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3,015,595

BONDED NON-WOVEN FIBROUS PRODUCTS

Vincent J. Moser, Willow Grove, and Benjamin B. Kine, Levittown, Pa., assignors to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware
No Drawing. Filed Apr. 9, 1958, Ser. No. 727,245
12 Claims. (Cl. 154-46)

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, including 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.

Urea-formaldehyde and melamine-formaldehyde condensates have been suggested for use as binders for the fibers in non-woven fabrics but when employed alone they produce undesirably stiff products which are unsuitable for textile use because of poor draping qualities and harsh feel or hand. In addition, the products bonded therewith cannot be employed satisfactorily in articles of dress which may need bleaching more or less frequently. Examples thereof are interliners for the collars and cuffs of shirts, especially the relatively open-weave type used for summer wear. The bleaching of such articles with the hypochlorites commonly used results in discoloration and loss in strength of the goods, especially when the bleaching is followed by heating or ironing. The application of such condensates in conjunction with certain addition polymers, such as described in United States Patent 2,823,142 produces a bonded product which initially has 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. Besides, the products of this patent show discoloration (yellowing) and loss of strength on bleaching.

It is an object of the present invention to provide fibrous products made with a binder formed of a composition comprising certain addition copolymers and certain thermosetting resin-forming condensates which can be applied without the disadvantages mentioned above that are characteristic of previously applied binders of this type. A further object of the invention is to provide a bonded fibrous product of non-woven character in which the addition copolymer is reacted with the condensate of the binder composition after application to the fibrous product whereby the binder composition is adapted to be converted, as by heating with or without the presence of a suitable catalyst as will be pointed out more particularly hereinafter, to an infusible and insoluble condition so that both the addition polymer and the condensate become so chemically bound together in the product that dry-cleaning solvents do not alter the hand or draping quality of the bonded product. 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 char-

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acteristics 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. Another object of the invention is to produce bonded fibrous products comprising wool, nylon, or other proteinaceous fibers which are protected from yellowing caused by bleaching with chlorine-containing bleaching agents. Other objects and advantages of the invention will be apparent from the description thereof hereinafter.

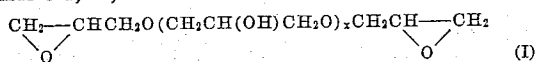
In accordance with the present invention, improved bonded fibrous products of non-woven character are obtained using as the binder certain addition copolymers of acrylamide or methacrylamide in conjunction with a water-soluble or water-dispersible aminoplast or epoxy thermosetting resin-forming condensate. It has been found that the presence of the amide groups in the addition copolymer results in the chemical combination of the copolymer with the aminoplast or epoxy resin during the curing or baking of the latter condensate in the fibrous product. Surprisingly, it has been discovered that the employment of the amide copolymers in conjunction with the aminoplast condensate in the proportions hereinafter designated results in a reduction of the tendency of fibrous products bonded therewith to be discolored and to lose strength when subjected to heat after being bleached with chlorine-containing agents such as the hypochlorites commonly employed in the textile industry. This is surprising since the copolymer contains nitrogen atoms which would be expected to increase the tendency toward chlorine damage simply because additional nitrogen would be present in the bonded fibrous product.

The amide copolymers are those formed of mixtures of 1% to 10% by weight of acrylamide or methacrylamide with at least one comonomer selected from the group consisting of acrylonitrile, methacrylonitrile, and the esters of an acid selected from the group consisting of acrylic acid and methacrylic acid with benzyl alcohol, cyclohexanol, and aliphatic alcohols having from 1 to 18 carbon atoms. The proportions of acrylonitrile and of methacrylates of lower alcohols such as methyl methacrylate and ethyl methacrylate should be such that the T_g of the polymer does not exceed 5° C. and preferably does not exceed -10° C. in order to obtain the best draping qualities and optimum softness of hand. It is essential that the copolymer does not contain any chlorine. It is also essential that the copolymer contains no more than 89% by weight of methyl acrylate or ethyl acrylate or a mixture of these two comonomers. It is essential that the proportion of acrylamide or methacrylamide or of mixtures of the two does not exceed 10% by weight since it has been found that copolymers containing a greater proportion of the amide component result in a binder which is subject to extreme swelling and even disintegration during laundering or dry-cleaning in spite of the presence of the aminoplast or epoxy resin for reaction therewith. Preferably, the amount of acrylamide or methacrylamide or of the total of any mixture of these amides in the copolymer is between 2½% and 5% by weight. It has been discovered that this small proportion of acrylamide in the copolymer serves to provide the optimum combination of insolubility, heat-resistance, solvent-resistance, softness, and resistance to change of hand and draping qualities on dry-cleaning and laundering.

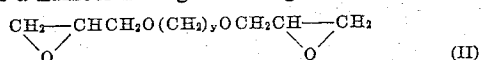
The aminoplast condensates which may be employed are the low molecular weight or monomeric reaction products of formaldehyde with urea, thiourea, biuret, or other homologs or derivatives thereof, such as N,N'-ethyleneurea, N,N'-ethyleneurea, N,N'-dimethylurea,

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 thermosetting resin condensates, e.g. of methyl and ethyl alcohols, for example, dimethoxymethylmonomethylolmelamine. Preferably, the extent of condensation of these resin-forming aminoplast condensates is such that they are still soluble in water or self-dispersible therein to a colloidal condition.

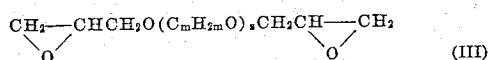
The epoxy thermosetting resin-forming condensates may be either water-soluble or self-dispersible in water. The water-soluble types may be any of those having the Formulas I, II, and III:



where x is a number having an average value of 1 to 3;

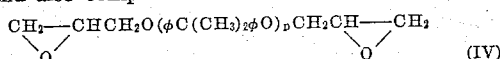


where y is a number having an average value of 2 to 4; and



where m is an integer having a value of 2 to 4, and z is a number having an average value of 1 to 5.

The water-insoluble but self-dispersible condensates containing epoxide groups include the compounds of Formula II above wherein y has an average value of 5 to 10 and also compounds of Formula IV:



where ϕ is the *p*-phenylene group, and p is a number having an average value of 1 to 3.

The proportion of the addition copolymer containing amide groups to the thermosetting resin-forming condensate is from 5:1 to 19:1 by weight, preferably between 9:1 and 10:1. In the lower part of the range near the ratio of 5:1, it is desirable to employ copolymers containing a greater proportion of a softening acrylate or methacrylate to assure a desirable soft hand. On the other hand, at the upper end of the range near the ratio of 19:1, the harder copolymers having T_g values from 5° up to about 17° C. may be employed without obtaining an excessively stiff, harsh feel or hand.

The copolymers may be prepared in any suitable fashion but for most practical purposes those obtained as aqueous dispersions by the emulsion copolymerization of the various comonomers are most practical. The aqueous dispersion with or without dilution may itself serve as the vehicle of impregnation of the fibrous product after the addition of the aminoplast or epoxy condensate thereof with or without acidic catalyst.

The acidic catalyst, if used, may be introduced into the aqueous dispersion containing the copolymer and the condensate or it may be applied to the non-woven fibrous mat or web separately before or after application of the aqueous dispersion of the copolymer and condensate. The catalyst may be used in an amount of ¼% to ½% by weight of the total weight of the aqueous dispersion if included in such aqueous dispersion of the copolymer and condensate. If applied separately, it is preferably applied in such amount and at such a concentration as to provide approximately ½% to 2% by weight of the catalyst on the weight of condensate employed. The acidic catalyst may be an acid itself or it may be a potentially acidic material which serves as a latent catalyst which liberates acid on heat. Examples thereof include ammonium chloride, diammonium hydrogen phosphate, zinc fluoroborate, zinc perchlorate, or a salt of an amine such as the hydrochloride of mono-

ethanolamine, diethylamine, triethylamine, 2-methyl-2-aminopropanol-1, and the like.

As pointed out hereinabove, the copolymer contains a plurality of amide groups by which it is adapted to be insolubilized and rendered infusible on heating with the aminoplast or epoxy condensate with or without a suitable catalyst. Hence, the cured or baked fibrous product provides resistance to laundering, dry-cleaning and spotting, to various chemicals, and to heat. The bonded fibrous products of the present invention can be heated to a moderate temperature 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. The binder compositions of the present invention apparently also provide great versatility of adhesion in that they are characterized not only with good adhesion to hydrophilic fibers like cotton, regenerated cellulose rayons and the like, but also 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 soon. 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 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 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 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 invention, a fibrous product, the fibers of which may consist entirely of non-proteinaceous fibers which are incapable of felting, is impregnated with the aqueous dispersion of the condensate and the water-insoluble linear polymer containing the amide groups. The molecular weight of the polymers should be from about 100,000 to about 10 million. The fibers are present in the form of a so-called "non-woven" mat or web in which they are haphazardly distrib-

uted. 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 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 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 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 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 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 scaly, wool-like fibers described and claimed in the copending application of Nathaniel A. Matlin, Serial No. 576,462, filed April 5, 1956, now United States Patent 2,866,256, may be used in forming the fibrous product. Such wool-like fibers are capable of use in the formation of non-woven fibrous products in which the thermoplastic character of such fibers may be made use of to effect binding of the fibers even without the employment of the binders herein disclosed; and, of course, such wool-like fibers can be employed in conjunction with relatively non-adhesive fibers such as cellulose, nylon, wool, and so on.

The binder of the present invention is preferably applied in the form of an aqueous dispersion obtained by the addition of the aminoplast or epoxy condensate with or without a catalyst to an aqueous dispersion of a polymer which may be produced by emulsion polymerization. Alternatively, a dried powder obtained from the first-mentioned dispersion may be dusted or sprayed on to the web or the fibers before, during, or after deposition. Surprisingly, dispersions of copolymers having T_1 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_1 values. As pointed out hereinbefore, however, it is preferred that the copolymer have a T_1 which is not above 50° C. in order to obtain a soft product for textile use.

The T_1 value referred to herein 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 Patents 23, 87-90, 102 (September 1950). The T_1 value here used is that determined at 300 kg./cm².

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, acrylamide or methacrylamide 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 copolymer formed. The same procedure may be used in reverse order to graft the acrylamide or methacrylamide 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 acrylamide or methacrylamide may be introduced at the beginning, at any intermediate stage or at the end as desired.

The binder dispersion or powder 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 or powder 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 or powder 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 or powder 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.

The binder of the present invention may be applied in conjunction with other binders, such as glue. 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.

If desired, the aqueous dispersion of the polymer and condensate may also contain a wetting agent to assist penetration of the fibrous wet 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 dioctylsuccinic acid 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 amide groups is generally applied at a concentration of 2% to 60% solids and preferably at a concentration of 20% to 40% binders solids by weight.

The fibrous product of non-woven character may contain from 10% to 200% by weight, based on the weight of the fibers, of the copolymer-condensate binder 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 10% to 50% by weight of binder solids on fiber, the lower proportion, of course, giving the maxi-

mum porosity possible 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 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 10% 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 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, knotted, or felted character.

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 hereinabove, may be assisted by the use of an acidic catalyst.

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, $1\frac{1}{16}$ 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 5% of methacrylamide with 95% of butyl acrylate

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

0.4 part of octylphenoxyethoxysodiumsulfate (wetting agent)

2.5 parts of dimethylol-N,N'-ethyleneurea
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 has a weight ratio of about 33/67 fiber/binder. It is highly porous and has a soft and resilient feel. Bleaching with a hypochlorite solution can be followed by ironing without serious discoloration or loss of strength of the fibers.

(b) The procedure of part (a) is repeated with Pyrex glass fibers, except that the carded web weighed 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 containing 25.0 parts of an emulsion copolymer of 10% of n-butyl acrylate with 89% of ethyl acrylate and 1% of methacrylamide and the same aminoplast. A porous, soft and coherent non-woven web is obtained. Bleaching with a hypochlorite solution can be followed by ironing without serious discoloration or loss of strength of the fibers.

Example 3

The procedure of Example 1(a) is repeated using a similar aqueous dispersion containing 25.0 parts of an emulsion copolymer of 80% ethyl acrylate, 18.5% of 2-ethylhexyl acrylate, and 1.5% of methacrylamide. An exceptionally well-bonded web is obtained that is highly resistant to solvents and heat. Bleaching with a hypochlorite solution can be followed by ironing without serious discoloration or loss of strength of the fibers.

Example 4

The procedure of Example 1(a) is repeated using a similar aqueous dispersion containing 25.0 parts of an emulsion copolymer of 85% of ethyl acrylate, 14% of butyl acrylate, and 1% of acrylamide, but replacing the dimethylol-N,N'-ethyleneurea with 2.5 parts of an epoxy condensate of Formula I above in which x has an average value of 4. A coherent web like that of Example 3 but with a softer hand is obtained. Bleaching with a hypochlorite solution can be followed by ironing without serious discoloration or loss of strength of the fibers.

Example 5

The procedure of Example 4 is repeated on 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. After washing and drying, no ironing or pressing is needed to restore the shape, appearance, or hand of garments, such as blouses made of the fabric. This fabric can be bleached and then ironed without discoloration.

Example 6

A 50/50 white viscose-dyed Acrilan (polymer of 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:

- 25 parts of an emulsion copolymer of 95% n-butyl acrylate and 5% of methacrylamide
- 2 parts of t-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent)
- 2.5 parts of urea/formaldehyde/methanol condensate
- 0.5 part of diammonium phosphate
- 0.5 part of octylphenoxyethoxysodiumsulfate (wetting agent)
- 0.2 part of silicone antifoam

at ca. 300% wet pick-up. The web is dried 1.5 min. at 225° F., cured 5 min. at 350° F. Product: 55/45 fiber/binder weight ratio; good coherence, porous, soft, textile hand. Bleaching with a hypochlorite solution can be followed by ironing without serious discoloration or loss of strength of the fibers.

Example 7

An 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:

- 25 parts of an emulsion copolymer of 5% of methacrylamide and 95% of n-butyl acrylate
- 2 parts of t-octylphenoxypolyethoxyethanol containing about 35 oxyethylene units (emulsifier and dispersing agent)
- 3.5 parts methylated hexamethylolmelamine
- 0.5 part diethanolamine hydrochloride
- 0.5 part octylphenoxyethoxysodiumsulfate (wetting agent)
- 0.2 part silicone antifoam

at ca. 200% wet pick-up. Dried 1.5 min. 225° F., cured 3 min. at 350° F. Product: 55/45 fiber/binder; soft, resilient, resistant to laundering and dry-cleaning. This fabric can be bleached and then ironed without discoloration.

Example 8

The procedure of Example 7 is repeated on air-deposited webs of the following fibers:

- (1) 100% regenerated cellulose (2.0 denier, 1.5 inch staple) 2 oz./sq. yd. carded web.
- (2) 55% polyamide 66 nylon and 45% regenerated cellulose both 5 denier, 1.75 inch staple,
- (3) 100% cotton (garnetted card waste, roving and yarns) 4 oz./sq. yd. carded web.
- (4) 35% cotton and 65% poly(ethylene glycol terephthalate) 1.25 oz./sq. yd. carded web.

The fabrics could be bleached and then ironed without serious discoloration.

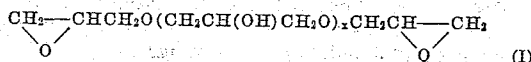
Example 9

The procedure of Example 7 is repeated substituting for the urea condensate 4 parts of a trimethylolmelamine. A coherent web is obtained which could be bleached and then ironed without serious discoloration.

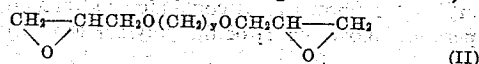
It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. As an article of manufacture, a non-woven fibrous product resistant to dry-cleaning and laundering in which the fibers are distributed in random array, fibers in the product being bonded together by 2 to 200% by weight, based on the weight of fibers in the product, of a binder comprising an insoluble, infusible reaction product of (1) a water-insoluble addition polymer of 1% to 10% by weight of methacrylamide and 90% to 99% by weight of at least one compound selected from the group consisting of acrylonitrile and esters of an acid selected from the group consisting of acrylic acid and methacrylic acid with an alcohol selected from the group consisting of benzyl alcohol, cyclohexanol, and alkanols having 1 to 18 carbon atoms, said polymer having a T_g of not over 17° C., and (2) a water-dispersible thermosetting resin-forming condensate selected from the group consisting of (a) condensates of formaldehyde with urea, N,N'-ethyleneurea, and melamine, and (b) polyepoxides of the Formulas I, II, III, and IV:

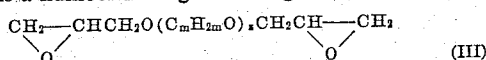


where x is a number having an average value of 1 to 3;

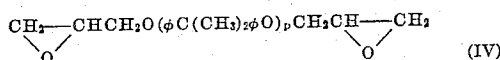


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where y is a number having an average value of 2 to 10;



where m is an integer having a value of 2 to 4, and z is a number having an average value of 1 to 5; and



where ϕ is the p-phenylene group, and p is a number having an average value of 1 to 3, the amount of condensate (2) being from 5% to 17% by weight of the polymer (1).

2. An article as defined in claim 1 in which the aminoplast is a condensate of formaldehyde with N,N'-ethyleneurea.

3. An article as defined in claim 1 in which the fibers comprise at least 50% by weight of cellulosic fibers.

4. An article as defined in claim 1 in which the fibers comprise at least 50% by weight of nylon fibers.

5. An article as defined in claim 1 in which the fibers comprise at least 50% by weight of smooth-surfaced artificial fibers.

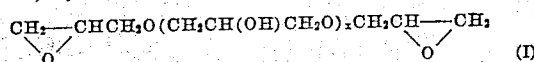
6. An article as defined in claim 1 in which the fibers comprise at least 50% by weight of fibers selected from the group consisting of cellulosic fibers, nylon fibers, vinyl resin fibers, fibers of polymers of acrylonitrile, poly(ethylene glycol terephthalate) fibers, and mixtures thereof.

7. An article as defined in claim 1 in which the fibers comprise nylon fibers and the condensate is a polyepoxide.

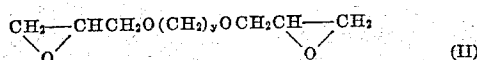
8. An article as defined in claim 1 in which the aminoplast is a condensate of formaldehyde with melamine.

9. An article as defined in claim 1 in which the aminoplast is a condensate of formaldehyde with urea.

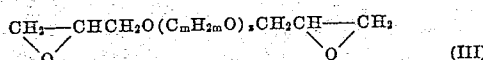
10. A process of making a non-woven fabric which comprises collecting a mass of fibers in random array, bringing into contact with the fibers a binder comprising an aqueous dispersion containing (1) 2% to 60% by weight of a water-insoluble addition polymer of 1% to 10% by weight of methacrylamide and 90% to 99% by weight of at least one compound selected from the group consisting of acrylonitrile and esters of an acid selected from the group consisting of acrylic and methacrylic acid with an alcohol selected from the group consisting of benzyl alcohol, cyclohexanol, and alkanols having 1 to 18 carbon atoms, said polymer having a T_1 of not over 17° C., and (2) 5% to 17% on the weight of the polymer of a water-dispersible thermosetting resin-forming condensate selected from the group consisting of (a) condensates of formaldehyde with urea, N,N'-ethyleneurea, and melamine, and (b) polyepoxides of the Formulas I, II, III, and IV:



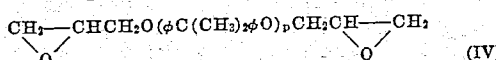
where x is a number having an average value of 1 to 3;



where y is a number having an average value of 2 to 10;



where m is an integer having a value of 2 to 4, and z is a number having an average value of 1 to 5; and

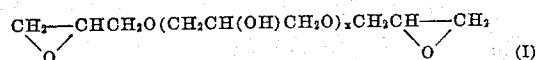


where ϕ is the p-phenylene group, and p is a number having an average value of 1 to 3, thereby depositing a total amount of (1) and (2) in the range of 2 to 200% by weight, based on the weight of fibers in the product, and drying the fibrous mass containing the binder at a temperature above the T_1 of the polymer to effect fusion of

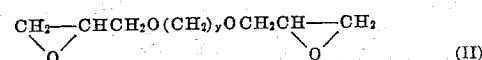
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the polymer and bonding of the fibers thereby, and heating the dried fibrous product at a temperature of 110° to 350° C. to insolubilize the binder.

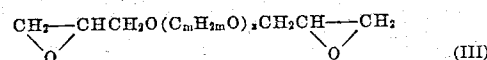
11. As an article of manufacture, a non-woven fibrous product resistant to dry-cleaning and laundering in which the fibers are distributed in random array, fibers in the product being bonded together by 2 to 200% by weight, based on the weight of fibers in the product, of a binder comprising an insoluble, infusible reaction product of (1) a water-insoluble addition polymer of about 2½% to 5% by weight of methacrylamide and about 95% to 97½% by weight of at least one compound selected from the group consisting of acrylonitrile and esters of an acid selected from the group consisting of acrylic acid and methacrylic acid with an alcohol selected from the group consisting of benzyl alcohol, cyclohexanol, and alkanols having 1 to 18 carbon atoms, said polymer having a T_1 of not over 17° C., and (2) a water-dispersible thermosetting resin-forming condensate selected from the group consisting of (a) condensates of formaldehyde with urea, N,N'-ethyleneurea, and melamine, and (b) polyepoxides of the Formulas I, II, III, and IV:



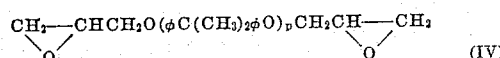
where x is a number having an average value of 1 to 3;



where y is a number having an average value of 2 to 10;

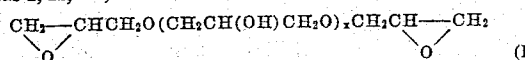


where m is an integer having a value of 2 to 4, and z is a number having an average value of 1 to 5; and

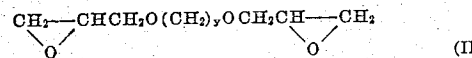


where ϕ is the p-phenylene group, and p is a number having an average value of 1 to 3, the amount of condensate (2) being from 5 to 17% by weight of the polymer (1).

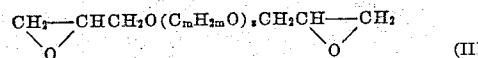
12. A process of making a non-woven fabric which comprises collecting a mass of fibers in random array, bringing into contact with the fibers a binder comprising an aqueous dispersion containing (1) 2 to 60% by weight of a water-insoluble addition polymer of about 2½% to 5% by weight of methacrylamide and about 95% to 97½% by weight of at least one compound selected from the group consisting of acrylonitrile and esters of an acid selected from the group consisting of acrylic and methacrylic acid with an alcohol selected from the group consisting of benzyl alcohol, cyclohexanol, and alkanols having 1 to 18 carbon atoms, said polymer having a T_1 of not over 17° C., and (2) 5 to 17% of the weight of the polymer of a water-dispersible thermosetting resin-forming condensate selected from the group consisting of (a) condensates of formaldehyde with urea, N,N'-ethyleneurea, and melamine, and (b) polyepoxides of the Formulas I, II, III, and IV:



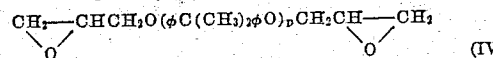
where x is a number having an average value of 1 to 3;



where y is a number having an average value of 2 to 10;



where m is an integer having a value of 2 to 4, and z is a number having an average value of 1 to 5; and



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where ϕ is the p-phenylene group, and p is a number having an average value of 1 to 3, thereby depositing a total amount of (1) and (2) in the range of 2 to 200% by weight, based on the weight of fibers in the product, and drying the fibrous mass containing the binder at a temperature above the T_i 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° to 350° C. to insolubilize the binder.

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