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PAPER COMPOSED OF SYNTHETIC FIBERS, AND FIBROUS BINDER FOR USE IN THE MANUFACTURE THEREOF

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This invention relates generally to the manufacture of paper, and has particular reference to paper composed of synthetic fibers. Coordinately, the invention relates to an improved binder which makes it possible and commercially practical to make such paper on standard paper-making machines and in accordance with conventional paper-making techniques.

A primary problem in the manufacture of paper made wholly from synthetic fibers is the inability of such fibers to form secure inter-fiber bonds. This problem is particularly acute in the manufacture of light-weight papers.

It has been found that thermoplastic polymer latices are potentially useful bonding agents for organic synthetic fiber papers. One suggested method is the spraying of the latex on the wet fiber web while the web is carried on the forming wire of the paper-making machine. A critical problem in drying is presented, since the latex has a tendency to cause the web to adhere to the drying roller. Furthermore, the formation of steam by evaporation of the water phase of the latex as the web passes over the drying roller causes the latex to flow to the upper surface of the sheet. This results in a finished paper having all the latex binder on one surface thereof and consequently possessing very poor binding qualities on the other surface. In order to overcome this difficulty it is necessary to make substantial departures from the conventional paper-making process and to use cumbersome mechanical procedures.

Another method proposed by the prior art is to precipitate the polymer on the surface of the synthetic fibers prior to forming the fibers into a web. This is done by various "beater saturation" techniques which are well established in the manufacture of latex treated papers made from natural cellulosic fibers. Due to the fact that the synthetic fibers are rod-like in shape and their surfaces are smooth and relatively hydrophobic they present poor surfaces for the depositon of polymer latices. Attempts to deposit polymers on such fibers in any substantial amount frequently resulted in free resin particles which were unattached to the fiber and caused wire clogging and sticking to the dryers and felts, etc. In addition, synthetic fibers coated in this manner also tend to form large fiber clumps or "ropes" in the fiber slurry, which makes paper-making difficult or impossible. Moreover even if the paper is finally formed and dried, an insufficient amount of polymer deposits on the fiber and consequently the resultant paper has poor wet strength and the like.

One of the objects of the invention is to provide a fibrous binder of novel character whose utilization makes it possible to bind together in the form of a paper web synthetic fibers which are incapable by themselves to bond together to an adequate self-sustaining degree.

Another objective is to provide an improved all-synthetic paper which incorporates this binder and whose primary synthetic fibers are consequently securely bonded together.

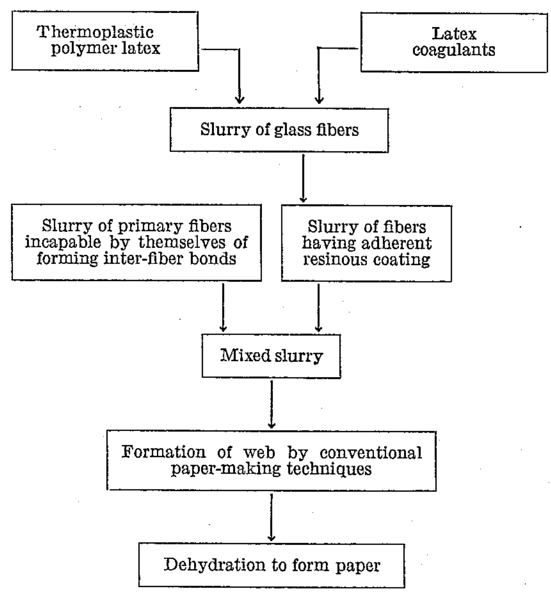
By the practice of this invention, papers of excellent strength, both in the wet web and in the dry sheet, can be produced; and it is possible and practical to manufacture strong highly useful light-weight synthetic fiber papers at relatively low cost and by conventional paper-making procedures.

It is among the more particular objects of this invention to provide a binder which will cause normally non-binding fibers to cling together both in the wet web and the dry sheet.

It is further among the objects of this invention to provide a means whereby paper may be manufactured entirely from synthetic fibers without significantly altering the texture, appearance and other physical properties of the primary fibers themselves; and to provide a paper made wholly of synthetic fibers in which the thermal, chemical, and electrical properties can be maintained within a desirable range.

The invention is predicated upon the use of a special binder composed of thin hydrophilic fibers heavily coated with thermo-plastic polymers having wet tack. Among the polymers found suitable for this purpose are polyacrylic esters, polyacrylonitriles, polyvinyl chlorides, polyvinyl acetates, and nitrile rubbers.

A simplified flow diagram of the improved paper-making procedure is as follows:



While, generally speaking, any hydrophilic fiber or mixture of such fibers is satisfactory, best results have been obtained with fibers composed of glass and having diameters of less than about 2.5 microns. The fiber diameter should be as small as possible; however, economic and other considerations dictate a preferred range of from 0.2 to 1.5 microns.

The polymer-fiber ratio should be somewhat below complete saturation of the fiber by the polymer and generally from 2 to 25 parts by weight of polymer to 1 part by weight of the glass or other hydrophilic fiber. Best results are obtained with from 3 to 10 parts of polymer to 1 part of hydrophilic fiber.

The binder contemplated by this invention is prepared by slurrying hydrophilic fibers (such as glass or rayon) in water, and introducing into the slurry an anionic aqueous dispersion of thermo-plastic polymer. Precipitation of the polymer onto the hydrophilic fiber is accomplished by introducing a precipitating agent such as alum, or various cationic resins such as urea-formaldehyde and melamine-formaldehyde.

It has been found desirable to agitate or beat the initial hydrophilic fiber slurry to aid in the production of a uniform dispersion of these fibers prior to the introduction of the polymer dispersion.

In manufacturing a paper, the binder as described is admixed in the desired proportion with a slurry of the primary synthetic fibers. The combined slurry is then introduced into the head box of a suitable paper-making machine and is formed into paper by conventional and well-known processes. Among the primary synthetic fibers found suitable are acrylics, polyesters, polyamides and regenerated celluloses.

The use of the improved binder results in sufficient fiber bonding on the wire of the paper-making machine to provide excellent wet web strength, and it has been found that the bonding increases as the sheet passes through the dryer section of the machine. Further increases in strength may be obtained by calendering, heat-treating or combinations thereof.

A wide range of different properties of the paper manufactured by the use of the present invention can be obtained by judicious selection of primary fiber or fibers, and of the polymer or polymers employed in the binder; also by varying the fiber-to-binder ratio, and the finishing treatment. The ratio of primary (non-binding) fibers to the binder (resin-coated) fibers may vary from 1:2 to 32:1. Best results are attained when there are between one and four parts of primary fibers for each part of the binder. As an example of the result that may be achieved are papers composed entirely of synthetic fibers, weighing less than ½ ounce per square yard, and having tensile strengths as high as 6,000 pounds per square inch.

Aqueous dispersions of acrylonitrile and acrylic ester polymers have been found to be particularly satisfactory in the preparation of this binder. The polymer must be such that it will form a strongly adherent coating on the glass or other hydrophilic fibers and will have a sufficient degree of wet tack to adhere to the adjacent primary fibers as the web is formed on the paper-making machine wire. On the other hand the wet tack must not be so great that fiber clumps are formed in the dilute suspension. Additionally, the polymer must be capable of forming strong permanent bonds with the primary fibers themselves after drying has taken place.

The following specific examples are indicative of the breadth and scope of this invention:

Example 1

One part by weight of glass fibers having an average diameter of about 0.5 micron is slurried in about 800 parts of water in a beater, with the water temperature at about 10° C. With the beater roll in the raised position, the slurry is circulated until the glass fibers are uniformly dispersed. An amount of Rhoplex ER equivalent to 6.3 parts by weight of latex solids is added and mixed thoroughly with the glass fibers and 2.5 parts by weight of 10% alum solution are added. (Rhoplex ER is Rohm and Haas Company's trademark for an anionic polyacrylic ester latex having a shear modulus of 60 kg. per sq. cm. at 10° C., 7 kg. per sq. cm. at 30° C. and 4 kg. per sq. cm. at 50° C.) Circulation is continued until precipitation of the latex is completed and a uniform dispersion of polymer-coated glass fibers is obtained. This slurry of fibrous binder is then admixed with a second slurry containing 12.5 parts of Orlon cut to a length of about ¼ inch. (Orlon is E. I. du Pont de Nemours & Co. trademark for its linear polyacrylonitrile fiber.) The combined slurry is sheeted and dried on a paper machine. The final product is a thin, highly porous paper weighing 0.36 oz. per square yard and having a tensile strength of 0.5 lb. per inch of width. After light calendering at 200° F., the tensile strength of this paper increases to 1.2 lbs. per inch and, after calendering through two nips at 300° F., the tensile strength is 2.2 lbs. per inch.

Example 2

One part of glass fibers having an average diameter of about 0.5 micron is slurried in about 250 parts of water in an agitated vessel, with the water temperature at about 70° C. The slurry is violently agitated until the glass fibers are uniformly dispersed. Three tenths part (dry basis) of Uformite 700 is added and the pH is adjusted to about 4 with sulfuric acid. (Uformite 700 is Rohm & Haas' trade mark for cationic urea-formaldehyde resin containing about 19% nitrogen.) An amount of Cypel sufficient to provide 6 parts of latex solids is diluted with several volumes of water and added to the glass fiber slurry. (Cypel is American Cyanamid Company's acrylonitrile polymer latex containing 43 to 45% solids by weight and having a pH of 9 to 10.5, viscosity 40 to 80 cp. and with a particle size less than 1 micron.) Agitation is continued until precipitation of the latex on the glass fibers is completed and a uniform dispersion of polymer coated fibers is obtained. This fibrous binder slurry is then admixed with a second slurry containing 8.8 parts of Orlon cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 8 oz. per square yard and after hot calendering has a tensile strength of 70 lbs. per inch.

Example 3

One part of glass fibers having an average diameter of about 0.5 micron is slurried in about 250 parts of water in an agitated vessel, with the water temperature at about 70° C. The slurry is violently agitated until the glass fibers are uniformly dispersed. Three tenths part (dry basis) of Uformite 700 is added and the pH is adjusted to about 4 with sulfuric acid. An amount of Rhoplex AC–55 equivalent to 5 parts by weight of latex solids and an amount of Rhoplex B–85 equivalent to 1 part by weight of latex solids are mixed, diluted with several volumes of water, and added to the glass slurry. (Rhoplex AC–55 is Rohm & Haas Company's trademark for an acrylic ester polymer in aqueous emulsion form containing 54 to 55% solids and having a pH of 9.0 to 9.5; and Rhoplex B–85 is Rohm & Haas Company's trademark for an acrylic ester polymer latex containing 38% solids and having a pH of 9.5 to 10. The former is a soft latex while the latter is a hard latex.)

Agitation is continued until precipitation of the latex on the glass fibers is completed and a uniform dispersion of polymer coated fibers is obtained. This fibrous binder slurry is admixed with a second slurry containing 14.6 parts of regenerated cellulose fibers cut to a length of about ⅜ inch. The combined slurry is sheeted and dried on a paper machine. The final product is a thin, highly porous paper weighing 0.4 oz. per square yard and having a tensile strength after hot calendering of 2.2 lbs. per inch.

Example 4

A binder is formed as in Example 3, except that the parts by weight of the Rhoplex AC–55 and Rhoplex B–85 are respectively 4.8 and 1.2. This fibrous binder slurry is admixed with a second slurry containing 12.2 parts of Dacron cut to a length of about ¼ inch. (Dacron is E. I. duPont's trademark for a terephthalic acid-ethylene glycol copolymer.) The combined slurry is sheeted and dried on a paper machine. The final product is a thick, bulky paper weighing 6 oz. per square yard.

Example 5

A binder is formed as in Example 2 and the binder slurry is then admixed with a second slurry containing 10 parts of nylon fiber cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1.2 oz. per square yard and after hot calendering has a tensile strength of 2 lbs. per inch.

Example 6

One part of glass fibers having an average diameter of about ½ micron is slurried in about 250 parts of water in an agitated vessel, with the water temperature at about 70° C. The slurry is violently agitated until the glass fibers are uniformly dispersed. Two-tenths part (dry basis) of Uformite 700 is added and the pH is adjusted to about 4 with sulfuric acid. An amount of Lecton RC–6302 sufficient to provide 6 parts of latex solids is diluted with several volumes of water and added to the glass fiber slurry. (Lecton RC–6302 is E. I. duPont's trademark for an acrylic dispersion containing 32.5% solids by weight, having a pH of 3.5, viscosity 5 cp., and a particle size of approximately 0.11 micron.) Agitation is continued until precipitation of the latex on the glass fibers is completed and a uniform dispersion of polymer coated fibers is obtained. This fibrous binder slurry is then admixed with a second slurry containing 10 parts of Orlon cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1.2 oz. per square yard and after hot calendering has a tensile strength of 6.5 lbs. per inch.

Example 7

A binder is formed as in Example 6 except that four-tenths of a part (dry basis) of Uformite 700 is used instead of two-tenths of a part. After the combined slurry formed as in Example 6 is sheeted and dried on a paper machine, the final product weighs 1.2 oz. per square yard, and after hot calendering has a tensile strength of 6.5 lbs. per inch.

Example 8

A binder is formed as in Example 6, except that three-tenths of a part of Parez 607 acid colloid is used in place of the Uformite 700, and the pH is adjusted to 4 with hydrochloric acid. Sufficient of the Lecton RC–6302 is used to provide 8 parts of latex solids. (Parez 607 is American Cyanamid's trademark for trimethylol melamine.) This fibrous binder slurry is then admixed with a second slurry containing 13.3 parts of Orlon cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1.2 oz. per square yard and the uncalendered paper has a tensile strength of 4.5 lbs. per inch.

Example 9

A binder is formed as in Example 8, except that three-tenths of a part of Uformite 467 is used instead of the Parez 607. (Uformite 467 is Rohm & Haas' trademark for anionic urea-formaldehyde resin.) The pH is adjusted to about 4 with alum. This fibrous binder slurry is then admixed with a second slurry containing 13.3 parts of Orlon cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1.2 oz. per square yard and after hot calendering has a tensile strength of 6 lbs. per inch.

Example 10

A binder is formed as in Example 8, except that three-tenths of a part of Uformite 700 is used instead of the Parez 607, and the pH is adjusted with sulfuric acid. The Lecton RC–6302 is used to an extent equivalent to 10 parts of latex solids. The slurry of fibrous binder is admixed with a second slurry containing 16 parts of Orlon, cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1.2 oz. per square yard and after hot calendering has a tensile strength of 6.5 lbs. per inch.

Example 11

A binder is formed as in Example 10, except that the glass fibers have an average diameter of about 2 microns, and the Lecton RC–6302 is sufficient to provide 6 parts of latex solids. The fibrous binder slurry is then admixed with a second slurry containing 10 parts of Orlon, cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1.2 oz. per square yard and after hot calendering has a tensile strength of 8 lbs. per inch.

Example 12

One part by weight of glass fibers having an average diameter of about 0.5 micron is slurried in about 250 parts of water in an agitated vessel, with the water temperature at about 70° C. The slurry is violently agitated until the glass fibers are uniformly dispersed. An amount of Rhoplex ER equivalent to 2 parts of latex solids is added and mixed with the glass fibers, and 2 parts by weight of 10% alum solution is added. (Rhoplex ER is Rohm & Haas Company's trademark for an acrylic ester polymer whose shear modulus (kg. per sq. cm.) is 4 at 50° C., 7 at 30° C., 60 at 10° C., and 300 at 3° C.), Agitation is continued until precipitation of the resin on the glass fibers is completed and a uniform dispersion of polymer coated glass fibers is obtained. This fibrous binder slurry is admixed with a second slurry containing 10 parts of Orlon cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1 oz. per square yard and after hot calendering has a tensile strength of 2.8 lbs. per inch.

Example 13

A binder is formed as in Example 12, except that glass fibers are used having an average diameter of 0.1 micron. The Rhoplex ER is used in an amount equivalent to 25 parts of latex solids, and 5 parts by weight of the alum solution is added. This fibrous binder slurry is admixed with a second slurry containing 10 parts of Orlon cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 0.6 oz. per square yard and after hot calendering has a tensile strength of 3.6 lbs. per inch.

Example 14

One part of glass fibers having an average diameter of about ½ micron is slurried in about 250 parts of water in an agitated vessel, with the water temperature at about 70° C. The slurry is violently agitated until the glass fibers are uniformly dispersed. Three-tenths part (dry basis) of Uformite 700 is added and the pH is adjusted to about 4 with sulfuric acid. An amount of Rhoplex AC–55 equivalent to 4.5 parts of latex solids and an amount of Rhoplex B–85 equivalent to 1.5 parts of latex solids are mixed, diluted with several volumes of water, and added to the glass fiber slurry. Agitation is continued until precipitation of the latex on the glass fibers is completed and a uniform dispersion of polymer coated fibers is obtained. This fibrous binder slurry is then admixed with a second slurry containing 3.7 parts of Orlon cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1.1 oz. per square yard and after hot calendering has a tensile strength of 5 lbs. per inch.

Example 15

The binder of Example 14 is formed, except that Lecton RC–6302 is used, equivalent to 8 parts of latex solids, instead of the combined Rhoplex compounds. The fibrous binder slurry is then admixed with a second slurry containing 45 parts of Orlon cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product is a soft, porous structure weighing 4 oz. per square yard.

Example 16

The binder of Example 14 is formed, using Hycar 1852 equivalent to 6 parts of latex solids, instead of the Rhoplex ingredients. (Hycar 1852 is B. F. Goodrich Chemical Company's trademark for butadiene-acrylonitrile polymer latex containing 38 to 42% solids by weight, and having a pH of greater than 9.0.) This fibrous slurry is then admixed with a second slurry containing 10 parts of Orlon cut to a length of about ¼ inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1.2 oz. per square yard and after hot calendering has a tensile strength of 4.5 lbs. per inch.

Example 17

A binder is formed as in Example 14, in which the Rhoplex is replaced by Everflex B equivalent to 6 parts of latex solids. (Everflex B is Dewey & Almy Chemical Company's trademark for a polyvinyl acetate latex containing 54 to 56% solids by weight, and having a pH of 4.0 to 6.5, viscosity 1,000 to 1,400 cp. and a particle diameter of less than 2 microns.) The fibrous binder slurry is then admixed with a second slurry containing 10 parts of Orlon cut to a length of about 1/4 inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs .9 oz. per square yard and after hot calendering has a tensile strength of 4.3 lbs. per inch.

Example 18

A binder is formed as in Example 14, the Rhoplex being replaced by Geon 576 in an amount equivalent to 6 parts of latex solids. (Geon 576 is B. F. Goodrich Chemical Company's trademark for polyvinyl chloride latex containing 54 to 56.5% solids by weight and having a pH of 8.0 and a viscosity of 27 to 47 cp. This latex contains 35 parts of dioctylphthalate per 100 parts of resin.) The fibrous binder slurry is then admixed with a second slurry containing 10 parts of Orlon cut to a length of about 1/4 inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 1.2 oz. per square yard and after hot calendering has a tensile strength of 6 lbs. per inch.

Example 19

A binder is prepared as in Example 14. This fibrous binder slurry is then admixed with a second slurry containing 236 parts of Orlon fibers cut to a length of about 1/4 inch. The combined slurry is sheeted and dried on a paper machine. The final product weighs 2.2 oz. per square yard and, after hot calendering, has a tensile strength of 2.8 lbs. per inch.

It will be understood that many of the details set forth in these examples, and other details herein alluded to for the purpose of explaining the invention, may be modified in various respects without necessarily departing from the spirit and scope of the invention. Therefore, except as otherwise specified, or as set forth in the appended claims, it is intended that the foregoing descriptive particulars be interpreted in an illustrative manner and not in a limiting sense.

What is claimed is:

1. A paper composed primarily of synthetic fibers incapable by themselves of bonding together in the form of a self-sustaining web, said paper containing uniformly distributed glass fibers having diameters less than about 2.5 microns and coated with a thermoplastic polymer of good wet tack quality in the ratio of 2 to 25 parts by weight of coating to 1 part by weight of glass fibers, said coated fibers serving as a binder for the non-bonding primary fibers.

2. A paper according to claim 1 wherein said non-bonding fibers are taken from the class consisting of acrylics, polyesters, polyamides and regenerated celluloses.

3. A paper according to claim 1 wherein the glass fibers have diameters from 0.2 to 1.5 microns.

4. A paper according to claim 1 wherein the coating on the glass fibers is present in the ratio of 3 to 10 parts by weight of coating to 1 part by weight of glass fibers.

5. A paper according to claim 1 wherein the ratio of non-bonding fibers to coated glass fibers is from 1:2 to 32:1.

6. A paper according to claim 1 wherein the ratio of non-bonding fibers to coated glass fibers is from 1:1 to 4:1.

7. A process of forming a paper composed of primary fibers incapable by themselves of bonding together in the form of a self-sustaining web, which consists in preliminarily coating separate glass fibers having diameters less than about 2.5 microns with an adherent resinous coating of good wet tack quality in the ratio of 2 to 25 parts by weight of coating to 1 part by weight of glass fibers, introducing and mixing a slurry of said coated fibers into a slurry containing the primary fibers of which the paper is to be made, forming a web of the resultant mixture, and dehydrating it to convert it into a self-sustaining paper.

8. A process according to claim 7 wherein said coating is taken from the class consisting of polyacrylic esters, polyacrylonitriles, polyvinyl chlorides, polyvinyl acetates and nitrile rubbers.

9. A process of forming a paper according to claim 7 wherein the glass fibers have diameters from 0.2 to 1.5 microns.

10. A process of forming a paper according to claim 7 wherein the coating is applied to the glass fibers in the ratio of 3 to 10 parts by weight of coating to 1 part by weight of glass fibers.

11. A binder for use in the manufacture of a paper composed of fibers incapable by themselves of bonding together to an adequate self-sustaining degree, consisting of a dilute aqueous slurry of separate glass fibers having diameters less than about 2.5 microns, each glass fiber being coated with a thermoplastic polymer having wet tack, the polymer-fiber ratio being from 2 to 25 parts by weight of polymer to 1 part by weight of the glass fibers.

12. A binder according to claim 11, wherein said polymer is taken from the class consisting of polyacrylic esters, polyacrylonitriles, polyvinyl chlorides, polyvinyl acetates, and nitrile rubbers.

13. A binder according to claim 11 wherein the diameters of said glass fibers are from 0.2 to 1.5 microns.

14. A binder according to claim 11 wherein the polymer-fiber ratio is from 3 to 10 parts by weight of polymer to 1 part by weight of the glass fibers.

15. A process for the preparation of a binder for use in the manufacture of paper composed of fibers incapable by themselves of bonding together to an adequate self-sustaining degree, comprising the formation of a dilute aqueous slurry of glass fibers having diameters less than about 2.5 microns, agitating said slurry to separate and uniformly disperse said fibers, then introducing into said slurry an anionic aqueous dispersion of a thermoplastic polymer having wet tack, said aqueous dispersion of polymer being added in an amount sufficient to provide a polymer-fiber ratio of 2 to 25 parts by weight of polymer to 1 part by weight of the glass fibers, and precipitating said polymer on said glass fibers by addition of a precipitating agent.

16. A process according to claim 15 wherein the thermoplastic polymer is taken from the class consisting of polyacrylic esters, polyacrylonitriles, polyvinyl chlorides, polyvinyl acetates and nitrile rubbers.

17. A process according to claim 15 wherein said precipitating agent is taken from the class consisting of alum, cationic urea formaldehyde resins, and cationic melamine formaldehyde resins.

18. A process according to claim 15 wherein the diameters of said glass fibers are from 0.2 to 1.5 microns.

19. A process according to claim 15 wherein said aqueous dispersion of polymer is added in an amount sufficient to provide a polymer-fiber ratio of 3 to 10 parts by weight of polymer to 1 part by weight of the glass fibers.

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