive member comprising:
a. a cellulose fiber substrate having a thermoplastic resin surface size and containing from about 50 to 80 percent by weight of glass fibers having lengths ranging from 1 to 10 millimeters and diameters ranging from 0.09 to 3 microns, and
b. at least one layer of a photosensitive material contained on the surface of said substrate.

2. An electrophotographic member comprising:
a. cellulose fiber paper substrate having a thermoplastic resin surface size and containing from about 50 to 80 percent by weight of glass fibers having lengths ranging from 1 to 10 millimeters and diameters ranging from 0.09 to 3 microns, and
b. at least one photoconductive insulating layer contained on the surface of said substrate.

3. The member of claim **2** in which the photoconductive insulator layer comprises zinc oxide in a binder.

4. The photosensitive member of claim **1** wherein the cellulose fiber is a bleached softwood Kraft fiber.

5. The photosensitive member of claim **1** wherein the thermoplastic resin surface sizing is selected from the group of butadine/styrene copolymers, polyacrylic resins and polyviny/polyvinyl alcohol copolymers.

6. The photosensitive member of claim **5** wherein the photosensitive layer is a polycrystalline layer of silver halide.

7. The photosensitive member of claim **5** wherein the photosensitive layer is a silver halide emulsion.

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