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METHOD OF FORMING AN INORGANIC WATER-LAID SHEET
CONTAINING COLLOIDAL SILICA AND CATIONIC STARCH
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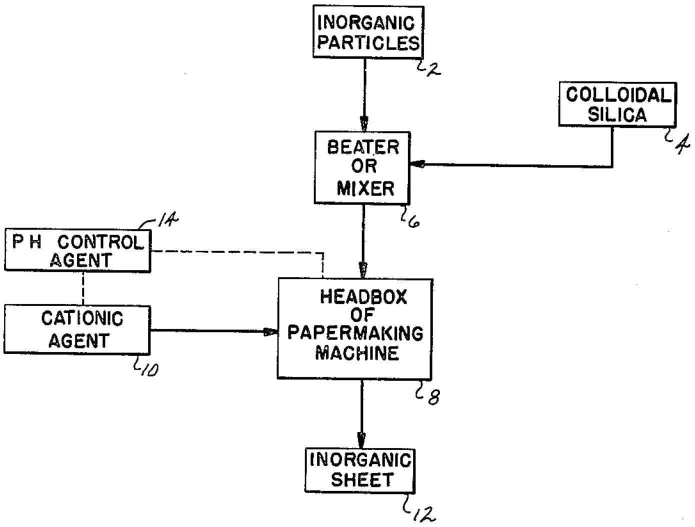

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3,253,978

METHOD OF FORMING AN INORGANIC WATER-LAID SHEET CONTAINING COLLOIDAL SILICA AND CATIONIC STARCH

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This application is a continuation-in-part of our copending application Serial No. 125,112, filed July 19, 1961, now abandoned.

The present invention relates to sheet structures of inorganic fibers or particles, and to the process for their manufacture.

It is an object of the present invention to provide a novel inorganic sheet product of relatively high strength and porosity and substantially uniform structure.

Another object is to provide a porous inorganic sheet product substantially free from organic binders and characterized by relatively strong bonding between the inorganic particles, relatively high strength and porosity as well as resistance to solvents.

A further object is to provide a porous sheet product of high strength comprised of inorganic fibers which are firmly bonded together and which is characterized by resistance to attack by acids and alkalis and by substantial resistance to heat.

Still another object is to provide a novel and highly efficient method for making inorganic sheet products having relatively high strength and porosity and substantially uniform structure.

Other objects and advantages will be readily apparent from the following detailed description and the appended claims.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others and the article possessing the features, properties, and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

In the drawing:

The figure is a diagrammatic illustration of a process in accordance with the present invention.

It has now been found that the foregoing and related objects can be attained by a process in which the inorganic particles are initially thoroughly admixed with colloidal silica to provide a substantially homogeneous aqueous slurry or dispersion which is fed into the headbox of the papermaking machine while simultaneously introducing therewith a solution of a cationic agent, which dispersion and solution interact to deposit the inorganic fibers and colloidal silica upon the wire of the papermaking machine in substantially uniform admixture to form a web, the cationic agent also being incorporated therein in a minor amount. The web is then dried and may be treated in accordance with conventional papermaking practice.

Referring to the attached drawing, a process embodying the present invention is generally illustrated by the diagrammatic flow sheet. Here the inorganic particles **2** and colloidal silica **4** are admixed to form a substantially homogeneous aqueous dispersion in a papermill beater or mixing device **6**. The resultant admixture is then fed into the headbox **8** of a papermaking machine into which is being fed simultaneously a solution or dispersion of a cationic agent **10**, and the two feeds intermix in the headbox but a very stort time before the inorganic particles and colliodal silica deposit upon the wire of the papermaking machine to form the inorganic sheet product **12** of the present invention. A portion of the cationic agent **10** is also retained in the web. As will be pointed out more fully hereinafter, the pH may be adjusted by metering a buffer or acid solution **14** into the headbox **8** or by incorporating it into the solution of cationic agent **10**.

The inorganic particles may be either in fiber or flake form, and fibers may be desirably utilized in admixture with the flakes for increased strength in the sheet product. By the present invention, various inorganic particles can be utilized including glass fibers, quartz fibers (acid-leached glass), ceramic fibers such as aluminum silicate (sold as Fiberfrax by Carborundum Company), mineral wool fibers (a mixture of iron, magnesium, calcium and aluminum silicates, and silicon dioxide); mica flakes, glass flakes and quartz flakes.

Since the glass flakes will generally tend to produce a more brittle sheet structure, care must be exercised in handling to avoid cracking the sheet, particularly during reeling and other operations involving substantial flexure. As pointed out above, inorganic fibers may be desirably employed even in a minor amount to lend flexural strength to the product.

Generally, the fibers utilized are preferably of papermaking length, i.e. predominately greater than 1⁄32 inch length, and may range to even more than 1½ inches in size depending upon dispersibility in water to form dilute slurries, and ceramic fibers (Fiberfrax) of 2–3 inches in length have been employed. The diameter of the fibers does not appear to be particularly significant since glass fibers of up to 12 microns diameter have been satisfactorily employed. The flake particles are generally quite small by reason of the process for their manufacture.

The term "inorganic particles" as used herein refers to inorganic fibers or flakes including glass fibers, quartz fibers, ceramic fibers, mineral wool, glass flakes, quartz flakes, mica flakes, and combinations thereof.

The colloidal silica is admixed with the inorganic particles in an amount equal to at least 2 percent by weight of the inorganic particles and may be used in amounts of up to about 30 percent by weight. Generally, the amount of collodial silica utilized will vary with the intended end use for the product and with the nature of the inorganic particle, i.e. whether it is a fiber or flake. The strength of a given sheet product, both dry and wet, will tend to increase with increase in the colloidal silica content, but the flexibility will decrease and the sheet will become more brittle.

With fibers, the lower portion of the above range, i.e. about 2–15 percent, will produce a strong sheet product having a relatively high degree of flexibility; however, the percentage of colloidal silica may be increased for even greater strength. Generally for flexible sheet applications, it is preferred to use 3–8 percent by weight of colloidal silica.

With flakes, it is generally necessary to use higher percentages of silica, i.e. 15–30 percent, for strong sheet products to be maximum binding of the individual flakes, and the actual amount necessary will be dependent in part upon the size of the individual flake particles. For example, with mica and glass flakes, about 20–30 percent by weight has been found most satisfactory.

The colloidal silica comprises extremely fine particles of silica such as described in United States Patents No. 2,574,902, No. 2,577,485 and No. 2,980,558. The particles are generally of a diameter less than about 100 millimicrons and preferably predominately of a mean diameter less than 15 millimicrons, and are generally considered to be comprised of silica molecules of a relatively low degree of polymerization. The colloidal silica particles are readily dispersible in water to form colloidal dispersions or sols.

Although the colloidal silica may be added in dry form directly to the inorganic fibers or flakes and water in preparing the base furnish, it is preferable to disperse the silica in water separately under conditions affording greater control over the dispersing operation and undesired dusting of the very fine particles. Furthermore, it is possible to purchase such colloidal sols directly from the manufacturers.

Exemplary of such colloidal silica materials are Ludox LS, MS and HS, all aqueous sols containing about 30 percent solids sold by E. I. du Pont de Nemours & Company; and Cab-O-Sil, a colloidal silica powder sold by Cabot Corporation of Boston, Massachusetts.

The admixing of the colloidal silica and inorganic particles should be sufficient to ensure substantially homogeneity. This can be accomplished in a papermill beater during a brushing operation using light roll pressure or during a simple mixing operation with the roll raised off the bed plate, or it can be accomplished by a conventional mixing apparatus or during the continuous mixing in the storage chest for the headbox.

Because of the relative brittleness of flakes and ceramic fibers, these materials should not be subjected to any substantial pressure during the mixing operation, and so the beater roll should be raised off the bed plate for mixing such materials where a papermill beater is employed.

The cationic or positively charged agent must not interfere with the ultimately desired properties of the sheet, such as porosity, or with the papermaking operation. It has been found that the cationic agent must be added to the headbox in an amount of about 0.5–10.0 percent by weight of the solids content of the inorganic particle and coloidal silica furnish which is being added thereto simultaneously. Amounts in excess of 10 percent by weight produce no significant additional benefit. The cationic agent is preferably employed in an amount of about 1–3 percent by weight of the solids in the furnish so as to obtain maximum effect commensurate with low organic content in the final sheet.

The cationic agent is conveniently added to the headbox in an aqueous solution (generally a colloidal solution) of about 1–5 percent by weight and preferably about 2–3 percent by weight, and is dispensed into the headbox in a controlled amount by means of a metering pump or bucket system.

Of the various cationic agents presently known, cationic starches have proven to be consistently satisfactory in operation by reason of their true ionic activity, ease of handling and noninterference with the papermaking operation. Such cationic starches are generally amine-modified starches which are considered to be starch ethers using an amino- or imino- group to provide a positive charge.

Exemplary of such amine-modified starches are: Cato 8 (a modified cornstarch) and Cato Amylon (a hybrid starch containing 55–60 percent amylose), both sold by National Starch and Chemical Corporation of Plainfield, New Jersey; Starbond W (a modified potato starch) sold by Morningstar-Paisley Corporation of New York, New York; and Keotac 22–5 (a modified cornstarch) sold by Hubinger Company, Keokuk, Iowa.

These cationic starches are best added to the headbox in an aqueous solution (colloidal) of about 1–5 percent by weight and preferably about 2–3 percent by weight. The solution is readily prepared by mixing the starch in cold water, heating the mixture to a temperature of about 160–200° F., and continuing the agitation for about 10–30 minutes to effect the desired colloidal solution.

The pH of the headbox dispersion should generally be maintained in the range of about 2.7–6. For glass fibers, quartz fibers, mineral wool fibers, and glass flakes, the pH is preferably maintained in the range of about 2.8–4. Ceramic fibers preferably utilize a pH of about 4–6. Mica flakes, however, are most effectively treated in a headbox dispersion having an essentially neutral or slightly alkaline pH of about 6.5–8.0.

The pH of the headbox can be adjusted by addition of a noninterfering acid salt or acid agent such as potassium aluminum sulfate (alum) or of mineral acids such as hydrochloric acid. The pH can be readily adjusted by use of mineral acids in conjunction with a metering device operating in response to variations in the acidity of the headbox dispersion. Alternatively, an acid salt may be added to the headbox at a predetermined rate and conveniently in the cationic agent dispersion.

Prior to the headbox, control of the pH of the dispersion is quite significant for certain of the inorganic particles. Generally, the glass, quartz and mineral wool materials should be mixed into a slurry and stored at a pH of about 2.7–6.0, and preferably about 2.7–4.0. The ceramic fibers are mixed in an unadjusted aqueous medium or at a slightly alkaline pH, i.e., at about 6.5–8.0 and should be stored in an alkaline slurry. Mica flakes should also be mixed under essentially neutral or slightly alkaline conditions, i.e., at a pH of about 6.5–8.0. In the instance of the ceramic fibers and mica flakes, the desired neutrality or mild alkalinity will generally be provided by inherent alkalinity of the colloidal silica.

Although cylinder machines and conventional Fourdrinier machines may be employed, the sheet is most desirably formed in a papermaking machine utilizing an inclined Fourdrinier wire since more dilute dispersions may be employed with greater uniformity in the sheet structure and greater control of the porosity of the final sheet. In such inclined Fourdrinier papermaking machines, the inorganic particle dispersion is generally maintained at 0.1–1.0 percent by weight solids and preferably at about 0.20–0.30 percent for optimum results. Higher consistencies may be readily employed on cylinder and conventional Fourdrinier machines so long as a sheet porosity of at least about five cubic feet per minute is obtained.

It is imperative that the cationic agent be added to the inorganic particle slurry but a very short time before the particles start to deposit upon the wire. In a fluid system moving rapidly in the headbox, the two dispersions can be admixed by feeding thereinto at closely spaced points within the headbox so as to obtain optimum intermixing commensurate with almost instantaneous deposition of the inorganic particles upon the wire after admixing.

The various inorganic particles can be used in combination to obtain the benefits of each. As pointed out previously, this is particularly true in the use of fibers in combination with flakes to obtain a less brittle sheet product.

It will be apparent that organic fibers may also be incorporated in the sheet of the present invention for particular application. However, generally the presence of any substantial percentage of organic materials in such sheet products is considered deleterious for most intended applications. With the process of the present invention, the sheet product may be produced essentially free from organic materials since the retained amount of cationic agent is generally quite small and may be further adjusted by reduction in the ratio of cationic agent to inorganic particles and silica fed into the headbox. For example, in a ratio of 3:100 using amine-modified starch, the amount of total organics in the finished sheet (including residual organics in the water used for the slurry) is 1 percent or less.

Although the theory of the present invention is not fully understood, it is believed that the cationic agent, which forms a colloidal dispersion in which the particles carry a positive charge, overcomes the small negative charge on the colloidal silica particles in their initially formed uniform slurry with the inorganic particles. The colloidal silica particles then appear to act as if positively charged and are attracted to the surface of the inorganic fibers or flakes which act as if negatively charged. As a result, the colloidal silica is substantially homogeneously distributed upon the surface of the inorganic particles throughout the sheet and bonds the particles together strongly, providing both dry strength and a most significant degree of wet-strength. Since this is a charge mechanism it is important that the cationic agent be added to the system just prior to sheet formation, otherwise it is not fully effective.

The cationic agent should not gel the colloidal silica, which gelling would be most undesirable since substantially discrete silica particles are essentially for the present invention. For example, other known cationic agents, such as alum, dicyandiamide formaldehyde, epichlorhydrin-polyamide and melamine formaldehyde, when mixed with colloidal silica produce almost instantaneous gelation indicating that the retention of the silica by such agents is purely mechanical. The cationic starch, on the other hand, will not gel the silica even after prolonged periods of time. Additionally, gelation of the silica tends to cause poor drainage and sticking to the papermaking wire as well as reduced porosity resulting from the sheet's tendency to tighten. However, the cationic agent may tend to produce a flocculating action when admixed with the inorganic particle-silica furnish, particularly when glass fibers are employed, and this action is best controlled by utilizing close control of the pH for optimum operation, particularly where higher percentages of cationic agent are employed.

The inorganic sheet products obtained in accordance with the method of the present invention generally exhibit a porosity of greater than 5 c.f.m. as measured on a Frazier permeometer. The porosity of these sheets, of course, will vary depending upon the exact composition thereof. As is evident from the process, as described hereinbefore, the cationic starch will constitute only a minor portion of the total weight of the sheet, i.e., 0.5–10 percent and preferably 1.0–3.0 percent, while the silica will account for about one quarter or less by weight, i.e., about 2–27 percent and preferably about 2–15 percent. The remainder of the sheet, up to 97.5 percent by weight, will consist essentially of the inorganic particles mentioned hereinbefore.

The inorganic sheet products of the present invention are suitable for a wide number of applications. Because of their inherent wet-strength, they are adapted to coating or impregnation with various aqueous or organic solvent solutions such as for manufacture of electrical tape. The fibrous structures have a high degree of absorbency due to their porosity and are suitable for manufacture of photo-tape products containing solutions of developer and the like. They have been widely evaluated with most satisfactory results as filters for air, fuel, and acids.

It has also been proposed to use these sheet products for plastic overlay sheets, in electroluminescent paneling and in the manufacture of ceramic decals wherein the sheet would be printed with a decal and subsequently fired to provide a glazed coating.

Various of the sheet products made in accordance with the present invention have been thoroughly evaluated and enthusiastically received as insulating materials for both cryogenic and high-temperature applications.

Other materials may also be included in the sheet. In particular, carbon particles may be admixed with inorganic fibers and colloidal silica to provide a base furnish which will result in a carbon-filled sheet, as fully described in our copending application Serial No. 125,113, filed July 19, 1961, now U.S. Patent No. 3,149,023.

Exemplary of the efficacy of the present invention are the following specific examples wherein various inorganic sheet products were produced in accordance with the present invention.

Example 1

To a conventional paper mill beater were furnished 85 pounds of AAA glass fiber (diameter of about 0.5–0.8 micron), 15 pounds A glass fiber (diameter 1.5–2.5 microns), both fibers being predominately about $\frac{1}{32}$–$\frac{1}{4}$ inch in length and sold by the Johns-Manville Company, 1 quart commercial hydrochloric acid and 1200 gallons of water. The pH of the mixture was approximately 3.0. This mixture was initially defibered for ten minutes with the roll of the beater raised off from the bed plate, and was then lightly brushed to separate the fibers for fifteen minutes.

At the end of the brushing operation 40 pounds of a colloidal silica aqueous sol containing 30 percent solids was added (Ludox LS, E. I. du Pont de Nemours & Company). The colloidal silica was mixed with the fibers for ten minutes and thereafter in the storage chest for the papermaking machine.

A solution of cationic agent was prepared by mixing 15 pounds of cationic starch (Cato 8, National Starch and Chemical Corporation) in 40 gallons of cold water, heating the mixture to 190° F., agitating for fifteen minutes, and thereafter diluting with water to a total volume of 60 gallons.

The glass fiber-silica slurry was further diluted to a consistency of 0.25 percent by weight solids and fed into the headbox of a papermaking machine using an inclined Fourdrinier wire. At the same time, the cationic agent solution was fed into the headbox at a rate providing approximately 1.2 percent by weight starch based upon the solids in the glass-silica slurry. Simultaneously, hydrochloric acid was metered into the headbox to maintain the pH at approximately 3.4.

The glass fibers and silica deposited almost instantaneously upon the wire along with a portion of the cationic agent to form a web which was removed from the Fourdrinier wire and dried in accordance with conventional practice.

The base sheet thus formed had a basis weight of 40 pounds (480 sheets—24" x 36") and a thickness of 13 mils. The tensile strength was 2131 grams per inch in the machine direction and 1169 grams per inch in the cross direction. The density was determined at 0.203 gram per cubic centimeter and the porosity at 5.53 c.f.m. on the Frazier permeometer. The Mullen was determined at 1.5 pounds and the wet tensile strength was 750 grams in the machine direction and 431 in the cross direction.

This sheet product has been found particularly advantageous for use as a jet fuel filter. It is also adapted for converting processes in both aqueous and solvent processes, as an impregnant carrier, for cryogenic insulation, photo-saturant tape, electrical tape, and manufacture of hollow tubes to serve as cores for electrical windings.

Example 2

A quartz fiber sheet was formed in a similar fashion to Example 1.

To the beater were initially supplied 15 pounds of AAA microquartz fiber, 35 pounds of AA microquartz fiber, 1 quart hydrochloric acid and 1200 gallons of water. This mixture was defibered for ten minutes and then subjected to a light brushing operation for ten minutes.

To this mixture was then added 10 pounds of a colloidal silica aqueous sol [(30 percent solids) Ludox LS, E. I. du Pont de Nemours & Company], and the resultant slurry was mixed for ten minutes.

The slurry was fed to the headbox of the papermaking machine and admixed therein with a cationic starch solution as set forth in Example 1, the pH again being maintained at approximately 3.4 by metering in hydrochloric acid.

The resultant sheet had a basis weight of 45 pounds and a thickness of 16.5 mils. The tensile strength was 2000 grams in the machine direction and 1508 grams in the cross direction. The density was determined at 0.179 gram per cubic centimeter, the Mullen as 1.7 pounds and the porosity at 19.9 c.f.m. on the Frazier permeometer. The wet tensile strength was 338 grams in the machine direction and 195 grams in the cross direction.

This sheet has been found highly satisfactory for high temperature insulation materials.

Example 3

A similar sheet was prepared from ceramic fibers. The beater furnish in this instance comprised 40 pounds of long, fine-staple Fiberfrax (fibers of fused alumina-silica, sold by Carborundum Company of America) and 40 pounds of washed Fiberfrax (shot-free), 50 pounds of colloidal silica sol (Ludox LS) and 1200 gallons of water. The long-staple fibers were predominately 2–3 inches in length and about 7 microns in diameter, and the washed fibers were predominately about 1/64 inch in length and about 2.5 microns with some fibers ranging up to 1½ inches in length.

This mixture was defibered for five minutes in the paper mill beater and transferred to the chest wherein agitation was continued. The resultant slurry was further diluted to a consistency of 0.25 percent by weight solids and fed into the headbox of the papermaking machine wherein the remainder of the papermaking formation was the same as in Example 1.

The resultant sheet had a basis weight of 24 pounds and was 6 mils in thickness. The tensile strength was 463 grams in the machine direction and 460 grams in the cross direction. The density was found to be 0.259 gram per cubic centimeter; the Mullen 1.4 pounds and the porosity 85 c.f.m. on the Frazier permeometer. The wet tensile strength was 214 grams in the machine direction and 175 grams in the cross direction.

The sheet is particularly suitable for use as high temperature insulation, electrical insulation and hot liquid filtration.

Example 4

A similar sheet product containing predominately mineral wool fibers was similarly prepared.

The furnish to the beater in this instance comprised 5 pounds AAA microglass fiber, 50 pounds mineral wool fibers of predominately about ¼ inch length and about 1.5–2.5 microns diameter (PMC–35, Eagle Pitcher Company), 1 quart hydrochloric acid and 1200 gallons water. This mixture was defibered in the beater for ten minutes and then admixed with 40 pounds of colloidal silica sol (Ludox LS). The remainder of the papermaking operation was substantially identical to that outlined in Example 1.

The resultant sheet product had a basis weight of 61 pounds and a thickness of 15 mils. The tensile strength in the machine direction was 994 grams and in the cross direction was 892 grams. The density of the sheet was 0.274 gram per cubic centimeter, and the porosity was found to be 33.2 c.f.m. on the Frazier permeometer. The Mullen was 0.8 pound. The wet tensile strength was 569 grams in the machine direction and 483 grams in the cross direction.

This sheet product is desirably employed for high temperature insulation and for lamination with Masonite or building board to provide fire-proofing.

Example 5

The sheet in this instance utilized glass flakes.

To a mixer were added 42.7 percent by weight glass flakes having an average thickness of 3 microns (Microflake Glass, Pittsburgh Plate Glass Company), and 57.3 percent by weight of a 30 percent solids colloidal silica sol (Ludox LS). The pH of the aqueous mixture was adjusted to approximately 2.8 by use of hydrochloric acid. The mixing operation was a light one to avoid fragmentation of the flakes. The dispersion was diluted with water to a consistency of approximately 0.25 percent by weight solids and a solution of cationic starch was introduced into the headbox at a rate calculated to provide 1.5 percent by weight based upon the solids in the flake-silica furnish. The pH of the headbox dispersion was adjusted by hydrochloric acid approximately 3.0.

The resultant web had a basis weight of 40 pounds and a thickness of 5 mils. The average dry tensile strength was 900 grams and the average wet tensile strength was 600 grams.

This glass flake sheet product has been found highly desirable as an electrical insulation material.

Example 6

The sheet in this instance utilized mica flakes.

To a mixer were added 42.7 percent by weight mica flakes (Integrated Mica Corporation) and 57.3 percent by weight of a 30 percent solids colloidal silica sol (Ludox LS). The pH of the dispersion was not adjusted and was at about 7.0. The solids were mixed in the water under mild conditions so as to avoid fragmentation of the mica flakes and the dispersion was further diluted to a consistency of 0.25 percent by weight in the headbox. A solution of cationic agent was simultaneously introduced into the headbox at a rate calculated to provide approximately 1.5 percent by weight cationic starch based upon the solids in the mica flake-silica furnish. The pH of the headbox dispersion was approximately 7.0.

The resultant sheet had a basis weight of 40 pounds and a thickness of 6 mils. The average dry tensile strength was 1200 grams and the average wet tensile strength was 650 grams.

This particular sheet product has been evaluated as being most satisfactory as an electrical insulating material and as a heat insulating material.

Example 7

The sheet in this instance utilized glass fiber.

The base furnish comprised 35.4 percent by weight of AAA (Grade 106) microglass fiber, 6.3 percent AA (Grade 110) microglass fiber, 4.2 percent colloidal silica sol (Ludox LS), and 54.1 percent activated carbon (LC–300, National Carbon). These components were thoroughly admixed in water and fed to the headbox at a consistency of about 0.25 percent by weight solids. The pH in the headbox was maintained at about 3.0 by means of hydrochloric acid.

The resultant sheet was found to be 10 mils in thickness and have a basis weight of 35 pounds. The average tensile strength was 850 grams of the porosity was determined to be 6 c.f.m. on the Frazier permeometer.

Example 8

This example illustrates the improved strength characteristics obtained by adding a cationic material according to the present invention.

Approximately 17 liters of water and 50 ml. of 5% HCl were placed in a Valley beater. To the acid solution was added 83 grams of Code 106 (Johns-Manville Co.) glass microfiber, 14 grams of Code 110 (Johns-Manville Co.) glass microfiber and 3 grams of ¼″ chopped glass strand (9 microns). The glass was dispersed at fast speed for 10 minutes and then brushed with a two pound weight for six minutes. Thereafter, 40 grams of colloidal silica (12 grams solid—Ludox LS) was added and dispersed. A handsheet made from this furnish was designated Sample 8–A.

An aliquot of the above furnish was modified by dispersing 5 cc. of a 1% solution of cationic starch (Cato 8—National Starch and Chemical Corporation) in a handsheet mold just prior to draining and forming the sheet. This sheet was labeled Sample 8–B.

The results of physical tests made on both sheets are tabulated below:

Test	Sample 8–A	Sample 8–B
Basis weight (24 x 36 x 80), lbs	17.3	16
Gauge, mils	4.8	4.1
Tensile Strength—Dry, gms./in	388	990
Tensile Strength—Wet, gms./in	34	251
Mullen, lbs	0	1.4

Example 9

This example illustrates the effect of adding the cationic agent just prior to sheet formation.

One hundred grams of glass microfiber (Code 106) were dispersed by means of a laboratory Valley beater in about 17 liters of water and acidified with 50 ml. of 5% HCl. The dispersion was then brushed with a 2 pound weight for 6 minutes and the resultant furnish was used for the following samples.

Sample 9–A.—An aliquot of the above furnish (approximately 3 grams dry fiber weight) and 6 ml. of a 1% solution of a dicyandiamide formaldehyde condensate (Warco F71) were mixed well and then allowed to stand for 10 minutes. Colloidal silica (Ludox LS) was added in an amount equal to 12% of the furnish and after standing for 10 minutes a handsheet was made. This sheet was labeled Sample 9–A. Due to the slow drainage time repeat handsheets were made in order to time the flow of white water through the wire.

Sample 9–B.—An aliquot of the above furnish and approximately 2% starch solids (Cato 8) were mixed well. Then colloidal silica (Ludox LS) was added in an amount of 12% of the furnish and the entire mixture was agitated for 15 minutes. The handsheet made from the resultant mixture was labeled Sample 9–B.

Sample 9–C.—To an aliquot of the above furnish was added colloidal silica (Ludox LS) to the extent of 12% of the furnish. Handsheets labeled Sample 9–C were prepared by adding approximately 2% starch solids (Cato 8) to the handsheet mold just prior to sheet formation.

The test results on the above handsheets are as follows:

Test	Sample 9–A [1]	Sample 9–B	Sample 9–C
Tensile Strength—Dry, gms./in	725	289	513
Tensile Strength—Wet, gms./in	278	33	195
Basis weight (24 x 36 x 480), lbs	29	28.3	28
Porosity at ½" W.G., c.f.m	0	6.8	7.3
Gauge, mils	6	8.5	8
Drainage, seconds	87	22	8

[1] Difficulty in removing sheets from wire, tended to stick.

While there appears to be some retention of colloidal silica in Sample 9–A, such a sheet requires an excessively long and impractical drainage time (about ten times that of Sample 9–C) and exhibits no porosity, which property is, of course, necessary for filtration purposes. Further, when the starch was added before the silica, poor strength was obtained.

It can be seen from the foregoing specification and specific examples that the present invention provides a novel and highly desirable inorganic sheet product having high strength and readily controllable physical characteristics including high porosity and flexibility.

As will be readily apparent to persons skilled in the art, various modifications and adaptions may be effected without departing from the spirit and scope of the invention.

We claim:

1. The method of forming an inorganic sheet comprising forming a substantially homogeneous aqueous slurry of inorganic particles and colloidal silica; feeding said slurry to the headbox of a papermaking machine while simultaneously feeding therewith a solution of a cationic starch to form a mixture with said slurry, said cationic starch solution admixing with said slurry shortly before deposition of the inorganic particles upon the wire of the papermaking machine and being present in an amount sufficient to provide about 0.5–10.0 percent by weight of the solids in said slurry; and causing said mixture to deposit upon the screen of a papermaking machine to form a web having the inorganic particles firmly bonded together with colloidal silica uniformly distributed across the surfaces of the inorganic particles.

2. The method in accordance with claim **1** wherein said inorganic particles are of a material selected from the group consisting of fibers and flakes, wherein said fibers are selected from the group consisting of glass, quartz, ceramic, mineral wool and combinations thereof and said flakes are selected from the group consisting of glass and quartz, and wherein the pH of said aqueous mixture in the headbox is maintained at about 2.7–6.0.

3. The method in accordance with claim **1** wherein said inorganic particles are mica flakes and wherein the pH of said aqueous mixture in the headbox is maintained at about 6.5–8.

4. The method in accordance with claim **1** wherein said cationic starch is an amine-modified starch.

5. The method of forming an inorganic sheet comprising forming a substantial homogeneous aqueous slurry containing essentially inorganic particles and colloidal silica, said inorganic particles and silica being present in a weight percentage of about 70–98 and 2–30 respectively; feeding said slurry into the headbox of a papermaking machine while simultaneously feeding therewith a solution of a cationic starch in an amount sufficient to provide about 0.5–10.0 percent by weight of the solids in said slurry, said cationic starch solution admixing with said slurry shortly before deposition of the inorganic particles upon the wire of the papermaking machine; and causing said admixture to deposit upon the screen of the papermaking machine to form a web having the inorganic particles firmly bonded together with colloidal silica uniformly distributed across the surfaces of the inorganic particles.

6. The method in accordance with claim **5** wherein said inorganic particles are predominately fibers selected from the group consisting of glass, quartz, ceramic, mineral wool and combinations thereof, and wherein the pH of said headbox mixture is maintained at a pH of 2.7–6.0.

7. The method in accordance with claim **5** wherein said inorganic particles are mica flakes and wherein the pH of said headbox admixture is about 6.5–8.0.

8. The method in accordance with claim **5** wherein the inorganic particles are ceramic fibers and wherein the pH of said headbox admixture is about 4.0–6.0.

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DONALL H. SYLVESTER, *Primary Examiner.*