This invention relates to bonded non-woven fibrous or filamentous products having a carded fiber structure or comprising fibrous mats in which the fibers or filaments are distributed haphazardly or in random array. The invention also relates to methods for producing the bonded non-woven fibrous products or shaped articles therefrom. The bonded non-woven fibrous products are not only useful in the production of articles of either flat or three-dimensional shape, but also as insulating material and the like as will be described more particularly hereinafter.

Hereinafter, the expression "random array" is intended to include the array of fibers in a carded web wherein partial orientation is frequently present as well as other arrays in which the fibers are in a completely haphazard distributional relationship.

Heretofore, binders of natural rubber latex and aqueous dispersions of synthetic rubbers, such as butadiene copolymerized with styrene, acrylonitrile, and so on have been suggested as binders for bonding the fibers in non-woven fabric structures, but these materials have various disadvantages, among which is the tendency to impart an off-white appearance or cast to the bonded products, and this tendency is so strong it is difficult to overcome even by the use of optical bleaches or by the use of white pigments, such as titanium dioxide. Also, the synthetic rubbers are unsatisfactory for making products that are exposed to sunlight, such as outer wearing apparel, because of lack of resistance to ultraviolet radiation. These rubbery binders also produce a rubbery hand which appears to the consumer insofar as the feel of the product is concerned. When binders of polyvinyl acetate, chlorides, or their copolymers are used, the hand becomes papery, by which is meant that the product has a crisp, brittle hand and conveys the impression of thinness and fragility. It also produces a noise on crumpling that is typical of papers.

The application of thermoplastic polymers such as vinyl acetates of acrylic or methacrylic acid produces products in which the binder remains permanently thermoplastic with consequent tendency to change when subjected to excessive temperatures. The simple acrylic and methacrylic acid esters are also characterized by relatively poor adhesion to hydrophobic types of fibers, such as nylon, vinyl resins and cellulose esters and such polyelectrolytes as polyethylene glycol terephthalate. Furthermore, many of the binders heretofore employed, including the aqueous dispersions of rubber, synthetic rubbers, and acrylic esters, cannot be washed, scoured, or dry-cleaned. Also, these binders have a strong tendency to migrate to the surfaces of fibrous products during drying of the products to which the dispersions have been applied.

It is an object of the present invention to provide fibrous products made with a binder which can be applied by way of an aqueous system without the disadvantages mentioned above that are characteristic of previously applied aqueous binder systems. A further object of the invention is to provide a bonded fibrous product of non-woven character in which the binder is adapted to be converted to an insusceptible and insoluble condition as by heating with or without the presence of a suitable catalyst as will be pointed out more particularly hereinafter. It is a further object of the present invention to produce bonded fibrous products of non-woven character from fibers which are incapable of felting, whether of natural or synthetic origin, and especially those which, unlike wool, are of non-proteinaceous character and have relatively smooth surfaces extending longitudinally of the fibers, and because of these surface characteristics are incapable of being converted into a felted product by normal felting operations. A further object of the invention is to provide bonded fibrous products of non-woven character wherein the binder may be substantially uniformly distributed through the body of the structure and has reduced tendency to migrate preferentially to the surfaces of the structure. Other objects and advantages of the invention will be apparent from the description thereof hereinafter.

The bonded fibrous products of the invention comprise a binder derived from an essentially water-insoluble linear polymer containing amino groups which in the final bonded products are apparently cross-linked to an insoluble condition. The versatility of the binder used in the present invention is such as to be readily adapted to various methods of production of the fibrous products. The bonding of the fibers is effected with a clear, substantially colorless binder which has good adhesion to all sorts of fibers and filaments and even to those of siliceous character which, in the past, have been difficult to handle because of the difficulty of finding colorless binders which are adequately adhesive toward the siliceous material such as glass. The binders of the present invention are also substantially free of discoloration when subjected to elevated temperatures, such as those used for drying, fusing, or curing.

The binder of the present invention contains a plurality of amino groups by which it is adapted to be insolubilized and rendered insusceptible on exposure to or without suitable catalysts which are generally of acidic character. Hence, the cured or baked fibrous product provides improved resistance to laundering, dry-cleaning and spotting, to various chemicals, and to heat as compared to the aqueous systems, such as rubber latex or aqueous dispersions of synthetic rubbers or acrylic or vinyl esters, heretofore applied. The bonded fibrous products of the present invention can be heated to a much higher temperature than those of the prior art using the binders mentioned above without suffering discoloration, increase in stiffness or deleterious decomposition. They are characterized by excellent resistance to ironing in which operation they are not subject to tackiness as would be true of the thermoplastics heretofore used.

The amino groups apparently also provide a greater versatility of adhesion in that the binders of the present invention are characterized not only by good adhesion to hydrophilic fibers like cotton, regenerated cellulose rayons and the like, but also are characterized by excellent adhesion to hydrophobic types of fibers, such as the nylon and especially the polyamide types, the vinyl resins such as copolymers of vinyl chloride with vinyl acetate or with acrylonitrile, polymers of 70 to 90% acrylonitrile with other monomers such as vinyl chloride, vinyl acetate, any of the vinyl pyridines such as 2-vinyl pyridine or mixtures of such auxiliary comonomers, polyelectrolytes and cellulose derivatives, such as cellulose acetate, cellulose acetate butyrate, and the like. Because of the characteristic adhesion of the binder of the present invention to both hydrophilic and hydrophobic types of fibers, the fibrous products are characterized by excellent resistance to...
“pilling” and abrasion. The binder of the present invention is adapted to be dried and then cured to insoluble and infusible condition so that the bonds cannot be disturbed even under severe conditions of heat. The fibrous products using the binder of the present invention have the advantage also that they can be embossed durably in wet condition or during the first drying but before complete drying. This is evidenced by the fact that if the drying is effected on a suction screen through which the excess water is drained from the fibrous product, the pattern of the screen is permanently imparted to one face of the product and even calendering under normal procedures and temperatures does not destroy this pattern effect. While the binder may be preferentially applied, if desired, to portions of the fibrous product, such as one or both of the faces thereof, it is characteristic of the binder of the present invention that if such preferential treatment is not desired, substantially uniform distribution may be obtained because of the reduced tendency of the binder after initial distribution throughout the body of the fibrous product to migrate to the surfaces thereof during drying. The binder of the present invention may also contain, besides the amino-containing polymer, thermostetting aminoplast condensates such as of urea or melamine or the like with formaldehyde and the catalyst used for accelerating the condensation of the aminoplast to insoluble and infusible condition serves simultaneously and/or concurrently for the curing of the amino-containing polymer to the insoluble and infusible condition.

The cured or insolubilized binders are unaffected by water or organic solvents, such as styrene, even at moldering temperatures, whereby the bonded fibrous products are adapted to be used as molding preforms or molding inserts for the production of molded articles from various thermosetting resins as will be pointed out in more detail hereinafter. The binders are also free of cold flow and are resistant to flow at elevated temperatures, whereby shifting of the fibers or filaments in the bonded product is substantially completely prevented even at elevated temperatures during subsequent molding with such products being used as reinforcing inserts or forms.

In accordance with the present invention, a fibrous product, the fibers of which consist entirely of non-proteinaceous fibers which are incapable of felting, is impregnated with an aqueous dispersion of a water-insoluble linear polymer of monomethylenically unsaturated monomeric units comprising at least 3 percent by weight of units containing amino groups. The polymer may be applied as a powder, but it is preferable to apply it in the form of an aqueous dispersion. The molecular weight of the polymers should be from about 100,000 to about 10 million.

The amino groups may be in free amine form, in salt form or in the form of a quaternary ammonium salt, and in the specification and claims reference to amino groups is intended to embrace all of these three forms.

The linear polymer may consist of units each of which contains an amino group (provided the homopolymer is water-insoluble) or it may contain at least 3% by weight of units in the copolymer having amino groups. Generally, water-insoluble copolymers containing units of which from 3 to 20% by weight contain the amino groups are more practical. It is preferred to employ copolymers containing from 3 to about 20% of units containing amino groups when soft, flexible products are desired. However, polymers containing a larger proportion of units having amino groups even up to 100% are useful when a relatively stiff product is desired or when soft products are desired and the amine-containing units also contain large alkyl or alkylene groups totalling 8 or more carbon atoms.

The aqueous dispersion is preferably obtained by emulsion polymerization in the presence of an emulsifying agent of at least one monomer containing an amino group, such as a monomer having the structure of one of Formulas I and II following:

\[
\begin{align*}
R' \quad & \quad \text{where:} \\
R & \quad \text{is selected from the group consisting of } H \text{ and } CH_3, \\
A & \quad \text{is selected from the group consisting of } -O-, \\
- & \quad \text{and } -O-N-. \\
\end{align*}
\]

in which R² is selected from the group consisting of H and saturated aliphatic hydrocarbon groups having 1 to 12 carbon atoms,

Rⁿ is selected from the group consisting of straight and branched chain alkylene groups having 2 to 10 carbon atoms, of which at least two extend in a chain between the adjacent N atom and A group,

R”, when not directly connected to R’, is selected from the group consisting of H, hydroxyalkyl groups containing 2 to 4 carbon atoms and saturated aliphatic hydrocarbon groups having 1 to 10 carbon atoms,

R”’, when not directly connected to R”, is selected from the group consisting of H, hydroxyalkyl groups containing 2 to 4 carbon atoms and saturated aliphatic hydrocarbon groups having 1 to 10 carbon atoms,

R’ and R”’, when directly connected together, form with the N atom a residue of a heterocyclic nucleus selected from the group consisting of morpholine, piperazine, pyridine, pyrrolidine, and N-alkyl-piperazine in which the alkyl group has 1 to 18 carbon atoms, such as methyl, ethyl, isopropyl; and

\[
\begin{align*}
\text{II} \\
\end{align*}
\]

R² is selected from the group consisting of H and saturated aliphatic hydrocarbon groups having 1 to 12 carbon atoms, and

n is an integer having a value of 1 to 4.

Examples of the compounds of Formula I include:

N-(p-dimethylamino)propyl methacrylamide
N-((p-dimethylamino)ethyl acrylamide
N-(p-dimethylamino)ethyl methacrylamide
10-aminocrotyl vinyl ether
8-aminoctyl vinyl ether
diethylaminohexyl methacrylate
diethylaminoethyl vinyl ether
5-aminoethyl vinyl ether
3-aminoctyl vinyl ether
2-aminoethy vinyl ether
2-aminoctyl vinyl ether
2-aminoctyl vinyl ether
2-dimethylaminomethyl acrylate
dimethylaminoethyl acrylate
N-(3,5,5-trimethylhexyl)aminoethyl vinyl ether
N-cyclohexylaminoethyl vinyl ether
1 Butylaminoethyl acrylate
2-(1,1,3,3-tetramethylamino)ethyl methacrylate
N-t-butyllaminoethyl vinyl ether
N-methylaminoethyl vinyl ether
N-2-ethylhexaminoethyl vinyl ether
N-4-occtylaminoethyl vinyl ether
β-morpholinomethyl methacrylate
4-(β-acryloyloxyethyl)-pyridine
β-pyrrolidinoethyl vinyl ether
5-aminoctyl vinyl sulfide,
β-hydroxethylaminoethyl vinyl ether,
(N-β-hydroxyethyl - N - methyl)aminoethyl vinyl ether,
and hydroxyethylidimethyl(vinylxoyethyl) ammonium hydroxide.

Preferred monomers of this general class are those of the formula I:

\[
\text{Ia} \quad \text{CH}_2=\text{CHOCH}_2\text{H}_2\text{N(R)}\text{C}_2\text{H}_5\text{OH}
\]

where R is a lower alkyl group having 1 to 6 carbon atoms.

The polymers obtained therefrom are especially resistant to solvents and hot washings or laundering in alkaline aqueous liquids.

Examples of the 4-vinyl pyridine of Formula II include:

- 4-vinyl pyridine
- 2,6-dimethyl-4-vinyl pyridine
- 3-dodecyl-4-vinyl pyridine, and
- 2,3,5,6-tetramethyl-4-vinyl pyridine.

Another class of amine-containing monomers that may be used is that of Formula III:

\[
\text{III} \quad \text{CH}2=\text{C}(\text{R})\text{COONH}_2
\]

where R and R' are defined above. Examples include:

- 3-(4-pyridyl)-propyl methacrylate,
- 2-(4-pyridyl)-ethyl methacrylate, and
- 2-(4-pyridyl)-ethyl acrylate.

The fibers are present in the form of a so-called "non-woven" mat in which they are haphazardly distributed. The mat may be formed by carding when the fibers are of such a character, by virtue of length and flexibility, as to the amenable to the carding operation. Natural fibers like jute, sisal, ramie, hemp, and cotton may be used, as well as many artificial fibers or filaments including rayon, those of cellulose esters such as cellulose acetate, vinyl resin fibers such as those of polyvinylchloride, copolymers of vinyl chloride with vinyl acetate, vinylidene chloride or acrylonitrile containing a major proportion of vinyl chloride in the polymer molecule, polyacrylonitrile and copolymers of acrylonitrile with vinyl chloride, vinyl acetate, methacrylonitrile, vinyl pyridine, or with mixtures of such monomers and containing a major proportion from 75 to 95% of acrylonitrile in the copolymer molecule; also condensation polymers such as polyamides of nylon type, polyesters such as ethylene glycol-terephthalaldehyde polymers and the like. The thin web or fleece obtained from a single card may be treated in accordance with the present invention, but generally it is necessary and desirable to superpose a plurality of such webs to build up the mat to sufficient thickness for the end use intended particularly in the making of heat insulation. In building up such a mat, alternate layers of carded webs may be disposed with their fiber orientation directions disposed at 60° or 90° angles with respect to interposing layers.

Mats may also be formed by the deposition of fibers, either natural or artificial, from an air stream. Thus, continuous filaments may be fed to a cutter or breaker which discharges the fibers into the discharge side of a blower. Suitable conduits are provided to guide the fibers to a collecting screen or air-pervious structure for collecting the fibers in the form desired. The screen may be in the form of an endless traveling belt passing through the lower portion of a frame into the upper portion of which the blown fibers are introduced by the conduits. A suction box may be disposed beneath the upper course of the traveling screen to assist in the deposition of the fibers thereon. Instead of having a traveling flat screen, a stationary formed screen may be used. For example, it may take the form of a hat-shaped cone such as that used in the felt hat-making industry. Alternatively, it may have any other form suitable to produce the desired shape of the fibrous product, such as a rectangular tray. Again, suction may be applied beneath the screen to assist deposition of the fibers thereon.

The fibers and filaments may be formed by direct spraying from a solution or molten mass thereof. This is a conventional procedure for the formation of glass fibers or mineral wool fibers as well as those of nylon or of thermoplastic materials, such as vinyl resins of the type mentioned hereinabove, adapted to be dissolved in a suitable solvent, such as acetone or dimethylformamide, or to be melted. The solution or melt is, of course, directed to suitable nozzles or jet-forming orifices and a high pressure fluid stream, such as of cold or hot air or of insert gases such as nitrogen or even of steam, is directed against the stream of filaments-forming material to disrupt them and coagulate them as fibers in the vicinity of the orifices. Electrostatic spinning methods may also be employed for this purpose. As in the case of the use of blowers, the disrupted and dispersed fibers may be directed to the top of a settling tower and be allowed to settle, with the aid of suction devices, upon a suitable traveling or stationary screen at the bottom of the tower. This procedure is adaptable to the production of fibers of siliceous materials such as glass or mineral wool as well as to thermoplastic resin fibers mentioned above.

Another procedure may involve the extrusion to continuous filaments, either from solutions of the filament-forming material or from molten masses thereof, and the cutting or breaking of the filaments to fibers of a predetermined length which may be fed to a hopper at the top of a settling tower into which they may be discharged by conventional feeding devices, and at the bottom of which a traveling or stationary screen may be deposited for collection of the fibers.

The fibers and filaments that may be used in the present invention may be natural or artificial as stated above. The selection of the particular material of which the fiber is made frequently depends upon the use intended of the product. For example, siliceous fibers are extremely valuable in the production of molded articles because of the exceptional strength obtained by their use. However, when the bonded fibrous products are used for filtration purposes, fibers of certain resins may be preferred to provide resistance to attack by acids or alkalies that may be present and be filtered. Thus, polymers containing a high percentage of acrylonitrile or of vinyl chloride or even of such highly halogenated resins as polytetrafluoroethylene or polychlorotrifluoroethylene may be more useful in such cases. For certain purposes, it may be desirable to form the fibrous products from a mixture of flbers of different types. An example is the use of a mixture of thermoplastic fibers of potentially adhesive character with other fibers which lack such potentially adhesive character. A fibrous product comprising such a mixture may be heated to the appropriate temperature to render the potentially adhesive fibers tacky to effect binding of the fibers in the product by this procedure as well as by the binders of the present invention.

The binder of the present invention is applied in the form of an aqueous dispersion which may be produced by the emulsion polymerization of monomers containing amino groups, preferably with other monomerically unsaturated or monomerically saturated comonomers. The comonomers may be selected to provide various properties in the binder. Thus, they may provide a soft and flexible binder or they may provide a hard and stiff binder which imparts corresponding stiffness to the bonded fibrous product. Surprisingly, dispersions of copolymers having Ti values of 30° C. and over can be effectively applied to form coherent bonded "non-woven" fabrics, even though these dispersions ordinarily do not form continuous films.
when applied to textile fabrics and dried at temperatures above their respective $T_i$ values. Useful monomers which tend to yield soft and flexible polymers when copolymerized with one of the amino monomers mentioned above are those which yield solid polymers which have a $T_i$ below 15° to 20° C. The $T_i$ value referred to is the transition temperature or inflection temperature which is found by plotting the modulus of rigidity against temperature. A convenient method for determining modulus of rigidity and transition temperature is described by J. Williamson, Brit. Plastics 23, 87-90, 102 (September, 1950). The $T_i$ value here used is that determined at 300 kg./cm.$^2$.

The polymerizable, neutral, monomers which form soft, solid polymers in the presence of free radical catalysts include any primary and secondary alkyl acrylate, even with alkyl substituents up to eighteen or more carbon atoms, primary or secondary alkyl methacrylates with alkyl substituents of five to eighteen or more carbon atoms, or other monovinylidene compounds as defined above which are polymerizable with free radical catalysts to form soft solid polymers, including vinyl esters of saturated monocarboxylic esters of two or three carbon atoms. The preferred monovinylidene compounds are the stated acrylates and methacrylates and of these the most practical esters are those with alkyl groups of not over 12 carbon atoms.

The preferred monomers which by themselves yield soft polymers may be summarized by the formula

$$\text{CH}_2=\text{C}-\text{OOOR}^\prime \quad \text{CH}_2=\text{C}-\text{OOOR}$$

where $R'$ is hydrogen or the methyl group and $R^\prime$ represents, when $R'$ is methyl, a primary or secondary alkyl group of 5 to 18 carbon atoms, or, when $R'$ is hydrogen, an alkyl group of not over 18 carbon atoms, or better, of two to 12 carbon atoms. They are esters of acrylic or methacrylic acid which acids may be represented by the formula

$$\text{CH}_2=\text{C}-\text{OOOR}^\prime \quad \text{CH}_2=\text{C}$$

wherein $n$ is an integer having a value of 1 to 2.

Typical compounds coming within the above definition are methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, sec-butyl acrylate, amyl acrylate, isoamyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, 3,5,5-trimethylhexyl acrylate, decyl acrylate, dodecyl acrylate, cetyl acrylate, octadecyl acrylate, isooctyl acrylate, n-amyl methacrylate, sec-amyl methacrylate, hexyl methacrylate, 2-ethylbutyl methacrylate, octyl methacrylate, 3,5,5-trimethylhexyl methacrylate, decyl methacrylate, dodecyl methacrylate, octadecyl methacrylate, and butoxyethyl acrylate or methacrylate.

As polymerizable monovinylidene monomers, which by themselves form hard polymers, there may be used alkyl methacrylates having alkyl groups of not over four carbon atoms, also tert-amyl methacrylate, tert-butyl or tert-amyl acrylate, cyclohexyl or benzyl acrylate or methacrylate, acrylonitrile, or methacrylonitrile, these constituting a preferred group of the compounds forming hard polymers. Styrene, vinyl chloride, chlorostyrene, vinyl acetate and p-methylstyrene also form hard polymers.

Preferred monomers, which by themselves form hard polymers, may be summarized by the formula

$$\text{CH}_2=\text{C}-\text{X} \quad \text{CH}_2=\text{C}-\text{X}$$

wherein $R'$ is hydrogen or the methyl group and wherein $X$ represents one of the groups $-$CN, phenyl, methyl, phenyl, and ester-forming groups $-$COOR, wherein $R'$ is cyclohexyl or, when $R'$ is hydrogen, a tert-alkyl group of four to five carbon atoms, or, when $R'$ is methyl, an alkyl group of one to four carbon atoms. Some typical examples of these have already been named. Other specific compounds are methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, sec-butyl methacrylate, and tert-butyl methacrylate. Acrylamide and methacrylamide may also be used as hardening components of the copolymers.

It is frequently desirable to copolymerize the amino-containing monomer with a mixture of two or more different comonomers, one or more of which are selected from the hard category just mentioned and another of which is selected from the soft category. An example of this would be a copolymer of 8% to 55% ethyl acrylate, 44% to 90% of methyl methacrylate and from about 3% to about 6% of dimethylaminooethyl methacrylate.

The polymers used as binders of the present invention may also be graft or block copolymers wherein one or more, but not all, of the monomers are first polymerized and then one or more of the other monomers are copolymerized with the first polymer obtained. Thus, an amino-containing monomer may first be homopolymerized or copolymerized with one or more, but less than all, of the comonomers to be introduced into the ultimate copolymer, and then the last monomer or monomers are added to the system and copolymerized. Then a single or a mixture of the first homopolymer or copolymer formed. The same procedure may be used in reverse order to graft the amino-containing units on to a previously formed homopolymer or copolymer of other monomeric units. Again, a plurality of monomeric units may be introduced in succession and the amino-group-containing monomer may be introduced at the beginning, at any intermediate stage or at the end as desired.

For certain purposes, the copolymers of the present invention having a $T_i$ of about 30° C. or lower may be preferred. These set on drying at room temperature to bind the fibers with a soft flexible binder bridging the fibers at their points of intersection or intercrossing with a firm grip. Their flexibility adapts the fibrous product to be readily conformed to shaped contours which may be of value in cases where an insulating product or mat is desired to be bent into the shape of a structure to be covered therewith as in the wrapping of a pipe or cylindrical vessel. Such wrapping can be effected without extensive rupture of the bonds between the fibers and without excessive compacting of the mat, which thereby largely retains its bulky character with numerous small air-spaces and high heat-insulating value and is subsequently rendered permanent by the baking operation. However, for certain purposes, it is preferred to use dispersions of copolymers having a $T_i$ of 35° C. or higher, such as from 35° to 100° C. In order to effect optimum bonding of the fibers with such a dispersion, it is necessary that the drying be effected at temperatures above the $T_i$ temperature of the particular copolymer. At lower temperatures, the polymer dispersions in particular form in which the particles are of the order of size of the dispersed resin particles in the aqueous dispersion whereby effective bonding is obtained only where the small particles are lodged within or close between the intercrossed fibers. The other particles serve to modify the hand of the web or mat but do not contribute appreciably to the cohesion of the web. By drying the treated fibrous product at temperatures above the $T_i$ value, fusion or coalescence occurs giving rise to substantial masses adequate in size to bind the fibers at their intersections even when the fibers are separated by relatively large spaces as compared to the size of the original polymer particles in the dispersion. The peculiar advantage of the use of dispersions of polymers, having the elevated $T_i$ value of at least about 35° C., is that in the operation of applying the dispersion to the fibrous mass, as by spraying, any excess that is deposited on the walls of the
spraying chamber dries at the prevailing room temperature below 35° C. to discrete particles or a powder which is readily removed from the equipment merely by brushing. To take advantage of this property, care is taken to avoid any substantial elevation of the temperature in the application equipment, such as the spraying equipment or chamber, appreciably above room temperature in cases where the T\textsubscript{g} value of the copolymer is in the neighborhood of 35° C. Of course, when higher T\textsubscript{g} values of 55° to 100° C. characterize the polymer, considerable elevation of the temperature in the spraying equipment may be present without encountering coalescence in the excess material deposited in the walls of the equipment, provided the temperature surrounding such equipment does not approach too closely (say within 10° C.) the temperature of the T\textsubscript{g} value of the particular polymer involved.

In the preparation of bonded fibrous products of the present invention, which are intended to serve as preforms in the making of molded products, the use of polymers having higher T\textsubscript{g} values also has the advantage that the preform is much stiffer in character and encounters less risk of disturbance of the fibers during the handling of the preform in preparing it for the molding operation per se.

The dispersions adapted to be used as the binder-applying medium of the present invention are most advantageously prepared by emulsifying with a dispersing agent and polymerizing preferably under the influence of a free radical catalyst, an amino monomer or a mixture of the monomers of which at least 3 percent is one of the amino-containing monomers above.

Anionic, cationic, and non-ionic emulsifiers or dispersing agents may be used. Less advantageously, water-insoluble polymers comprising at least 3% of amino-containing monomeric units produced in any other way may be dispersed in water by means of suitable dispersing agents.

The dispersions may contain as little as 1% and as much as 60% of the resinous copolymer on a weight basis. It is, however, more practical—hence preferred—to produce dispersions which contain about 30% to 50% resin-solids. Generally, the dispersion is diluted to 1% to 35%, and preferably 2% to 30%, resin content at which it is readily adaptable to be applied as by spraying, dip-coating, or by transfer rolls.

The binder dispersion may be applied to the dry fibers after the formation or deposition of the web or mat so as to penetrate partially into or completely through the interior of the fibrous product. Alternatively, the binder dispersion may be applied to the fibers as they fall through the settling chamber to their point of deposition. This is advantageously obtained by spraying the binder dispersion into the settling chamber at some intermediate point between the top and the bottom thereof. By so spraying the fibers as they descend to the point of collection, it is possible to effect a thorough distribution of the binder among the fibers before they are collected into the product. In the production of certain fibrous products wherein a hot molten mass of a polymer, such as nylon or a fused siliceous mass or glass, is disrupted by jets of heated air or steam, the binder dispersion may be sprayed directly on the fibers while still hot and very shortly before their deposition so that quickly after deposition the binder is set and bonds the fibers in proper relationship. Preferably, however, application of the binder dispersion to the fibrous product is made at room temperature to facilitate cleaning of the apparatus associated with the application of the binder dispersion. The binder dispersion may be applied to one or both surfaces of the fibrous product or it may be distributed through the interior as well. While the binder may be applied in powdered form in each of the situations just mentioned, in all cases application of the aqueous dispersion is preferred.

While chemical reaction probably occurs between the binders of the present invention and fibers, such as those of cellulosic type, which contain reactivity groups, it is intended that the invention should be limited to this theory operation. The binder of the present invention may be applied in conjunction with other binders. For example, another type of binder, such as glue or resin-forming condensates, especially aminoplasts such as urea-formaldehyde melamine-formaldehyde and the like, may be applied either to the interior or to the external surfaces of the fibrous product while the binder of the present invention is applied to the external surfaces or to the interior of such products. Similarly, the use of potentially adhesive fibers within the fibrous product may also be resorted to in conjunction with the use of a binder of the present invention. The aqueous polymer dispersion may also contain dissolved therein a water-soluble thermostetting condensation product, especially the aminoplasts, namely the low molecular weight or monomeric reaction products of an aldehyde, and especially formaldehyde with urea, thiourea, triurea, or other homologues or derivatives thereof, such as aldehydeurea, N,N'-dimethylurea, N,N'-diethyurea, N,N'-diethylyurea, N,N'-dimethoxymethylurea, N,N'-dimethoxyethyurea, tetramethoxyurea, tetramethyloxymethylurea, tetraethoxyurea, etc. Similar condensation products of formaldehyde with triazines, such as melamine, may also be employed, such as dimethylol-N,N-dimethylmelamine and alcohol-modified melamine-formaldehyde thermosetting resin condensates, e.g. of methyl and ethyl alcohols, for example, dimethoxymethyl-monomethylmelamine.

The use of an auxiliary aminoplast with the amino-containing polymers of the present invention serves to modify the hand, and frequently increases the strength and resistance to creasing, wrinkling, and crushing. The auxiliary aminoplast binder may be used in an amount up to 25% by weight of the weight of polymer containing amino groups, 2% to 11% being preferably employed when the combination binder system is used.

Whether or not an aminoplast binder is used in conjunction with the polymer containing amino groups, there may be introduced into the system either into the aqueous dispersion of the polymer or by separate application to the non-woven fibrous mat or web before or after application of the aqueous dispersion of the polymer, a catalyst for accelerating the curing of the binder through the amino groups. The catalyst may be used in an amount up to 2%, preferably about ½ to 1% on the weight of the polymer. The catalyst used may be selected to avoid excessive deterioration of the fibers used in the particular fibrous product, but it is in any case an acidic or potentially acidic material, the latter serving as a latent catalyst and liberating acid on heating. For example, when cellulosic fibers are employed, a latent ammonium salt, such as ammonium chloride or diammonium phosphate or a latent amine hydrochloride salt, may be employed such as the hydrochloride of triethanolamime, monoethanolamine, diethylenamine and so on. The same catalyst may act as the catalyst for the aminoplast, if such is used.

If desired, the aqueous dispersion of the polymer containing amino units may also contain a wetting agent to assist penetration of the fibrous web or mat to which it is applied, and it may contain either a foaming agent to provide the binder in a foamed condition in the final product or it may contain a defoamer when the ingredients of the aqueous dispersion have a tendency to rise to foaming, and in a particular case such foaming is undesirable. The conventional wetting agents, such as the sodium salt or dioctylsulfosuccinate may be used and the conventional foaming and defoaming agents may be employed, such as sodium soaps, including sodium oleate for foaming and octyl alcohol or certain silicones for defoaming.
Generally, the proportion of the binder of the present invention to the weight of the fiber component of the fibrous product may vary widely depending on the character of the product desired. For the production of preforms, intended to be converted into molded articles, it is preferred to employ from 2 to 10% of the binder of the present invention based on the weight of fibers. In the production of insulation masses, the amount of binder employed may fall in the lower part of the range just specified if the binder is applied primarily adjacent to the surface or surfaces of the product or if it is applied in conjunction with other binders. The aqueous dispersion of the polymer containing the amino groups is generally applied at a concentration of 2 to 50% solids and preferably at a concentration of 20 to 40% binder solids by weight.

The fibrous product of non-woven character may contain from 2 to 400% by weight of binder on the weight of the fibers depending on the purpose for which the product is to be used. When the binder is to serve mainly to bond the fibers together to form a coherent unitary structure in which the maximum porosity is retained in conjunction with a minimum change of natural fiber hand, there may be employed from 2 to 50% by weight of binder solids on fiber, the lower proportion of binder being particularly advantageous in providing a minimum change in the natural fiber hand although even with the larger proportion in this range, the porosity is mainly retained and the fiber hand is still evident. The products thus obtained are quite useful for many sanitary uses such as table napkins, bibs, table cloths, sanitary napkin covers, disposable diapers, disposable sheets, and surgical dressing and compresses. It is characteristic of the binder applied in the proportions just stated that there is relatively little or no "window paning," that is, the interstices between fibers is left open leaving a highly porous bulk product. Of course, the density of the product can be affected or modified by the application of pressure to varying extents prior to or, in many cases, even after the curing of the product.

Fibrous products of non-woven character using from 40 to 150% by weight of the binder of the present invention on the weight of the fibers are generally quite useful for garment uses to provide interlining fabrics for coats, dresses, and so on, or to provide outer wearing apparel fabrics, such as blouses, skirts, shirts, etc. The garments made of these fabrics need no ironing or pressing to restore their appearance, shape, and hand after hand-washing, machine-laundering and dry-cleaning operations. Because the general household and apparel uses mentioned above, fibrous products of the invention, in which 2 to 100% by weight of binder on the weight of fiber is employed, find many light industrial uses as wiping cloths, lining materials for packaging as filters, and packings and gaskets for industrial machinery.

Fibrous products of the present invention, in which 100 to 400% by weight of binder on the weight of fiber is used, are especially useful for heavy industrial uses where durability and resistance to wear are desired, such as in industrial gaskets, packings, filters, and so on. The products containing 20 to 200% of the binder of the present invention on the weight of the fiber are useful as laminating layers, either as interlayers or backing sheets in conjunction with plastic films and sheets as of polyethylene, nylon, and so on, or in conjunction with textile fabrics of woven, braided, knitted, twisted, or felted character.

It is essential that the drying of the treated fibrous product, that is the fibrous product carrying the binder dispersion, be effected at a temperature above the T<sub>c</sub> of the binder. This polymer in order to effect proper coalescence and bonding of the binder it is necessary to activate it if the T<sub>c</sub> of the copolymer is about 30° C. or lower, no special heating is necessary to effect bonding, but it may be advantageous to accelerate the drying of the binder to the set condition. To render the binder infusible, curing at elevated temperatures is effected. Curing temperatures may be as high as 400° C. for setting the binder, but preferably are in the range from about 110° C. to 350° C. The curing serves to render the binder insoluble and infusible and, as stated hereinafter, may be assisted by the use of an acidic catalyst.

As pointed out herebefore, the application of the polymer containing amino groups is adapted to provide fibrous products having a wide range of characteristics. When the binder is present in an amount of about 2 to 50% on the weight of the fibers in the fibrous product, the latter retains a textile hand and can have either a soft or a stiff texture depending on the proportion of amino groups in the polymer and the characteristics of any comonomers used in making it. Using polymers containing 3 to 20% of units containing amino groups in conjunction with such comonomers as result in providing a T<sub>c</sub> value of the copolymer of 20° C. or less and preferably not over 5° C., a soft resilient texture is obtained in conjunction with a textile feel or hand and the cured product is quite resistant to laundering, dry-cleaning and spotting to various chemicals and heat. In all of the fibrous products previously mentioned, where the binder may be present in the proportion of 2 to 50% as in the non-woven products, the amino acid proportions up to 400% on the weight of the fiber, the products are characterized by freedom from discoloration and excellent resistance to ultraviolet light, to laundering, to dry-cleaning and spotting, to various chemicals, and heat as in ironing, and durability of any embossed pattern. They are also characterized by good adhesion of the binder to the fibers.

The binder of the present invention may be made in essentially colorless form and has the advantage that, when so made, it undergoes no discoloration at the elevated temperature needed for the drying or baking of the fibrous products or even for the formation of molded articles with the fibrous products of the present invention used as preforms and ultimately occurring as a reinforcing component in the molded article. The binder of the present invention is resistant to flow at elevated temperatures so that a thermoplastic or thermosetting resin can be applied and the composite thereby obtained can be molded at elevated temperature without appreciably disturbing the disposition of fibers in the mass. Similarly, the binder is insoluble in water and organic solvents so that the presence of such materials during subsequent treatments cannot disturb the disposition of the fibers. Consequently, there is no "washing" Here in the preform with accompanying tendency to form resin-rich areas and fiber-rich areas in the molded article giving rise to such non-uniformity which tends to cause cracking or crazing in the molded articles and resulting weakness in the reinforced structure.

All of these properties render the binder outstandingly valuable in connection with siliceous fibers, such as those of glass or mineral wool, in the production of preforms adapted to be used for forming molded articles. The siliceous fibers are strongly bonded together by means of the binders of the present invention and especially those having a T<sub>c</sub> temperature above 35° C. and yet the binder is of such character as not to prevent proper integration of the siliceous fibers within the mass of molding resin. In the molded products, the presence of the binder has no adverse effect either on the appearance or the strength of the final articles. While siliceous resins or resin-forming materials of numerous thermoplastic and thermosetting types may be employed, the use of thermosetting types of polymers is particularly advantageous. Such a resin-forming material may comprise an unsaturated polyester resin, or a polyester of mixed maleic acid and phthalic acid (in a 50:50 ratio) with a glycol, such as propylene glycol, dissolved in styrene or other copolymerizable monothetically un-
saturated monomers having solvent properties for the low condensed polyester. Most binders heretofore used in the preforms become discolored during the molding operation and interfere with the penetration of the molding resin, especially when it is of a polyester type, so that the fused resin is poorly bonded to the portions of the fibers coated by the binder which in turn is manifested by a reduced transparency and corresponding lack of continuity and homogeneity. The binder of the present invention is resistant to such discoloration. In addition, it does not interfere with the penetration of the resin-forming material to the fibers of the preform during the molding operation. This provides excellent transparency and a high degree of homogeneity and continuity in the product. Also, the binders of the present invention having the higher Ti values and accompanying higher stiffness assure the maintenance of the distribution of the fibers during the handling of the preform up to the molding operation.

The fibrous products of the present invention are capable of numerous uses, many of which have been mentioned above. Thus, the fibrous mats bonded with the improved binders of the present invention may serve as heat or sound insulation materials, as filters for air systems or liquid systems, as permeable membranes as in storage batteries or electrolytic condensers, as cushioning or padding materials for upholstering purposes and so forth.

As pointed out hereinafter, fibrous mats or fabrics of siliceous fibers are extremely valuable as reinforcements for molded products using the bonded fibrous mat or fabric as a preform with appropriate molding powders or syrups. For example, the bonded mat or the bonded laminar fabric assembly may be introduced into a closed mold system with an appropriate amount of a thermosetting resin powder or liquid, such as of thermosetting condensates of urea-formaldehyde, melamine-formaldehyde, phenol-formaldehyde or polyesters, such as those described in U.S. Patents 2,255,313 and 2,607,756. From 5 to 45% by weight of the molded article may be composed of the reinforcing fiber network when a mat is used as the preform or, in the case of a fabric reinforcement, from 5 to 65% by weight of the molded product may consist of the composite of bonded fabric laminations.

Instead of using a thermosetting resin-forming material as the molding resin, there may be used thermoplastic types of resins such as the vinyl or acrylic types of resins. For example, polymers and copolymers of vinyl acetate, vinyl chloride, acrylonitrile, styrene, acrylic and methacrylic acid esters; e.g. the methyl, ethyl, propyl, or butyl esters thereof, and so on. Advantageously, a polymer or copolymer may be dissolved in its corresponding monomer or mixture of monomers to provide a solution that may readily be introduced into the mold.

The following examples are illustrative of the fibrous products and the methods for making them in accordance with the present invention and parts and percentages are by weight unless otherwise indicated.

**Example A**

A dispersion of a copolymer was prepared by emulsifying 95 parts by weight of n-butyl acrylate with 5 parts by weight of 2-aminoethoxy vinyl ether in about 300 parts by weight of water with about 6 parts by weight of an ethylene oxide condensation product of an octyl phenol containing between 30 and 50 oxyethylene units per molecule. To the emulsified monomers 0.3% by weight of ammonium persulfate, 0.06% by weight of sodium hydrosulfite, and 1% triethanolamine were added to catalyze the copolymerization which was carried out for a period of about fifteen minutes during which the temperature rose from 20°C to 45°C.

**Example B**

A dispersion of a copolymer is prepared by emulsifying 80 parts by weight of ethyl acrylate with 15 parts of butyl acrylate and 5 parts of 4-vinylpyridine in about 300 parts by weight of water with about 2 parts by weight of sodium lauryl sulfate and 6 parts by weight of an ethylene oxide condensation product of an octyl phenol containing between 30 and 50 oxyethylene units per molecule. To the emulsified monomers 0.5% by weight of ammonium persulfate, 0.06% by weight of sodium hydrosulfite, and 1% triethanolamine are added to catalyze the copolymerization which is carried out for a period of about fifteen minutes during which the temperature rises from 20°C to 45°C.

**Example 1**

(a) A 75/25 viscose (3 denier, 1 inch staple)/bleached cotton (middling, 25½ inch) carded web weighing about 0.75 ounce/square yard is impregnated with an aqueous dispersion containing per 100 parts:

- 25.0 parts of β-aminoethyl vinyl ether/butyl acrylate (5/95 by weight) emulsion copolymer.
- 2 parts of t-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent).
- 0.4 part of octylphenoxysulfosodium sulfate (wetting agent).
- 0.01 part silicone antifoam.

at a wet pick-up of about 600% on the weight of the fibers. The web is dried 1.5 minutes at 225°F, and cured 1.5 minutes at 350°F. The resulting non-woven fabric is about 40/60 fiber/binder weight ratio. It is highly porous and has a soft and resilient feel.

(b) The procedure of part (a) is repeated with Pyrex glass fibers, except that the carded web weighs ½ ounce per square yard and impregnation with the aqueous dispersion is effected at a wet pick-up of 300%, giving a weight ratio of 53/47 fiber to binder in the final fabric which is extremely porous and soft yet coherent.

**Example 2**

The procedure of Example 1(a) is repeated using a similar aqueous dispersion having the same concentration of copolymer but the copolymer therein is a copolymer of 5% by weight of β-morpholinoethyl methacrylate, 80% by weight of ethyl acrylate, and 15% by weight of n-butyl acrylate. A porous, soft and coherent non-woven web of outstanding whiteness is obtained quite similar to that of Example 1(a).

**Example 3**

(a) The procedure of Example 1(a) is repeated using a similar aqueous dispersion having the same concentration of copolymer but the copolymer therein is a copolymer of 10% by weight of n-butyl acrylate grafted by subsequent copolymerization on to 90% by weight of a previously homopolymerized 4-(β-acryloyoxethyl)pyridine.

(b) Good products are obtained when a simple emulsion copolymer of 95% n-butyl acrylate and 5% of 4-(β-acryloyoxethyl)pyridine is used in the same way.

**Example 4**

(a) The procedure of Example 1(a) is repeated using a similar aqueous dispersion having the same concentration of copolymer but the copolymer therein is a copolymer of 90% by weight of n-butyl acrylate and 10% by weight of β-(N-methylamino)ethyl vinyl ether. Similar products are obtained.

(b) Similar results are obtained when a simple emulsion copolymer of 95% by weight of n-butyl acrylate and 5% of 4-vinylpyridine or when the emulsion copolymer of Example A is used in the same way.
Example 5

The procedure of Example 1(a) is repeated using a similar aqueous dispersion having the same concentration of copolymer but the copolymer therein is a copolymer of about 14% by weight of \(\beta\)-(N-methyl-N-(\beta\-hydroxyethyl)amino)ethyl acrylate, 60% by weight of ethyl acrylate, and about 26% by weight of methyl methacrylate. Soft, coherent, solvent- and wash-resistant fabrics are obtained.

Example 6

The procedure of Example 1(a) is repeated using a similar aqueous dispersion having the same concentration of copolymer but the copolymer therein is a copolymer of 5% by weight of \(n\)-butyl acrylate and 5% by weight of the monovinyl ether of \(N\)-methylthiethanolamine. The products are highly resistant to alkaline wash liquors.

Example 7

(a) An all viscose (5 denier, 1.25 inch staple) carded web weighing about 2 ounces/square yard is printed in a design consisting of a plurality of spaced rings with an aqueous dispersion containing per 100 parts:

- 25.0 parts of \(\beta\)-pyrrolidinomethyl methacrylate/butyl acrylate/ethyl acrylate (10/20/70 by weight) emulsion copolymer
- 2 parts of \(t\)-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent).
- Sufficient methyl cellulose to give a Brookfield viscosity of about 2000 cps. at 75° F., with a No. 3 spindle at 30 r.p.m.

The web is dried one minute at 240° F., and cured two minutes at 300° F. The resultant non-woven fabric contains about 80/20, fiber/binder. The web is rendered coherent by the bonded annull and is porous throughout.

Example 8

A 50/50 white nylon/disperse-dyed bright acetate (both fibers 3 denier, 1.5 inch staple) random web obtained by air-deposition weighing about 1.5 oz./sq. yd. is impregnated with an aqueous dispersion containing per 100 parts:

- 27.0 parts of 5-aminopentyl vinyl ether/butyl acrylate, 20/80.
- 2 parts of \(t\)-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent).
- 3.0 parts of (dimethylol-N,N'-ethyleneurea).
- 0.5 part of ammonium chloride.
- 0.5 part of octylphenoxethoxysodiumsulfate (wetting agent).
- 0.01 part of silicone antifoam.

at about 300% wet pick-up. The web is dried 1.5 minutes at 225° F., cured six minutes at 350° F. Resultant non-woven fabrics is ca. 55/45, fiber/binder. It is quite porous and has an essentially textile hand. After washing and drying, no ironing or pressing is needed to restore the shape, appearance, or hand of garments made of the fabric.

Example 9

A 50/50 white viscose/dyed Acrilan (polymer or about 85% to 90% acrylonitrile) (both fibers 3 denier, 1.5 inch staple) random web obtained by air-deposition weighing about 1.75 oz./sq. yd. is impregnated with an aqueous dispersion containing per 100 parts:

- 27 parts of 95/5, butyl acrylate/2-vinylthioethylamine.
- 2 parts of \(t\)-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent).
- 3.0 parts of urea/formaldehyde/methanol condensate.
- 0.5 part of diammonium phosphate.
- 0.5 part of octylphenoxethoxysodiumsulfate (wetting agent).
- 0.02 part of silicons antifoam.

at ca. 300% wet pick-up. Dried 1.5 min. at 225° F., cured 5 min. at 350° F. Product: 55/45, fiber/binder; good coherence, porous, soft, textile hand.

Example 10

A 55/45 nylon/viscose (both fibers 5 denier, 1.75 inch staple) random web obtained by air-deposition is impregnated with an aqueous dispersion containing per 100 parts:

- 24.0 parts of N-methyl-N-2-(vinylthio)ethyamine/ethyl acrylate, 10/90.
- 2 parts of \(t\)-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent).
- 6.0 parts of urea-formaldehyde/methanol condensate.
- 0.5 part of octylphenoxethoxysodiumsulfate (wetting agent).
- 0.02 part of silicone antifoam.

at ca. 400% wet pick-up. Dried one min. at 240° F., cured five minutes at 300° F. Product: 45/55 fiber/binder; soft, resilient, resistant to laundering and dry-cleaning.

Example 11

An all cotton (garnetted card waste, roving and yarns) carded web weighing about 4 oz./sq. yd. is impregnated with an aqueous dispersion containing per 100 parts:

- 20.0 parts of \(N\)-\(\beta\)-ethoxyethyl-\(N\)-\(\beta\)-vinylxethoxyethyamine/ethyl acrylate, 80/20.
- 1.0 part of octylphenoxethoxysodiumsulfate (wetting agent).
- 2 parts of \(t\)-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent).
- 0.5 part silicone antifoam.

at ca. 200% wet pick-up. Dried five min. 240° F., cured five min. at 300° F. Product: 70/30, fiber/binder; good coherence, porous, soft, textile hand.

Example 12

In all nylon (50% 10-denier, 50% 3-denier, all 1.5 inch staple) random web obtained by air-deposition weighing about 1.25 oz./sq. yd. is impregnated with an aqueous dispersion containing per 100 parts:

- 35.0 parts 2-aminomethyl vinyl sulfoide.
- 2 parts of \(t\)-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent).
- 3.5 parts of urea/formaldehyde/methanol condensate.
- 0.5 part diethanolamine hydrochloride.
- 0.5 part octylphenoxethoxysodiumsulfate (wetting agent).
- 0.2 part silicone antifoam.

at ca. 200% wet pick-up. Dried 1.5 min. 225° F., cured three minutes at 350° F. Product: 55/45, fiber/binder; soft, resilient, resistant to laundering and dry-cleaning.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. As an article of manufacture, a non-woven fibrous product in which the fibers are distributed in random array, the fibers of which are predominantly fibers selected from the group consisting of cellulose fibers, polyamide fibers, vinyl resin fibers, and polyester fibers, fibers in the product being bonded together by a binder comprising (1) a water-soluble aminoplast and (2) a water-insoluble copolymer, having a molecular weight from 100,000 to ten million and a \(T_g\) value not over 30° C., of 3 to 20% by weight of a monoethylenically unsaturated monomer containing an amino group with 97 to 80% by
weight respectively of at least one ester of an alcohol having 1 to 18 carbon atoms with an acid of the formula

\[ \text{CH}_2\text{C}(\text{R})\text{O}=-\text{H} \]

where \( n \) is an integer having a value of 1 to 2, the amount of said aminoplast being from 2 to 25% by weight of the copolymer, said binder being cross-linked to an infusible condition in which it is also insoluble in organic solvents, the amount of binder being from 2 to 400% of the weight of fibers in the product, said product being substantially resistant to laundering and dry-cleaning.

2. A process of making a non-woven fabric which comprises associating, in random array within a web or mat, fibers selected from the group consisting of cellulosic fibers, polyamide fibers, vinyl resin fibers, and polyester fibers, bringing into contact with the fibers a binder comprising an aqueous dispersion containing (1) a water-soluble aminoplast and (2) 2 to 60% by weight of a water-insoluble copolymer, having a molecular weight from 100,000 to ten million and a \( T_1 \) value not over 30°C, of 3 to 20% by weight of a monoethylenically unsaturated monomer containing an amino group with 97 to 80% by weight respectively of at least one ester of an alcohol having 1 to 18 carbon atoms with an acid of the formula

\[ \text{CH}_2\text{C}(\text{R})\text{O}=-\text{H} \]

where \( n \) is an integer having a value of 1 to 2, the amount of aminoplast being from 2 to 25% by weight of the copolymer, the drying the fibrous mass containing the binder at a temperature above the \( T_1 \) of the polymer to effect fusion of the polymer and bonding of the fibers thereby, and heating the dried fibrous product at a temperature of 110°C to 350°C to render the binder insoluble in organic solvents.

3. A process of making a non-woven fabric which comprises associating, in random array within a web or mat, a mass of fibers comprising a predominant proportion of fibers selected from the group consisting of cellulosic fibers, polyamide fibers, vinyl resin fibers, and polyester fibers, bringing into contact with the fibers a binder comprising an aqueous dispersion containing (1) a water-soluble aminoplast and (2) 2 to 60% by weight of a water-insoluble copolymer, having a molecular weight from 100,000 to ten million and a \( T_1 \) value not over 30°C, of 97 to 80% by weight of at least one ester of an alcohol having 1 to 18 carbon atoms and an acid selected from the group consisting of acrylic acid and methacrylic acid with 3 to 20% by weight of a compound selected from the group consisting of those having one of the Formulas I and II following, the amount of aminoplast being from 2 to 25% by weight of the copolymer, drying the fibrous mass containing the binder at a temperature above the \( T_1 \) of the polymer to effect fusion of the polymer and bonding of the fibers thereby, and heating the dried fibrous product at a temperature of 110°C to 350°C to render the binder insoluble in organic solvents, Formulas I and II being:

\[ \text{CH}_2\text{C}(\text{R})\text{O}=-\text{H} \]

where:

- \( R \) is selected from the group consisting of \( \text{H} \) and \( \text{CH}_3 \)
- \( A \) is selected from the group consisting of \(-\text{O}=-\)
- \(-\text{O}=-\)
- \(-\text{O}=-\)
- \(-\text{O}=-\)

in which \( R^2 \) is selected from the group consisting of \( \text{H} \) and saturated aliphatic hydrocarbon groups having 1 to 12 carbon atoms,
where: $R^g$ is an alkylene group having 2 to 10 carbon atoms of which at least two extend in a chain between the N and O atoms, $R'$ is an alkyl group having 1 to 2 carbon atoms, and $R''$ is an alkyl group having 1 to 2 carbon atoms,
the amount of said aminoplast being from 2 to 25% by weight of the copolymer, said binder being cross-linked to an insusceptible condition in which it is also insoluble in organic solvents, the amount of binder being from 2 to 400% of the weight of fibers in the product, said product being substantially resistant to laundering and dry-cleaning.

6. As an article of manufacture, a non-woven fibrous product in which the fibers are distributed in random array, the fibers of which are predominantly fibers selected from the group consisting of cellulose fibers, polyamide fibers, vinyl resin fibers, and polyester fibers, fibers in the product being bonded together by a binder comprising (1) a water-soluble aminoplast and (2) a water-insoluble copolymer, having a molecular weight from 100,000 to ten million and a $T_1$ value not over 30° C., of copolymerizable monologically unsaturated molecules comprising 3 to 20% by weight of a monomer of the formula

$$H_2C\equiv CR\equiv N \quad \text{where:} \quad R^g \text{is an alkylene group having 2 to 10 carbon atoms of which at least two extend in a chain between the N and O atoms,}$$

where: $n$ is an integer having a value of 1 to 2, $R^g$ is an alkylene group having 2 to 10 carbon atoms of which at least two extend in a chain between the N and O atoms, $R'$ is an alkyl group having 1 to 2 carbon atoms, and $R''$ is an alkyl group having 1 to 2 carbon atoms,
the amount of said aminoplast being from 2 to 25% by weight of the copolymer, said binder being cross-linked to an insusceptible condition in which it is also insoluble in organic solvents, the amount of binder being from 2 to 400% of the weight of fibers in the product, said product being substantially resistant to laundering and dry-cleaning.

7. As an article of manufacture, a non-woven fibrous product in which the fibers are distributed in random array, the fibers of which are predominantly fibers selected from the group consisting of cellulose fibers, polyamide fibers, vinyl resin fibers, and polyester fibers, fibers in the product being bonded together by a binder comprising (1) a water-soluble aminoplast and (2) a water-insoluble copolymer, having a molecular weight from 100,000 to ten million and a $T_1$ value not over 30° C., of copolymerizable monologically unsaturated molecules comprising 3 to 20% by weight of a monomer of the formula

$$H_2C\equiv CR\equiv N \quad \text{where:} \quad R^g \text{is an alkylene group having 2 to 10 carbon atoms of which at least two extend in a chain between the N and O atoms,}$$

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