

Sept. 3, 1963

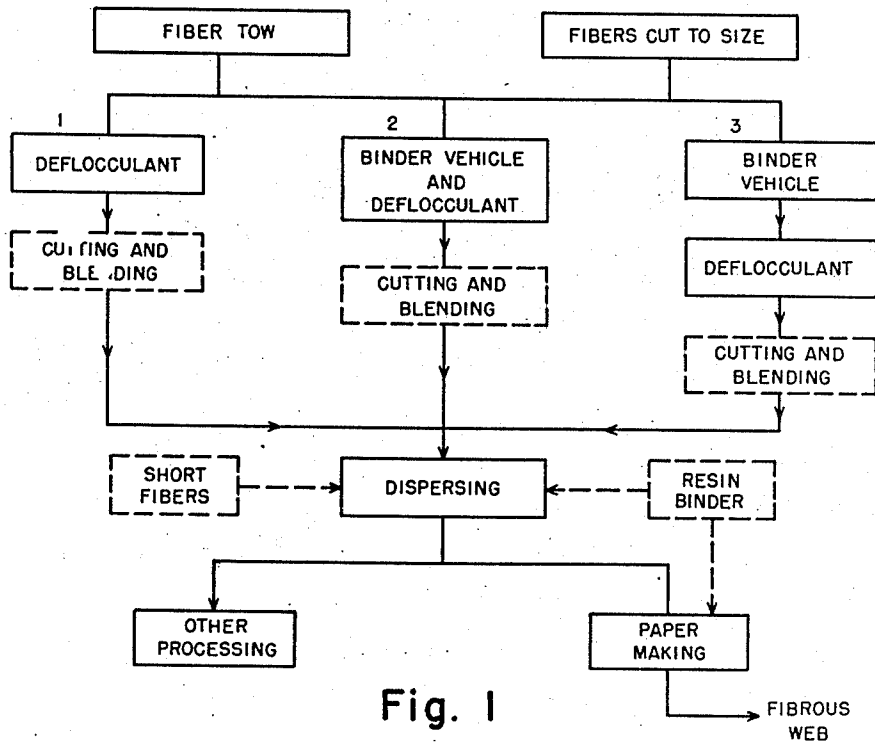
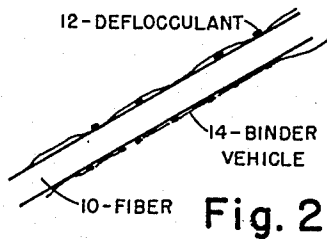
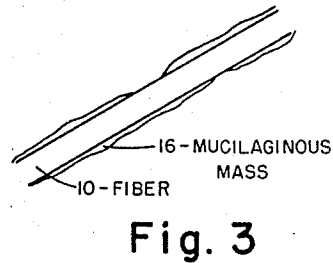
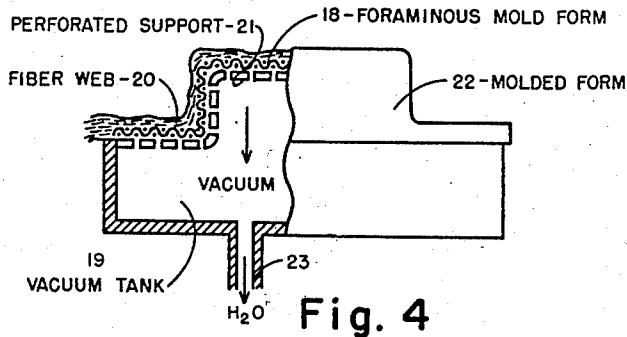
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3,102,838

FIBER TREATMENT AND RESULTING PRODUCT

Filed Feb. 23, 1960

2 Sheets-Sheet 1



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FIBER TREATMENT AND RESULTING PRODUCT

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2 Sheets-Sheet 2

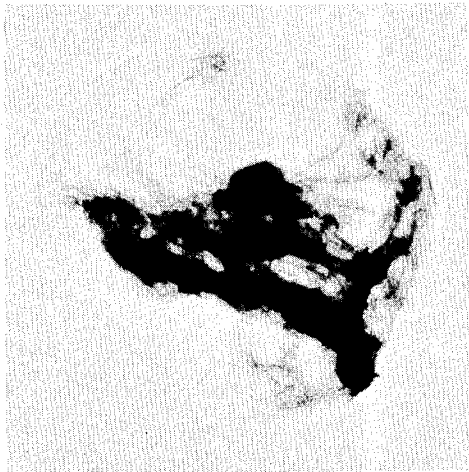


Fig. 5

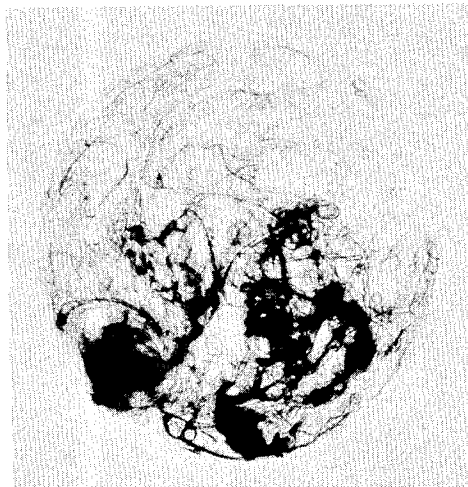


Fig. 6

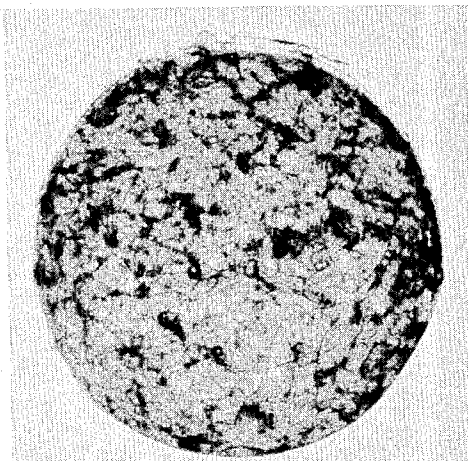


Fig. 7

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3,102,838

FIBER TREATMENT AND RESULTING PRODUCT

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Filed Feb. 23, 1960, Ser. No. 10,469
20 Claims. (Cl. 162-152)

This invention relates to pretreating fibers and more particularly to pretreating fibers to render them readily separable or dispersible in an aqueous liquid medium.

Although paper making is probably the most important and widely used process requiring the dispersion of fibers in water, there are a number of other processes in which it would be highly desirable to be able to disperse relatively long fibers (i.e., longer than three-eighths and up to several inches) in water or an aqueous liquid. Moreover, in view of the ever-increasing development of synthetic fibers which are of the nonfibrillated type, it would be highly desirable to be able to disperse these synthetic fibers in water and lay a web having good dry strength from them, whether of papermaking length or longer. If these fibers, particularly in relatively long lengths, could be disentangled and laid as a web having good formation, there would result papers with fabric-like characteristics.

Using known techniques it has been possible to make papers having good formation of cellulosic fibers that were one-quarter inch or less in length. When using the longer-length fibers, however, it has been necessary to use certain corrective measures, among which may be listed decreasing the consistency and adding relatively large amounts of a deflocculating agent. However, it has not been possible to make paper of fibers longer than about one-quarter inch even using these corrective measures. Furthermore, it has not been possible to water-lay synthetic fibers which are nonfibrillated, even if extremely short lengths of fibers were used, to form a paper having good dry strength. This in turn necessitated the adding of a considerable amount of a resin binder either to the stock or to the web after laying, which in turn meant that the resulting paper or water-laid web formed of the nonfibrillated synthetic fibers no longer possessed the characteristics of the fiber from which it was made, but of necessity had the characteristics of the binder.

If fibrillated synthetic fibers are used in lengths of about one-fourth inch or less, webs with satisfactory strength and formation can be made. However, heat-bonding of the final paper is preferable in the case of short fibers and required in the case of the longer (i.e., over one-fourth inch) to interlock or coalesce the interfelted fibrils.

In water-laying fibers of mineral origin, such as glass or asbestos, it has been necessary to resort to such techniques as carefully controlling the pH of the stock or adding lubricants or agents to the stock in sufficient quantity to deflocculate the fibers. Even then this has not been wholly successful when long fibers were used. Finally, there are other fibers which possess peculiar fiber structure, which prevents them from being water-laid. Wool fibers, for example, are serrated, and it has been difficult to water-lay wool by any techniques applicable to cellulosic materials.

There has then been no one technique or even a combination of techniques which has permitted the formation of water-laid webs from fibers exceeding three-eighths inch in length to give a final paper or fabric embodying the characteristics and only the characteristics of the fiber from which it has been made. Moreover, there is no one technique of water-laying long fibers which is adaptable to all fibers whether of natural, synthetic, or mineral origin;

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nor am I aware of a process which permits forming paper of satisfactory strength from papermaking length, nonfibrillated synthetic fibers. I have now found that by processing fibers in a specific way with a specific type of deflocculant that it is possible to water-lay all types of fibers of relatively long length to give a paper or fabric which has good tensile and flexural strength and which at the same time possesses characteristics which are substantially determined by the characteristics of the fibers from which the papers are formed. The process of this invention is also applicable to forming paper exhibiting good dry strength from short or papermaking lengths of nonfibrillated synthetic fibers.

It is therefore a primary object of this invention to provide pretreated fibers which can be easily dispersed in water whereby the fibers are separated and are available for further processing as individual fibers. It is a further object of this invention to provide a water-laid paper having a soft, fabric-like hand which is flexible and which at the same time exhibits good tensile and flexural strengths.

It is yet another object of this invention to provide nonwoven fabrics of a wide variety of fibers including those which cannot be fibrillated. It is another object to provide fabrics of the character described which retain the characteristics of the fibers from which they are made. It is yet another object of this invention to provide a water-laid fabric or paper having predetermined desired characteristics such as high thermal stability, good dielectric properties and the like. It is another object to provide a water dispersion of long fibers of relatively high consistency which may be used in a variety of processes.

It is another primary object of this invention to provide a process for pretreating long fibers to render them dispersible in water for further processing such as paper making or hydraulic spinning. It is still another object of this invention to provide a process for dispersing long fibers in water which permits the use of consistencies greater than those heretofore possible even using shorter fibers. It is another object to provide a process for making a water-laid fabric or paper from long fibers no matter what their origin. It is another object of this invention to provide a process of dispersing fibers in water which permits the attainment of a more economical use of a deflocculating agent. These and other objects will be apparent from the following description of this invention.

The process of this invention may be characterized as consisting of the step of affixing to the surface of fibers prior to dispersion in an aqueous medium a deflocculant which is a mucilage-producing material which swells in the aqueous medium thereby to produce a mucilaginous mass surrounding at least a portion of the fibers. The term "deflocculant" as used hereinafter is meant to include a material which is a potential deflocculant, i.e., one which, upon some additional treatment in the dispersion, behaves in the prescribed manner and forms the required mucilaginous mass around the fibers.

The pretreated fibers in accordance with this invention may be described as fibers which have affixed to their surfaces a deflocculant in an amount up to about 30% by weight of the fibers, the deflocculant being a finely-divided, mucilage-producing material which swells in an aqueous medium to produce a mucilaginous mass around the fiber. This mucilaginous mass permits the fibers to be readily disentangled and separated in the aqueous medium.

These pretreated fibers after proper dispersion in an aqueous medium may then be water-laid, using papermaking techniques, to form paper or webs of good tensile and tear strengths. The resulting water-laid web may consist essentially of individual fibers greater than three-eighths inch in length, the fibers being self-interlocked by virtue of their length to the extent that they impart good

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structural and flexural strength to the resulting dry web. The web may also consist of a mixture of papermaking length fibers (one-fourth inch and less) and of long fibers in which case web strength is apparently primarily due to the self-interlocking of the long fibers, to fibril interlocking of the papermaking length fibers if these are fibrillated, or to a combination of both. Finally, non-fibrillated synthetic fibers of papermaking length may be water-laid to form a paper having significant tensile and tear strengths imparted to the web by the deflocculant used. The physical characteristics of the papers prepared in accordance with this invention will be illustrated in specific examples.

The process of this invention also makes possible the formation of a water-laid web consisting of different types of fibers blended to impart an almost infinite variety of characteristics to the finished web. The web may also contain resin binders or fibers which in themselves may be activated to act as binders.

It will be seen from the above description of the product and process of this invention that the affixing of a particular type of deflocculant to the fiber surface before dispersion in an aqueous medium permits the water-laying of all types of fibers, and particularly those of relatively long length, without the use of the normal corrective measures described above. Furthermore the resulting web does not require any binder or after treatment to give it strength. However, a binder may be used, if desired, to obtain desired characteristics.

The resulting paper or fabric formed by the process of this invention has many uses, among which may be listed reinforcements for plastics, filters, one-use fabrics, and many of the varied uses now associated with nonwoven fabrics.

The product and process of this invention will be further described with reference to the accompanying drawings in which:

FIG. 1 is a low-diagram of the process;

FIG. 2 is a schematic representation of one of the pretreated fibers of this invention showing the deflocculant affixed to the surface prior to dispersion;

FIG. 3 illustrates the fiber of FIG. 2 after dispersion in water;

FIG. 4 is a representation, partly in cross-section, of apparatus for using the fiber dispersions of this invention to form molded shapes;

FIG. 5 is a photograph of a web formed from one-inch rayon fibers dispersed in water using no deflocculant;

FIG. 6 is a photograph of a web formed from one-inch rayon fibers dispersed in water containing a derivative of okra pods as a deflocculant; and

FIG. 7 is a photograph of a web formed from one-inch rayon fibers pretreated with the same quantity of okra derivative as in FIG. 6 before being dispersed in water in accordance with this invention.

As indicated above, the process of this invention is applicable to the pretreatment of any type of fiber whether it is of natural, synthetic, or mineral origin. Thus among the natural fibers may be listed those of a cellulosic nature such as cotton and linen, and those of a proteinaceous nature such as wool and silk. Derivatives of cellulose, such as cellulose acetate, are also included.

Many synthetic fibers are known and all are applicable in the practice of this invention. These synthetic fibers include the various rayons (acetate, triacetates, saponified acetates, cuprammonium and viscose), the polyamides such as nylon, the polyesters such as Dacron, the polyacrylics such as Acrilan, Orlon, Dynel and the like, as well as fibers formed from polytetrafluoroethylene, vinyl polymers and copolymers, the polyolefins such as polyethylene and from proteinaceous materials such as zein and casein. Moreover, these synthetic fibers may be of a thermoplastic or thermosetting nature inasmuch as no further processing, e.g., heat treating, etc. is required once they are water-laid. If, however, thermoplastic fibers

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are included in the web, heat treating may be used to fuse them to act in the role of a binder.

Finally the process of this invention is applicable also to fibers of mineral origin and these include glass, asbestos and fibers formed of other mineral derivatives, such as aluminum silicate.

The term fiber is one generally applied to a shape or configuration, the length of which is much greater than its greatest cross-sectional dimension. Fibers, of course, need not have circular cross-sections (but may be flat, oval or of a polygonal cross-section. Various terminology is used, depending upon the kind of fiber, to express cross-sectional size of the fiber and any one system of terminology is therefore not applicable to all of the kinds of fibers which are usable in this invention. Therefore, the term "fiber" as used herein is meant to include all configurations which have lengths much greater than cross-sections and which are long enough to form entangled masses when dispersed in a liquid.

It may, of course, be desirable to blend fibers of different lengths and also of different materials. If fibers of less than about one-fourth inch long are blended in with longer fibers, the short, normal papermaking length fibers need not be pretreated with the deflocculant according to the process of this invention. However, it may be desirable to add a deflocculant to the stock for the short fibers. Since the pretreatment of this invention is applicable to all types of fibers and the same process is used to water-lay all of them, fibers of all different kinds may be readily blended, thus providing an almost infinite variety of properties in the finished unwoven fabric.

The deflocculant used in the process of this invention has been defined as one which is a mucilage-producing material which swells in water to produce a mucilaginous mass surrounding at least a portion of the fiber. This characteristic of mucilage-producing may be further defined as the ability to swell in water and impart to water a ropy-like character which gives it the type or kind of consistency associated with uncooked egg whites. The degree to which such a consistency is imparted is a measurement of the ropiness, and hence of the mucilage-producing ability, of the deflocculant. Because of the physical characteristic of the water to which the mucilage-producing material has been added, it is possible to measure the effectiveness of the mucilage-producing material by measuring the volume of a water suspension of the material which spills over from a first container into a second container when the first container is tipped just to the point where the liquid begins to flow and held in that position without further tipping. The greater the quantity of the liquid agglomerate that flows into the second container under these conditions, the better is the ability of the mucilage-producing material to form the mucilaginous mass around the fiber.

In making evaluations of the mucilage-producing ability of a deflocculant in the manner described, a 0.25% suspension of finely divided deflocculant is made up in water, and the mixture is stirred to achieve a uniform suspension. Three hundred cc. of this mixture is then transferred to a first container (which is a 510 cc. brass straight-edged beaker) and the container is tipped only far enough to start liquid flow without further changing the position of this first container. A deflocculant which when added to water in this amount causes at least 25 cc. of the ropy liquid to flow over into a second container under these conditions is considered to be, for the purpose of this invention, mucilage-producing.

There are a number of plants, seeds and gums from which a dried, dehydrated, stable, mucilage-producing material may be extracted to be used as a deflocculant in the practice of this invention. Among the plants may be listed marsh mallow (*Althaea officinalis*, L.), hollyhock (*Althaea rosea*, L.), okra (*Abelmoschus esculentus*), rose mallow (*Hibiscus manicot*, L.), and *Malva rotundifolia*. In addition there are certain seed mucilages including, but

not limited to, linseed (*Linum usitatissimum*), quince (*Cydonia vulgaris*), and psyllium (*Plantago psyllium*) which are known to be mucilage-producing materials. Finally there are derivatives from polyacetylated gums and more particularly derivatives of cochlosperminic acid which possess a potential mucilage-producing property. Among these latter the most widely used is gum karaya, which when subjected to the action of a mild alkali undergoes deacetylation to form a material which is capable of forming the necessary mucilaginous mass to act as a deflocculant.

In preparing the mucilage-producing material from these plants, seeds and gum, it is necessary to extract the mucilage-producing content in a dry particulate form in a manner not to degrade the material to the extent that it will no longer impart ropiness to water.

There are a number of materials such as methyl cellulose, hydroxyethyl cellulose, starch, polyvinyl alcohol and the like which are known to swell in water and which have been used as fiber sizes or in other fiber treatments. These are not satisfactory for the practice of this invention for when used in this process they do not behave as effective deflocculants as do the required mucilage-producing materials. Even when up to fifty percent by fiber weight of these sizes is used, the formation (uniformity of fiber distribution) of the resulting web is poor. This will be illustrated further in the examples.

It has been found preferable to affix the deflocculant of this invention to the fiber surface in the form of finely-divided particulate matter. More preferably, the deflocculant should be sized finer than about 150 microns, i.e., it should pass a standard 100-mesh sieve. The deflocculant may be one which needs no further chemical treatment after the fiber is dispersed in the water or it may require a chemical treatment in the water. As an example of the first of these may be cited a dried, dehydrated product derived from okra pods, whereas a gum karaya which is subsequently deacetylated by the addition of ammonia in the stock is representative of the second type.

In the process of this invention the deflocculant, after it has served its purpose in the water suspension, may be washed out or it may remain within the web itself. If it does remain in the finished web, its presence does not detract from the web's characteristics, e.g., fabric-like hand and the like. When the fiber pretreatment is applied to short papermaking length synthetic fibers and they are formed into a web, the presence of the deflocculant in the finished web appears to contribute to the tensile and tear strengths of the web.

The amount of deflocculant used will of course depend upon its effectiveness as a mucilage-producing material, the rate at which it swells in water (which in turn is related to its particle size) and the like. However, it has been found that the deflocculant affixed to the fibers in the treating step should amount to from about 2 to 30% by weight of the fibers, with a preferred range being from about 10 to 20% by fiber weight. It is, of course, feasible to use more than 30% deflocculant, but it is usually not necessary and may be uneconomical.

The finely divided deflocculant is conveniently affixed to the fiber surface by means of a so-called "binder vehicle." However, the binder vehicle can be eliminated, if desired, provided the deflocculant can be made to adhere to the fiber surface without it. For example, the fibers can be treated first with steam to dampen the fiber surface and the deflocculant added to the treated fibers. Care must, of course, be taken not to wet the fiber surface to the extent that the deflocculant particles swell prematurely to form the mucilaginous mass prior to their dispersion in an aqueous medium. Steam treatment must then be that which will cause the deflocculant to adhere to the fiber surface without effecting any appreciable amount of deflocculant swelling.

The binder vehicle if used may be any of a large number

of liquids that may or may not be soluble in water. However, it is necessary that the binder be essentially a non-solvent for the deflocculant, inert to both the deflocculant and the fiber surface, and a nonswelling agent for the deflocculant. The binder vehicle is preferably a liquid which is easily removed either by washing out or by being sufficiently volatile to be removed in the papermaking drying process. A large number of binders have been successfully used and these include triethylene glycol, glycerin, so-called spindle oil, light petroleum fractions, kerosene, oleic acid, octyl alcohol and the like, and mixtures of these.

In affixing the deflocculant to the surface of the fibers by the use of a binder vehicle, it is possible to treat the fibers first with the binder vehicle and then with the deflocculant or to premix the binder vehicle and deflocculant and then treat the fibers. The binder vehicle and deflocculant are conveniently introduced onto the fibers in a mechanical device designed to open up and blend fibers, such as a carding machine or a garnetting machine. However, any technique which achieves the contacting of the fiber surface with the dry deflocculant and affixes it thereto is satisfactory.

The deflocculant may be affixed to the fibers while they are still in the form of a tow, after they have been formed into top, or after they have been cut to any desired length. If the fibers are treated in the form of top or tow, the top or tow may subsequently be cut before dispersion or may be dispersed in the water for any form of further processing.

Fibers which are to be used in paper making or in other processes after being reduced to the proper length are dispersed in water and the dispersion treated as in other normal papermaking operations. The stock does not have to be beaten for any length of time, usually an aging of about five minutes or a little more is sufficient. The fibers then remain effectively dispersed in the aqueous liquid medium over a prolonged period of time. The wet web may be formed on any type of papermaking equipment such as a Fourdrinier machine, a cylinder machine and the like. Because of the very effective use made of the deflocculant, it is possible to use consistencies up to about 0.25%, consistencies which are far higher than have ever been possible using fibers even no longer than one-fourth inch.

Once the wet web has been formed it is passed over a drum dryer or treated by any other paper drying technique and it is not necessary or even desirable to give the sheet thus formed any additional heat treatment, unless, of course, it contains a resin binder which requires such treatment. The sheet may be calendered, coated or otherwise treated in accordance with normal papermaking techniques.

Although the water dispersion of the fibers made in accordance with this invention may be used in processes other than paper making, the formation of a web or sheet has been used to evaluate the process of this invention. In making a paper it is necessary to achieve a good formation. The term formation connotes the fixed deposition of the fibers of a sheet of paper and includes all effects produced in the arrangement of the fibers before the sheet passes over the drying roll. Thus a paper having good formation will have the fibers evenly and uniformly distributed in the web and departures from the desired or necessary uniformity of distribution may be broadly designated as flocculation and attributed to the ineffectiveness of the deflocculant.

Before presenting examples illustrating the use of various fibers, deflocculants and binder vehicles, it will be helpful to examine drawings and photographs which further illustrate the novel aspects of this invention.

Referring now to the drawings, FIG. 1 is a flow diagram of the process of this invention showing alternate modifications in this process. The fibers to be pretreated may

be introduced as tow (i.e., multi-strands of continuous fibers) or as fibers cut to size. The deflocculant in dry form may be deposited on the fiber surface without a binder such as by flashing on by steam as indicated in modification 1 of FIG. 1; it may be put on with the binder vehicle as in 2; or the binder and the deflocculant may be put on in separate steps in that order as in 3. In each case, of course, if the fiber is introduced as tow, it may be cut after pretreatment as indicated in the steps indicated in dotted lines. Also if fibers of different lengths are to be used and the short fibers have not been treated, the latter may be blended in with the longer pretreated fibers before or after dispersing as indicated. Alternately, the fibers in tow form may be dispersed in water before cutting if they are to be used in processes other than paper making. If a resin binder is to be added, it may be introduced into the dispersion or after the web is formed as in known papermaking procedures. Alternate steps are shown for the process after the dispersing step providing for either further processing or for paper making.

FIGS. 2 and 3 are much enlarged diagrammatic sketches of what is believed to be a representation of the pretreated fiber before and after dispersion in water. In FIG. 2 an individual fiber 10 is shown to have on its surface small grains or particles of deflocculant 12 adhered thereto through a thin (not necessarily continuous) layer of binder vehicle 14. This is believed to be the situation after the fiber has been pretreated, but before it has been dispersed in an aqueous liquid. FIG. 3 represents the fiber and its surface after dispersion and shows the individual fiber 10 coated with a layer of mucilaginous mass 16 which has formed by virtue of the swelling of the deflocculant particles in the water. This mucilaginous mass 16 surrounding the fiber need not be continuous.

The process of this invention is particularly well adapted to the making of molded shapes and articles from water slurries of fibers, particularly long fibers. FIG. 4 illustrates the manner in which this may be accomplished. In the apparatus illustrated in FIG. 4 a foraminous mold form 18 is supported on a perforated support 21 such as a metal form having a number of holes or perforations. The assembly is positioned over a vacuum tank 19 and suitable apparatus is provided to pull a vacuum as indicated and to remove the water from the slurry as by line 23. The water slurry containing the fibers is poured over the foraminous mold form 18 to build up the fiber web 20 into a structural shape corresponding to the mold form 18. The resulting web after drying, and finishing if desired, is particularly well adapted for use as reinforcement in plastic articles. The molded structure may also be used as a finished article for such purposes as packaging and the like.

FIGS. 5-7 are photographs of paper made of rayon fibers, 0.7 mil in diameter and averaging about an inch in length. FIG. 5 represents an attempt to water-lay these rayon fibers in a circular 5-inch hand sheet mold from a stock having a consistency of 0.2% without the use of a deflocculant. (In each of these FIGS. 5-7, the photographs picture the entire hand sheet formed.) It will be seen that the result was a web which contained the bulk of the fibers entangled into a large thick mass showing no uniform distribution of the fibers whatsoever. The circular shape of the mold is not even discernible in FIG. 5.

The web illustrated in FIG. 6 represents an attempt to water-lay one-inch rayon fibers using a deflocculant in the usual manner, i.e., introducing it into the water used to form a stock. This stock was prepared by first dispersing in the water a dry, dehydrated okra pod extract which passed a 200-mesh sieve as a deflocculant and mixing it until the deflocculant was uniformly suspended. Then sufficient one-inch rayon fibers of the same type as used in making the web of FIG. 5 were added to form

a stock with a consistency of 0.2%. The amount of okra used was equivalent to 10% by weight of dry fibers. The same hand sheet mold was used and the resulting web, although an improvement over that of FIG. 5, showed no uniformity in fiber distribution, but rather several thickly entangled areas of fibers.

The photograph in FIG. 7 represents paper made of the same rayon fibers as in FIGS. 5 and 6, in accordance with the process of this invention. Prior to their dispersion in water the fibers were treated with the same okra pod extract used in the paper of FIG. 6 and in an amount equivalent to 10% of their weight. Treatment consisted of first mixing into the fibers a small amount of triethylene glycol, carding them once, then adding the okra extract (screened through 200 mesh) and carding the fibers a second time. The stock was made to have a consistency of 0.2% and was cast in the same circular hand sheet mold as in the case of FIGS. 5 and 6. In contrast to the very poor formation and presence of many entangled fiber masses in FIG. 6, the paper in FIG. 7 shows excellent formation with good uniform distribution of the fibers. Moreover the paper of FIG. 7 had good tensile and flexural strength compared to other synthetic fiber papers, a soft fabric-like hand and retained the characteristics of the original rayon fibers.

The mechanism of deflocculation is not completely understood and several theories have been offered to explain it, including considerations of charge effects and the like. In explaining the unexpected effectiveness of the deflocculants and process of this invention it may be postulated that the deflocculation of extremely long fibers is made possible by the fact that the deflocculant has been placed on the surface of the fiber where it can exert its most effective influence. In the prior art techniques it has always been customary to introduce the deflocculant directly into the water of the stock and as has been illustrated in FIG. 6, this is not effective in water-laying fibers over about one-fourth inch in length. Thus, in contrast to prior art practice, the deflocculant used in this invention does not have to be withdrawn from the stock by attraction to the fiber surface or by any other mechanism which causes it to contact the fiber surface.

The action of the deflocculant concentrated on the fiber surface may probably be explained as being a combination of several effects. Among these may be, first, the formation of a lubricant coating about the fiber, for the fibers have a slippery feel if removed from the water dispersion. Second, the ropiness imparted to water by the mucilage-producing material in the immediate vicinity of the individual fibers as the deflocculant swells in the water may materially alter the viscosity of the water around the fibers. Finally, it is also possible that the mucilaginous mass formed by the deflocculant around the individual fibers isolates them electrically, for each individual fiber is believed to have either a predominately negative or positive charge which means that a number of fibers will be attracted to each other, thus making fibers difficult if not impossible to separate in water dispersions.

The deflocculant of this invention affixed to the fiber prior to dispersion can and probably does contribute to each of these three effects in an efficient manner which permits very long fibers to be dispersed with an economical amount of deflocculant in a stock of consistencies which are feasible to handle.

The fact that the deflocculant is placed in a position to exert the greatest deflocculating effect and does not have to be withdrawn from the stock has been experimentally proven. Two grams of one-inch long rayon fibers were carded first with one gram of triethylene glycol as a binder vehicle and then with 0.2 gram of a dry, dehydrated okra pod extract (about 75 microns in size) as the deflocculant. The pretreated fiber was then stirred

into 1200 cc. of water at room temperature and the stock permitted to age for ten minutes. The dispersion was then poured through cheesecloth to remove the fibers, and the liquid was evaluated to determine its pour value as described above in connection with defining the mucilage-producing material used as a deflocculant. When 300 cc. of this liquid was placed in a first container (a 510 cc. straightedged brass beaker) and poured (as specified) into a second container, about 15 cc. spilled over in an agglomerated mass. Into a second 1200 cc. of water at room temperature was added 0.2 gm. of the same okra pod extract and the mixture stirred to give a uniform suspension. Then 2 grams of one-inch long rayon fibers was stirred in and the stock permitted to age for 10 minutes. The dispersion was then poured through cheesecloth to remove the fibers. This liquid had a pour value of 21 cc. An identical suspension of okra in water without fibers was found to have a pour value of 23 cc.; while pure water without any deflocculant has a pour value of between 10 and 12 cc. (It will be noted that the concentration of the dehydrated okra pod extract in these water suspensions was equivalent to 0.017%. Although the same technique was used to evaluate relative ropiness as in the above-described determination of pour value, the figures given below should not be confused with those given when concentrations of 0.25% are used to determine whether or not a material is deemed to be "mucilage-producing.")

These pour value figures show that when the deflocculant is affixed to the fiber surface before the fibers are dispersed in an aqueous medium the deflocculant swells, forms a mucilaginous mass and substantially all of it remains on the fibers, for the pour test value of 15 cc. compared to that for pure water of 10 to 12 cc. indicates that very little of the deflocculant has been suspended in the water in which the fibers were dispersed. The pour test value of 21 cc. obtained when the fibers were introduced into water in which the deflocculant had already been suspended is only slightly less than the pour test value of 23 cc. for the water suspension of the deflocculant alone, showing that a very small quantity of the deflocculant actually came in contact with the fibers and remained there to act as a deflocculant. This illustrates, then, why there is such a striking difference in the formation of the two hand sheets of rayon paper represented by FIGS. 6 and 7, for where the deflocculant is placed in the water, essentially all of it remains there and fails to prevent fiber entanglement. In contrast, when the deflocculant is affixed to the fiber surfaces prior to dispersing them, it remains around the fibers and achieves its optimum effect by preventing fiber entanglement and achieving good formation.

Although a resin binder is not required to give strength to a fiber web made from the pretreated fibers of this invention, it may be desirable to add resin binders to the web to increase its strength or give it other desired properties. The resin binders may be added at any convenient point in the papermaking process, to the wet web, or after the web is dried. A resin binder in finely divided particulate form may be deposited upon the fiber surface at the same time the deflocculant particles are added. Thus the resin binder may be carded on the fiber surface and held thereto by means of the binder vehicle. If the resin binder is used in this manner, the resulting fiber web after being formed can be treated to activate the binder. For example, a thermoplastic binder within the web would be heated to fuse the binder. Likewise a resin binder may be used in the form of a latex, a dispersion or a solution and may be added to the papermaking stock in the beater, in the papermaking machine, to the web after formation or to the finished web after it has dried.

Any of the resin binders which are normally incorporated into paper may be used. These include elastomers,

such as natural and synthetic rubbers; thermosetting resins as represented by the aldehyde-condensation resins; and thermoplastic resins such as the vinyl polymers and copolymers. The thermoplastic resins may also be added in fiber form to serve as fibers and resin binder.

The amount and type of resin binder added will be determined by the final properties desired in the web. In general, resin binders up to 50 to 60% by weight of the web may be added.

Because the process of this invention makes possible the dispersion of all fibers no matter what their origin, it means that all types of long fibers, whether fibrillated or nonfibrillated may be blended to form webs. This process of pretreating fibers also permits the blending of long (greater than five-eighths inch) fibers with shorter papermaking fibers whether the latter are fibrillated or nonfibrillated.

In blending the long pretreated fibers with normal papermaking fibers (e.g., kraft fibers) the blends may range from about 5% dry web weight of the long pretreated fibers up to, of course, 100% long fibers. In dispersing a mixture of long fibers with short papermaking fibers, the long fibers must first be pretreated to affix the deflocculant to their surfaces as required in this process. The short papermaking fibers do not require such pretreatment. However, it may be found desirable to add a deflocculant to the water for these short fibers.

It will be shown in Example 3 below that it is possible to pretreat nonfibrillated short (one-fourth inch or less) fibers with deflocculant and form these fibers into a web which has a measurable dry tensile strength. These short fibers may be reinforced with long fibers to impart added strength if desired. Thus, in a mixture of short nonfibrillated fibers pretreated in accordance with this invention and long pretreated fibers, the amount of long fibers may range from zero to 100% by weight, thus providing a complete range of this mixture of fibers. In blends of short nonfibrillated fibers and long fibers, each type of fiber must be pretreated prior to dispersion to affix the deflocculant on the fiber surfaces if a web with a measurable dry tensile strength is desired.

The process and product of this invention may be further illustrated in the following examples which are meant to be illustrative and not limiting. Inasmuch as the procedure for making the hand sheets of paper from the various fibers using a variety of deflocculants and binder vehicles was essentially the same in each case, this procedure is described in detail and the results of the examples are tabulated.

In making the hand sheets to evaluate the formation of the resulting web, two grams of the fiber was used along with the specified amounts of binder vehicle and deflocculant. Unless otherwise indicated, the binder vehicle was first carded on the fiber and then the deflocculant was carded on. The fibers thus pretreated were introduced into 1200 cc. of water at room temperature and the resulting stock was permitted to age for 10 minutes with occasional stirring. Without further dilution the stock was then cast on a round hand sheet mold 5 inches in diameter, and the web was couched and drum dried, the blotters used having been removed while the sheet was still damp. The sheets were examined visually for formation.

The examples are grouped to illustrate the application of this invention to various types and lengths of fibers, the type, amount and particle size of the deflocculant, the types of binder vehicles, the range of possible fiber blends, and the use of resin binders.

Examples 1-10 are summarized in Table I. These examples illustrate the application of this invention to natural fibers (Examples 1 and 2), to synthetic fibers (Examples 3-9), and to fibers of mineral origin (Example 10).

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Table I

Example No.	Fiber	Fiber length (inches)	Formation
1-----	Cotton batting-----	1	Good.
2-----	Wool-----	1	Do.
3-----	Rayon (about 2 denier)-----	0.25	Do.
4-----	do-----	1	Do.
5-----	do-----	3.5	Do.
6-----	Nylon (polyamide) (about 1 denier)-----	1	Do.
7-----	Cellulose acetate (textile fabric grade)-----	1	Do.
8-----	Dacron (polyester) (about 2 denier)-----	1	Do.
9-----	Acrlan (polyacrylic) (about 3 denier)-----	1	Do.
10-----	Asbestos (Chrysotile)-----	1	Do.

In preparing the hand sheets represented by Examples 1-10, triethylene glycol in an amount equivalent to 50% by fiber weight was used as the binder vehicle and a dried, dehydrated extract of okra pods which passed a standard 200-mesh sieve was used as the deflocculant (10% by fiber weight).

In addition to illustrating the application of the deflocculant pretreatment to all types of fibers (no matter of what origin and regardless of their surface characteristics), Table I also shows that extremely long fibers (3.5 inch fibers of Example 5) may be water-laid with resulting good formation. Finally, Example 3 illustrates that the shorter, papermaking length nonfibrillated fibers can be water-laid by the process of this invention. The web of Example 3 had a measurable tensile strength of the order of 1.3 pounds/inch in width and a tear strength of 32 grams. A similar web prepared from the same batch of rayon fibers without pretreatment of the fibers when dry had such little tensile strength that it could not be measured and a tear strength of only 13 grams.

The tensile and tear strengths were measured in accordance with standard procedures. Tensile strengths were made on one-half inch wide strips in a Schopper tensile tester. Results, however, are reported on the basis of one-inch widths as is customarily done. Tear strengths were determined on paper samples measuring 2.5 inches in the direction of the tear and by means of an Elmen-dorf tearing tester.

The examples in Table II illustrate the use of various deflocculants. In preparing these examples, one-inch rayon fibers (0.7 mil diameter) were used and triethylene glycol in an amount equivalent to 50% by weight of the fibers was employed as a binder vehicle. Both the binder vehicle and deflocculant were carded on the fibers. In the case of Example 16, the dehydrated okra pod extract was premixed with the triethylene glycol and the mixture was carded on the fibers.

Table II

Example No.	Deflocculant	Maximum size, μ	Amount, percent fiber wt.	Formation
11-----	Dehydrated okra pod extract-----	200-300	10	Poor.
12-----	do-----	150-200	10	Do.
13-----	do-----	150	10	Good.
14-----	do-----	75	5	Fair.
15-----	do-----	75	10	Good.
16-----	do-----	45	10	Do.
17-----	do-----	45	2	Fair.
18-----	Gum karaya ¹ -----	75	10	Good.
19-----	<i>Malva rotundifolia</i> extract-----	150	20	Do.

¹ 2 cc. ammonium hydroxide (30% NH_3) was added to the stock to deacetylate the gum karaya.

Examples 11 and 12 illustrate the necessity of using a finely divided deflocculant, for when it is affixed in particle sizes greater than about 150 microns in size, the deflocculant particles apparently do not swell rapidly enough to form the required mucilaginous mass surrounding the fibers. The use of only 5% deflocculant (Example 14) is effective but not as satisfactory as 10%

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by fiber weight (Example 15). However, when the deflocculant is in very finely divided particulate form (passes 325-mesh) and swells very rapidly in the aqueous dispersion medium, as little as 2% deflocculant based on dry fiber weight may be used (Examples 16 and 17). Although more than 30% by weight deflocculant is feasible, it is usually not economically practical. Examples 18 and 19 illustrate the use of two other deflocculants.

A number of other materials were used as deflocculants without success. These included polyvinyl alcohol, starch, bentonite, hydroxyethyl cellulose and methyl cellulose. These materials are known to swell in water and are frequently used as fiber treating agents. However, they are not mucilage-producing and therefore cannot form the required mucilaginous mass to surround the fibers. Even when these substances were used in amounts equivalent to 50% by fiber weight, the formation of the resulting web was very poor.

A large number of binder vehicles are illustrated in the examples of Table III. In making up the hand sheets represented by Examples 20-30, one-inch rayon fibers were used and the deflocculant, except for Example 29, was dehydrated okra pod extract (75 microns or less in size) applied in an amount equivalent to 10% by fiber weight. In Example 29, gum karaya was used as the deflocculant.

Table III

Example No.	Binder vehicle	Amount binder vehicle remaining, percent fiber wt.	Formation
20-----	Steam-----	0	Good.
21-----	Triethylene glycol-----	10	Fair.
22-----	do-----	25	Do.
23-----	do-----	50	Good.
24-----	Glycerine-----	50	Do.
25-----	Spindle oil ¹ -----	50	Do.
26-----	Kerosene-----	50	Do.
27-----	Oleic acid-----	50	Do.
28-----	Octyl alcohol-----	50	Do.
29-----	Spindle oil + oleic acid ² -----	50	Do.
30-----	Water-----	50	Poor.

¹ Light oil similar to ASE No. 10.

² Formed by mixing 18 gm. spindle oil, 2 gm. oleic acid and 4 gm. gum karaya (75 microns or less). Ammonium hydroxide added to dispersion to deacetylate karaya and to form ammonium oleate to emulsify the oil and thus enable it to be washed from the sheet.

Example 20 illustrates the fact that the deflocculant particles may be affixed to the fiber surface without the use of a binder vehicle. In Example 20 the rayon fibers were steamed until they had picked up about 15% of their weight in moisture. Immediately after steaming they were carded with the okra extract and then dispersed and cast as a hand sheet as specified. No premature swelling of the okra extract was observed, but sufficient moisture was present at the time of the introduction of the deflocculant to cause the okra derivative particles to adhere to the fiber surfaces. Little or no binder vehicle remained as in the case of Examples 21-29.

Example 30, in which water in the amount shown was used as the binder vehicle, illustrates the fact that the binder vehicle cannot be a swelling agent for the deflocculant swells prematurely. In the case of Example 30 when the deflocculant contacted the water serving as the binder vehicle, the fibers balled up and could not be carded or mechanically blended further to distribute the already swelled okra derivative.

The amount of binder vehicle that remains on the fiber surface at least until the fibers are dispersed may vary from zero to about 50% by dry fiber weight. A preferred range, if a binder vehicle is used, is from about 25 to 50%. The optimum amount of binder vehicle can be determined experimentally for any given fiber, deflocculant and binder vehicle combination.

The examples in Table IV illustrate fiber blends and the use of a resin binder. The blends of Examples 31

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and 32 were made using triethylene glycol as a binder vehicle (50% by weight) and dehydrated okra pod extract as a deflocculant (10% by weight) to pretreat the one-inch rayon fibers. The kraft and rope fibers were not pretreated. In preparing Example 33, both types of rayon fibers were pretreated with triethylene glycol and dehydrated okra pod extract, and in Example 34 the powdered vinyl copolymer was carded onto the fibers with the okra deflocculant, using triethylene glycol as the binder.

Table IV

Example No.	Fiber blend, percents by weight	Fiber length (inches)	Formation
31	Rayon—20% Kraft fiber—80%	1 papermaking	Good.
32	Rayon—20% Waste rope fiber—80%	1 papermaking	
33	Rayon—50% Rayon—50%	0.25 1	Do.
34	Rayon—65% Powdered Vinyl copolymer 1—35%	1 1	Do.

¹ Sold as VMCH by Bakelite Corp. A terpolymer of vinylchloride, vinylacetate and maleic anhydride.

The hand sheets of Examples 31 and 32 had the long rayon fibers evenly distributed throughout, imparting improved tensile and tear strengths to the sheets. These examples illustrate how normal papermaking cellulosic fibers may be reinforced with long pretreated fibers.

Example 33 represents a blending of pretreated short nonfibrillated fibers with long pretreated fibers. Hand sheets representing webs made from all short nonfibrillated fibers (Example 3) from a blend of short and long pretreated nonfibrillated fibers (Example 33) and from all long fibers (Example 4) were evaluated for tensile and tear strengths. Little, if any difference could be determined among these with respect to tensile strengths (due apparently to the fact that they were hand sheets) but the tear strengths were 32, 91 and 131 grams, respectively, showing that tear strength increased with an increase in the amount of long fibers present.

Finally, Example 34 illustrates the addition of a resin binder (in this case a thermoplastic binder) to a web formed from the pretreated fibers of this invention. After the hand sheet of Example 34 had been dried on the drum drier, it was baked for 15 minutes at 300° F. to fuse the vinyl copolymer. The cured sheet had a tensile strength of 2.6 pounds/inch, a marked increase over an all-rayon web.

It will be seen from the description of this invention that when fibers are pretreated in the prescribed manner they can be readily dispersed in water and the resulting dispersion used in further processing, e.g., to form a web of paper or unwoven fabric with good formation or fiber distribution. This process of pretreating is applicable to all types of fibers as illustrated by the wide variety of fibers in the examples given. The resulting water-laid web may be formed entirely of long fibers or may be modified by containing short papermaking fibers or short synthetic fibers. If desired, binders which are normally used in paper making may also be added. Although paper making is perhaps at present the most widely employed process requiring dispersion of fibers in water, the fact that the process of this invention now makes possible the ready dispersion of long fibers in water (no matter of what origin) means that many other processes, e.g., hydraulic spinning, etc., can now be developed to their fullest potential.

I claim:

1. Process for pretreating fibers prior to their dispersion in an aqueous liquid medium, characterized by the step of affixing to the surface of substantially dry individual fibers

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a deflocculant in an essentially dry finely-divided particulate state thereby to attach substantially all of said deflocculant to said fibers, said deflocculant being a mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25% and which swells when said fibers are dispersed in said liquid medium thereby to produce a mucilaginous mass surrounding at least a portion of the surface of said individual fibers.

2. Process for pretreating fibers prior to their dispersion in an aqueous liquid medium, comprising the steps of applying to the substantially dry individual fiber surfaces a binder vehicle and affixing to said fiber surface by action of said binder vehicle a deflocculant in an essentially dry finely-divided particulate state, said binder vehicle being inert to and a nonswelling agent for said deflocculant and said deflocculant being a mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25% and which swells when said fibers are dispersed in said medium thereby to produce a mucilaginous mass surrounding at least a portion of the surface of said individual fibers.

3. Process for pretreating fibers prior to their dispersion in an aqueous liquid medium, comprising the steps of mechanically blending substantially dry fibers in the presence of a binder vehicle and of a finely-divided deflocculant, said binder vehicle being inert to and a nonswelling agent for said deflocculant and said deflocculant being a mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25% and which swells when said fibers are dispersed in said medium thereby to produce a mucilaginous mass surrounding at least a portion of the surface of said individual fibers.

4. Process for pretreating fibers prior to their dispersion to render them separable in an aqueous liquid medium and bondable when water laid from said liquid medium, characterized by the steps of affixing to the surface of substantially dry individual fibers an essentially dry resin binder in finely-divided particulate form and a deflocculant in an essentially dry finely-divided particulate state thereby to attach substantially all of said deflocculant to said fibers, said deflocculant being a mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25% and which swells when said fibers are dispersed in said liquid medium thereby to produce a mucilaginous mass surrounding at least a portion of the surface of said individual fibers.

5. Process for making paper of fibers having a length greater than three-eighths inch, comprising the step of pretreating substantially dry individual fibers by affixing to the fiber surface a deflocculant in a finely-divided particulate state thereby to attach substantially all of said deflocculant to said fibers, dispersing the resulting pretreated fibers in an aqueous liquid medium and sheeting out said fibers thereby to form a web, said deflocculant being a mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25% and which swells when said fibers are dispersed in said liquid medium thereby to produce a mucilaginous mass surrounding at least a portion of the surface of said individual fibers.

6. Process in accordance with claim 5 further characterized by the step of adding to said aqueous liquid medium a reactant for said deflocculant.

7. Paper made by the process of claim 5.

8. Process for making paper, comprising the step of pretreating a first quantity of fibers having a length greater than three-eighths inch by affixing to the surface of said individual long fibers in a substantially dry state a deflocculant in a finely-divided particulate state thereby to attach substantially all of said deflocculant to said fibers, dispersing the resulting pretreated fibers in an aqueous medium, introducing a second quantity of fibers of papermaking lengths into said aqueous medium, and sheeting out said fibers thereby to form a web of blended fibers of different length, said deflocculant being a mucilage-producing material which imparts ropiness to water in

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concentrations as low as 0.25% and which swells when said fibers are dispersed in water thereby to produce a mucilaginous mass surrounding at least a portion of the surface of said individual fibers.

9. Process for making molded shapes from fibers having lengths greater than three-eighths inch, comprising the steps of affixing to the surface of substantially dry individual fibers a deflocculant in a finely-divided particulate state thereby to attach substantially all of said deflocculant to said fibers, dispersing the resulting pretreated fibers in an aqueous liquid medium, casting said fibers on a mold form thereby to form a web corresponding to the shape of said mold form and drying said web, said deflocculant being a mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25% and which swells when said fibers are dispersed in said liquid medium thereby to produce a mucilaginous mass surrounding at least a portion of the surface of substantially all of said individual fibers.

10. As a new article of manufacture fibers pretreated to render them separable when placed in an aqueous liquid medium, characterized by having affixed to the surface of individual substantially dry fibers a deflocculant in a finely-divided particulate state in an amount up to about 30% by weight of said fibers, said deflocculant being a mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25% and which swells when said fibers are dispersed in said liquid medium thereby to produce a mucilaginous mass surrounding at least a portion of the surface of said individual fibers.

11. Article in accordance with claim 10 wherein said fibers are of natural origin.

12. Article in accordance with claim 11 wherein said fibers are cellulosic.

13. Article in accordance with claim 10 wherein said fibers are of synthetic origin.

14. Article in accordance with claim 10 wherein said fibers are of mineral origin.

15. Article in accordance with claim 10 wherein said deflocculant is a stable, finely-divided dehydrated product derived from okra pods.

16. As a new article of manufacture, fibers pretreated to render them separable when placed in an aqueous liquid medium, characterized by having deposited on the surface of the individual fibers in a substantially dry state prior to their dispersion in said aqueous liquid medium a deflocculant as a finely-divided dry particulate material sized less than about 150 microns in an amount up to about 30% by weight of said fibers and affixed thereto by a liquid binder vehicle, said deflocculant being a mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25% and which swells when said fibers are dispersed in said liquid medium thereby to produce a mucilaginous mass surrounding at least a portion of the surface of said individual fibers, and said binder vehicle being inert to and a nonswelling agent for said deflocculant.

17. Fibers in accordance with claim 16 wherein said binder vehicle is a hydrocarbon oil.

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18. Fiber in accordance with claim 16 wherein said binder vehicle is a polyhydric alcohol.

19. As a new article of manufacture, fibers pretreated to render them separable when placed in an aqueous liquid medium and bondable when waterlaid to form a web, characterized by having deposited on the surface of the individual fibers in a substantially dry state prior to their dispersion in said aqueous liquid medium a deflocculant as a finely-divided dry particulate material sized less than about 150 microns and in an amount up to about 30% by weight of said fibers and an essentially dry resin binder in a finely-divided particulate form and affixed to said surface by a binder vehicle, said deflocculant being a mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25% and which swells when said fibers are dispersed in said liquid medium thereby to produce a mucilaginous mass surrounding at least a portion of the surface of said individual fibers, said resin binder being activatable after formation of said web thereby to bond said fibers, and said binder vehicle being inert to and a nonswelling agent for said deflocculant.

20. An aqueous liquid dispersion of fibers, said fibers being greater than three-eighths of an inch in length and being further characterized in that substantially all of them are at least partially surrounded by a mucilaginous mass separating the individual fibers in said dispersion, said mucilaginous mass being further characterized as being a water-swelled mucilage-producing material which imparts ropiness to water in concentrations as low as 0.25%, and having been affixed to said fibers as a pretreatment prior to their introduction into water to form said aqueous liquid dispersion.

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