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METHODS FOR MAKING BONDED NON-WOVEN FIBROUS PRODUCTS AND THE PRODUCTS OBTAINED

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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 useful in the production of articles of either flat or three-dimensional shape, such as insulating material and the like as will be described more particularly hereinafter. This application is a continuation-in-part of our copending application Serial No. 603,833, filed August 13, 1956, now abandoned.

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 that 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 be the result of a complete suppression of the fibrous character insofar as the feel of the product is concerned. When binders of polyvinyl acetates, 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 simple esters 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 resin fibers, cellulose esters and such polyesters 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 the fibrous products during drying of the products to which the dispersions have been applied.

United States Patent 2,823,142 discloses the application of soft acrylate addition polymers with certain thermosetting condensates to produce bonded non-woven fabrics which initially have a soft hand and desirable draping quality. However, on dry-cleaning the product, the addition polymer is gradually removed. Consequently

the soft hand and draping quality are both lost and the product, though the fibers thereof are still bonded by the thermosetting condensate, acquires a harsh hand and does not drape in a desirable fashion.

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, whether it consists of an addition polymer alone or of a mixture thereof with a thermosetting resin-forming condensate, is adapted to be converted to an infusible 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, 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 dicyandiamide 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 binder materials 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 dicyandiamide groups by which it is adapted to be insolubilized and rendered infusible on heating with 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 dicyandiamide groups apparently also provide a greater versatility of adhesion in that the binders of the present invention are characterized not only with good adhesion to hydrophilic fibers like cotton, regenerated cellulose rayons and the like, but they are also characterized by excellent adhesion to hydrophobic types of fibers, such as the nylons 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, polyesters such as poly(ethylene glycol terephthalate), and cellulose esters such as cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, and so on. 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 dicyandiamide-containing polymer, thermosetting 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 dicyandiamide-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 molding 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 resisns 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 products is substantially completely prevented even at elevated temperatures during subsequent molding with such products being used as reinforcing inserts or preforms.

In accordance with the present invention, a fibrous product, the fibers of which comprise a predominant proportion or consist entirely of fibers which are incapable of felting, is impregnated with an aqueous dispersion of a water-insoluble linear polymer of monoethylenically unsaturated monomeric units comprising 3 to 50% by weight of at least one monomeric compound having the structure of Formula I:

$$CH_2=C(R)CONHC(=NH)NHCN \qquad (I)$$

where R is selected from the group consisting of hydrogen and methyl.

The molecular weight of the polymers should be from about 100,000 to about 10 million. Generally, water-insoluble copolymer containing units of which from 3 to 20% by weight contain the dicyandiamide groups are most practical. It is preferred to employ copolymers containing from 3% to about 20% of units containing dicyandiamide groups when soft, flexible products are desired. However, polymers containing a larger proportion of units having dicyandimaide groups up to 50% are useful when a relatively stiff product is desired, or when soft products

are desired and the comonomers 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 of Formula I above.

The preperation of aqueous dispersions of polymers of these dicyandiamide monomers is disclosed in United States Patent 2,828,222. The subject matter of this patent which deals with the preparation of aqueous dispersions of homopolymers and copolymers containing at least 3% by weight of an unsaturated dicyandiamide monomer is incorporated herein by reference.

The fibers are present in the form of a so-called "non-woven" mat in which they are haphazardly distributed, or the mat may be formed by carding when the fibers are of such a character, by virtue of length and flexibility, as to be 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 polyvinyl chloride, 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 comonomers 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-terephthalate 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 necesary 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 intervening 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 tower into the upper portion of which the blown fibers are introduced by the conduit work. 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 hatmaking 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 inert gases such as nitrogen or even of steam, is directed against the stream or streams of filament-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 of 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 in the liquids to be filtered. Thus, polymers containing a high percentage of acrylonitrile or of vinyl chloride or even of such highly halogenated resins as polytetrafluoroethylene or poly(chlorotrifluoroethylene) may be more useful in such cases. For certain purposes, it may be desirable to form the fibrous products from a mixture of fibers 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 dicyandiamide groups with other monoethylenically unsaturated 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 T_i values of 50° C. and over can be effectively employed 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 comonomers which tend to yield soft flexible polymers when copolymerized with one of the dicyandiamide 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 I. Williamson, British Plastics 23, 87–90, 102 (September 1950). The T_i value here used is that determined at 300 kg./cm.^{2}.

The polymerizable, neutral comonomers 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 over two 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

$$CH_2=\underset{\displaystyle R'}{\overset{|}{C}}-COOR^x$$

where R′ is hydrogen or the methyl group and R^x 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.

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, octadecenyl 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, acrylamide, methacrylamide, and p-methylstyrene also form hard polymers.

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

$$CH_2=\underset{\displaystyle R'}{\overset{|}{C}}-X$$

wherein R′ is hydrogen or the methyl group and wherein X represents one of the groups —CN, phenyl, methylphenyl, and esterforming 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.

It is frequently desirable to copolymerize the dicyandiamide-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 methacrylyl dicyandiamide.

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 other monomers are copolymerized with the first polymer obtained. Thus, a dicyandiamide-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 or grafted on to the first homopolymer or column formed. The same procedure may be used in reverse order to graft the dicyandiamide-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 dicyandiamide-group-containing monomer may be introduced at the beginning, at any intermediate stage, or at the end, as desired.

The copolymers of the present invention have a T_1 of about 30° C. or lower. 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.

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, a mixture of monomers of which 3 to 50% is one of the dicyandiamide-containing monomers above.

Anionic, cationic, and non-ionic emulsifiers or dispersing agents may be used. Less advantageously, water-insoluble polymers comprising 3 to 50% of dicyandiamide-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 adapted to be applied as by spraying, dipping, printing, or by transfer rolls.

The binder of the present invention in the form of a 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 products. 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 or dusted 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.

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 products. Similarly, the use of potentially adhesive plied 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 dispersion may also contain dissolved therein a water-soluble thermosetting condensation product, especially the aminoplasts, namely the low molecular weight or monomeric reaction products of an aldehyde, and especially formaldehyde with urea, thiourea, biuret, or other homologues or derivatives thereof, such as N,N-ethyleneurea, N,N'-ethyleneurea, N,N'-dimethylurea, N,N'-diethylurea, N,N'-dimethoxymethylurea, N,N-dimethoxymethylurea, N,N'-diethoxyethylurea, tetramethoxymethylurea, tetraethoxyethylurea. Similar reaction products of formaldehyde with triazines, such as melamine may also be employed, such as N,N-dimethylmelamine and alcohol-modified melamine-formaldehyde thermo-setting resin condensates, e.g. of methyl and ethyl alcohols, for example, dimethoxymethyl-monomethylolmelamine.

The use of an auxiliary aminoplast with the dicyandiamide 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 dicyandiamide 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 dicyandiamide 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 dicyandiamide 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 or triethanolamine, monoethanolamine, diethylamine, and so on. The same catalyst may act as the catalyst for the aminoplast, if such is used. It is believed that the binder of the present invention reacts with such fibers as contain reactive groups, such as cellulosic fibers.

If desired, the aqueous dispersion of the polymer containing dicyandiamide 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 give rise to foaming, and in a particular case such foaming is undesirable. The conventional wetting agents, such as the sodium salt of 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. The aqueous dispersion of the polymer containing the dicyandiamide groups is generally applied at a concentration of 2 to 60% solids and preferably at a concentration of 20 to 40% binder solids by weight.

The fibrous product of non-woven character may contain from 20 to 200% 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 20 to 50% by weight of binder solids on fiber, the lower proportion, of course, giving the maximum porosity and 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 dressings 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 bulky product. Of course, the density of the product can be effected 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 fiber 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 drying operations. Besides the general household and apparel uses mentioned above, fibrous products of the invention in which 20 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 200% by weight of the binder on the weight of fiber is used, are specially useful for heavy industrial uses where durability and resistance to wear are desired, such as in industrial gaskets, packings, filters, and so on. Any of 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, knotted, 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_i of the binder copolymer in order to effect proper coalescence and bonding of the fibers. As pointed out above, since the T_i of the copolymer is about 30° C. or lower, no special heating is ordinarily necessary to effect bonding, but it may be advantageous to accelerate the drying of the binder to the set condition. To render the binder insoluble, 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° to 350° C. The curing serves to render the binder insoluble and infusible and, as stated hereinabove, may be assisted by the use of an acidic catalyst.

As pointed out hereinbefore, the application of the polymers containing dicyandiamide groups is adapted to provide fibrous products having a wide range of characteristics. When the binder is present in an amount of about 20 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 dicyandiamide groups in the polymer and the characteristics of any comonomers used in making it. Using polymers containing 3 to 20% of units containing dicyandiamide groups in conjunction with such comonomers as result in providing a T_i 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 20 to 50% as in the products just mentioned or in larger proportions up to 200% on the weight of the fiber, the products are characterized by freedom from discoloration and excellent resistance to ultraviolet light, to laundering (both home laundering and commercial laundering), to dry-cleaning and spotting, including dry-cleaning by means of solvent naphthas, carbon tetrachloride, perchloroethylene, and even by dimethylformamide, 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 is essentially colorless and has the advantage that it undergoes no discoloration at the elevated temperature needed for the drying or baking of such products.

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.

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 1

(*a*) A 75/25 viscose (3 denier, 1 inch staple)/bleached cotton (middling, 15/16 inch) carded web weighing about 0.75 ounce/square yard is impregnated with an aqueous dispersion containing per 100 parts:

25.0 parts of an emulsion copolymer of 60% ethyl acrylate, 25.5% methyl methacrylate, and 14.5% of methacrylyl dicyandiamide

2 parts of t-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent)

0.4 part of octylphenoxyethoxysodiumsulfate (wetting agent)

0.1 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 filass 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 56/44 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 methacrylyl dicyandiamide, 80% by weight of ethyl acrylate, and 15% by weight of n-butyl acrylate. A porous, soft and coherent non-woven web is obtained quite similar to that of Example 1(*a*).

Example 3

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 50% by weight of n-butyl acrylate grafted by subsequent copolymerization on to 50% by weight of a previously homopolymerized methacrylyl dicyandiamide.

Example 4

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 acrylyl dicyandiamide/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 2,000 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 annuli and is porous throughout.

Example 5

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 methacrylyl dicyandiamide/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 octylphenoxyethoxysodiumsulfate (wetting agent)
0.1 part of silicone antifoam

at about 300% wet pick-up. The web is dried 1.5 minutes at 225° F., cured 6 minutes at 350° F. Resultant non-woven fabric 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.

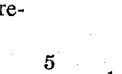
Example 6

The procedure of Example 4 is repeated with air-deposited webs obtained from the following fibers:

(*a*) 50% viscose rayon with 50% of a polymer of about 85% to 90% acrylonitrile available under the name "Acrilan,"
(*b*) 55% nylon (polyamide 66 type) with 45% viscose rayon,
(*c*) 100% cotton (garnetted card waste, roving and yarns),
(*d*) 100% nylon, and
(*e*) 35% cotton with 65% poly(ethylene glycol terephthalate) (Dacron).

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 consist of fibers selected from the group consisting of cellulosic fibers, polyamide fibers, vinyl resin fibers, and polyester fibers, fibers in the product being bonded together by a binder, substantially uniformly distributed through the body of the product, consisting essentially of a water-insoluble copolymer, having an apparent second order transition temperature of not over 30° C., of copolymerizable monoethylenically unsaturated molecules comprising 3 to 50% by weight of monomer molecules selected from the group consisting of methacrylyl dicyandiamide and acrylyl dicyandiamide in which the acrylyl group has the formula



and the methacrylyl group has the formula



and at least 50% by weight of at least one monomer selected from the group consisting of styrene, chlorostyrene, p-methylstyrene, vinyl chloride, vinyl acetate, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, esters of acrylic acid, and esters of methacrylic acid, said polymer being cured to an infusible condition in which it is also insoluble in organic solvents, said product being substantially resistant to laundering and dry-cleaning, the amount of binder being from 20 to 200% of the weight of fibers in the product.

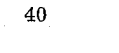
2. An article as defined in claim 1 in which the fibers consist entirely of cellulose fibers.

3. An article as defined in claim 1 in which the fibers consist entirely of a mixture of nylon and cellulosic fibers.

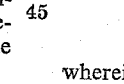
4. An article as defined in claim 1 in which the fibers consist entirely of a mixture of nylon and regenerated cellulose fibers.

5. An article as defined in claim 1 in which the fibers consist entirely of a mixture of nylon and cellulose acetate fibers.

6. As an article of manufacture, a non-woven fibrous product in which cellulose fibers are distributed in random array, fibers in the product being bonded together by a binder, substantially uniformly distributed through the body of the product, consisting essentially of a water-insoluble copolymer, having an apparent second order transition temperature of not over 30° C., of 3 to 20% by weight of methacrylyl dicyandiamide in which the methacrylyl group has the formula

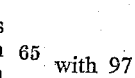


and 97 to 80% respectively of at least one ester of an alcohol having 1 to 4 carbon atoms with an acid of the formula



wherein *n* is an integer having a value of 1 to 2, said polymer being cured to an infusible condition in which it is also insoluble in organic solvents, said product being substantially resistant to laundering and dry-cleaning, the amount of binder being from 20 to 200% of the weight of fibers in the product.

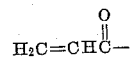
7. As an article of manufacture, a non-woven fibrous product in which cellulose fibers are distributed in random array, fibers in the product being bonded together by a binder, substantially uniformly distributed through the body of the product, consisting essentially of a water-insoluble copolymer, having an apparent second order transition temperature of not over 30° C., of 3 to 20% by weight of methacrylyl dicyandiamide in which the methacrylyl group has the formula



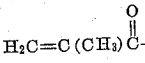
with 97 to 80% by weight of butyl acrylate, said product being substantially resistant to laundering and dry-cleaning, the amount of binder being from 20 to 200% of the weight of fibers in the product.

8. A process of making a non-woven fabric which comprises associating cellulose fibers in random array within a web or mat, bringing into contact with the fibers, substantially uniformly through the interior of the product, an aqueous dispersion of 2 to 60% by weight of a binder consisting essentially of a water-insoluble copolymer, hav-

ing an apparent second order transition temperature of not over 30° C. of copolymerizable monoethylenically unsaturated molecules comprising 3 to 50% by weight of monomer molecules selected from the group consisting of methacrylyl dicyandiamide and acrylyl dicyandiamide in which the acrylyl group has the formula

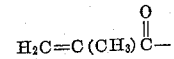


and the methacrylyl group has the formula

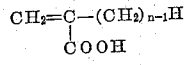


and at least 50% by weight of at least one monomer selected from the group consisting of styrene, chlorostyrene, p-methylstyrene, vinyl chloride, vinyl acetate, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, esters of acrylic acid, and esters of methacrylic acid, the amount of binder being such that on subsequent drying there is deposited from 20 to 200% by weight of binder solids based on the weight of fiber, 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.

9. A process of making a non-woven fabric which comprises associating cellulosic fibers in random array within a web or mat, bringing into contact with the fibers, substantially uniformly through the interior of the product, an aqueous dispersion of 2 to 60% by weight of a binder consisting essentially of a water-insoluble copolymer, having an apparent second order transition temperature of not over 30° C., of 3 to 20% by weight of methacrylyl dicyandiamide in which the methacrylyl group has the formula



and 97 to 80% respectively of at least one ester of an alcohol having 1 to 4 carbon atoms with an acid of the formula



wherein n is an integer having a value of 1 to 2, the amount of binder being such that on subsequent drying there is deposited from 20 to 200% by weight of binder solids based on the weight of fiber, 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.

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