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NON-WOVEN FABRIC BONDED WITH BUTYL RUBBER PHENOL-FORMALDEHYDE RESOL

Alfred L. Miller, Cranford, N.J., Edmund Maurice Buras, Jr., Silver Spring, Md., and Julian Berch, Washington, D.C., assignors to Esso Research and Engineering Company, a corporation of Delaware
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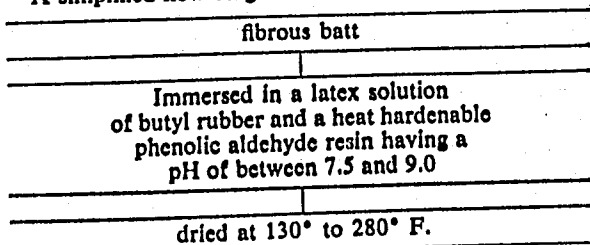
The present invention relates to improved non-woven fabrics. More particularly, it deals with cellulosic non-woven fabrics having increased tensile properties without undue increase in stiffness.

This is a continuation-in-part of U.S. Serial No. 544,281, filed November 1, 1955, now abandoned.

Non-wovens are conventionally made by impregnating a fiber batt, i.e., a mass of fibers having the consistency of, for example, household absorbent cotton, with a binder so as to hold the fibers together to form a textile-like fabric. The fibers of the batts may be uniformly oriented or randomly distributed according to the intended application of non-woven fabric to be produced. The unique nature of non-woven fabrics is well recognized in the art. Whereas woven fabrics can be engineered by suitable weave construction to produce strength with low stiffness and satisfactory drape, non-woven fabrics derive their ultimate strength and stiffness characteristics largely from the binder system. While non-woven fabric properties can be varied by selection of fiber type and characteristics, major changes in properties by this means are generally uneconomical. Rather, requisite properties are generally obtained through selection of the binder. For example, non-woven fabrics employing conventional polyvinyl acetate as a binder have good tensile properties although they are quite stiff and then are unsuitable for use in wearing apparel and decorative fabrics. Non-woven fabrics bonded with rubber-based binders require relatively large amounts of binder to obtain satisfactory strength, and this leads to rubberiness and undesirable tactile properties. Each of these binder systems can be modified by the addition of plasticizer, but this kind of modification gives softness at the expense of strength. Thus, there exists a demand for a non-woven fabric having good tensile properties without being excessively stiff.

The present invention solves this need. In accordance with the present invention, a binder system comprising a latex (aqueous dispersion) of butyl rubber, and a phenol-formaldehyde resin of the resol type, e.g., resorcinol-formaldehyde resin, when applied to a fiber batt, e.g., cellulosic fibers, gives, after drying, a non-woven fabric exhibiting good physical strength without undue stiffness. In general, it is preferred to employ an aqueous dispersion containing both the butyl rubber and phenol-formaldehyde resin to impregnate the fiber batt, the combined weight of butyl rubber and phenol-formaldehyde broadly ranging from 10 to 50, preferably 15 to 25, weight percent of the dried non-woven fabric. Soluble, heat-hardenable resin or dispersed, partly pre-polymerized phenol-formaldehyde resin may be employed.

A simplified flow diagram of the method is as follows:



The term "butyl rubber" denotes copolymers of a major proportion, e.g., 85 to 99.5 weight percent of a C₄ to C₈

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isoolefin such as isobutylene, 2-methyl-1-butene, etc. and a minor portion, preferably 15 to 0.5 weight percent, of a multiolefin of about 4 to 14 carbon atoms, e.g., myrcene. The multiolefin is preferably a diolefin such as isoprene, butadiene, or piperylene. The copolymer is prepared at temperatures below 0° C. in the presence of a Friedel-Crafts catalyst. The copolymer has a Staudinger molecular weight between about 20,000 to 300,000, and an unsaturation level represented by an iodine number between about 0.5 to 20, i.e., a low unsaturation rubber. Butyl rubber is well known in the art. For example, see "Synthetic Rubber" by Whitby (1954) and U.S. Patent No. 2,356,128 to Thomas et al. describing its preparation. As used in the specification and claims, the term "butyl rubber" denotes the above type of rubbery copolymer.

It is well known to produce latices of butyl rubber. For example, a solution of butyl rubber in a hydrocarbon or other solvent, generally a C₄ to C₁₀ aliphatic, may be emulsified with water generally in the presence of salt of a C₈ to C₁₈ organic phosphinate and a monovalent salt of dihydrogen ortho-phosphate. Alternatively, the latices may be prepared by the use of other emulsifier systems containing carboxylate soaps, sulfonate and non-ionic emulsifiers such as sodium dodecylbenzene sulfonate or the ethylene oxide adducts of phenols. The latices thus prepared contain about 10 to 35 weight percent rubbery solids, and can be further concentrated by distillation or passing an inert gas through the latex at about 150° to 200° F. so as to strip off liquid, i.e., hydrocarbon solvent for the butyl. A more detailed description of the preparation of butyl rubber latices may be had by referring to co-assigned U.S. Patent No. 2,595,797.

In the preparation of the fiber-treating dispersion latices such as those described above, a phenolic compound and an aldehyde which are capable of condensing or polymerizing to form a heat-hardenable phenol-aldehyde resin are mixed. The preferred phenolic compounds are appreciably water-soluble polyhydric phenols having hydroxyl groups in meta relationship such as resorcinol, phloroglucinol, orcinol, cresorcinol and m-xylorcinol although other polyhydric phenols and even mono-hydric phenols such as phenol itself may also be employed. The preferred aldehyde is formaldehyde, or its polymers, although other appreciably water-soluble aldehydes such as acetaldehyde or furfural may be substituted wholly or in part for the formaldehyde. The concentration of the phenol and the aldehyde is preferably from 1 to 10% of each on the total amount of the dispersion but this may be varied if desired.

Since alkalis such as sodium and potassium hydroxide catalyze the polymerization or condensation of the phenol and the aldehyde to form the resin, i.e., it is of the resol type, these may be present in the dispersion together with the synthetic latex, the phenol and the aldehyde.

The caustic-containing phenol-formaldehyde dispersion may be aged for a period up to about 72 hours, preferably for about 6 to 24 hours, either before or after mixing with the butyl latex. Alternatively, a partially pre-polymerized resin may be used.

Other additives may be included in the binder, such as viscosity control agents, colorants, and finishing agents (e.g., water repellents). The presence of these additives may require adjustment of the quantities of the basic binder components outside of the limits specified above.

When applying the phenol-formaldehyde resin and butyl rubber latex simultaneously, such as an aqueous solution containing resorcinol and formaldehyde together with butyl rubber, the following range of ingredients is preferred:

The butyl rubber solids constitute 1 to 40, preferably 1 to 25, weight percent of the total mixture. The concen-

tration of resorcinol-formaldehyde components can vary between 0.1 and 0.8 total mole of phenol and aldehyde per 100 parts of butyl rubber solids. The molar ratio of resorcinol to formaldehyde can vary from 1 to 5. The pH of the mixture is normally adjusted to between 7.5 to 9.0 by the addition of alkaline materials, such as sodium hydroxide, prior to impregnating the fiber batt.

The fiber batt is normally a cellulosic material such as cotton or rayon. The binder mixture is applied in such quantity that, after drying, the combined weight of the added solids preferably ranges from 15 to 25% of the weight of the fiber. Drying temperatures lie preferably within the range of 130 to 280° F., to remove moisture while polymerizing the phenol-aldehyde resin. Any of the conventional impregnating methods may be employed, such as padding, spraying, dipping and the like. Hot air drying for a period of 0.5 to 30 minutes is normally utilized.

It is to be clearly understood that the present invention is distinguished from the use of phenolic resins for binding fiber cords to rubbery articles, such as is carried out in producing tire cords. In such an operation, a bond is created between the preformed textile cord or an already formed fabric and the rubbery material, the bond involving a rubber cure system, e.g., sulfur linkages, of the elastomer. In contrast, the present invention deals with binding together a multitude of random non-woven filaments or fibers (fiber to fiber) to produce a bound unconstructed random fiber fabric, binding taking place principally at their closest points of contact. Binders that are suitable for non-wovens will not always work in tire cord adhesion, e.g., polyvinylacetate. Similarly, materials suitable for adhering cords on woven fabrics to rubbers will normally give a product of excessive stiffness if used to bind non-woven fabrics.

The combination of a low unsaturation butyl rubber latex and phenol-formaldehyde resins of the resol type as applied to non-woven cellulosic fibers is unusual in giving increased tensile strength without excessive stiffness (bending lengths of over four inches for nonwovens whose area weight is approximately 7 oz./sq. yard). Use of high unsaturation rubbers, e.g., nitrile rubber, etc., with phenolic resins results in non-woven fabrics of poor stiffness characteristics. Although the present invention is not limited to the following explanation, it is believed that the unusual nature of the present composition is due to the fact that phenolic resins such as resorcinol-formaldehyde will cure relatively highly unsaturated rubbers (during drying) whereas they will not cure low unsaturation butyl.

The various aspects and modifications of the present invention will be made more clearly apparent by reference to the following examples.

In all of the following examples, a typical butyl rubber latex, hereinafter referred to as "butyl rubber latex A," was employed. Butyl rubber latex A had the following inspection:

(1) Polymer properties—

Copolymer of about 98 weight percent isobutylene and about 2 weight percent isoprene
Unsaturation—1.3 to 1.7 mole percent
Mooney viscosity, 8 minutes at 212° F.—70–90
Molecular weight—200,000–400,000

(2) Total solids—53 to 55 weight percent (rubber solids 49.8 to 51.7 weight percent)

(3) Specific gravity—0.96 gr./cc. at 70° F.

(4) pH—5 to 6

(5) Particle size: 0.5 micron (average), 0.05 to 1 micron (range).

Non-woven fabrics in all cases were made by putting a fiber batt between a carrier, i.e., cheesecloth or fine metal screening, and then drenching the assembly with a bath containing the various binder systems indicated. The saturated batt and carrier was passed through squeeze rolls to remove excess binder. The impregnated batt was

then dried at a temperature of 240–250° F. for 20–25 minutes in a forced air circulating oven.

The thickness was measured with a Compressometer according to ASTM D461–56 No. 8. The binding length was measured by the cantilever method described in ASTM D1388–55T. The tensile properties were measured on an Instron Tester using a ST cell, according to ASTM cut-strip-method for non-woven fabrics D1117–58. The solid add-on was calculated from the increase in conditioned weight of the dried non-woven fabric.

EXAMPLE 1

A cotton fiber batt of about 12" x 20" was dipped in butyl rubber latex A at a pH of 6.5 and dried as indicated above. In the same manner, cotton batt was impregnated with a latex of polyvinylacetate, a conventional binder. The polyvinylacetate latex had a solids content of 55%, a Brookfield viscosity of 800–1000 centipoises, a pH of 4 to 6, and a residual monomer content below 1%.

In another experimental run, a butyl rubber latex A was mixed with a resorcinol-formaldehyde solution in accordance with the following recipe:

	Weight percent
Latex rubber solids	25
Resorcinol	1.9
Formaldehyde	1.2
Water	72

The pH of the latex mix was adjusted to pH 8.3 by the addition of a base solution, i.e., 10% sodium hydroxide. The mixture was then aged for about 24 hours. Thereafter a 5 oz./sq. yard cotton batt was impregnated with the latex and dried at 240° F. for 20 minutes.

The physical properties of the non-woven fabrics formed by the use of each of the above binder systems are set forth in Table I.

Table I

	Butyl	Butyl plus Resorcinol-Formaldehyde	Polyvinylacetate
Solids Add-on, percent	23.6	21.0	27.0
Init. Tens. Mod./Solids Add-on, p.s.i./percent/100	2,100	14,700	43,600
Yield Strength/Solids Add-on, lb./in./percent/100	10.9	50.1	52.4
Breaking Strength/Solids Add-on, lb./in./percent/100	30.4	83.3	75.0
Bending Length, in.	2.0	3.8	>4.0

As shown in Table I, non-woven fabrics employing polyvinylacetate have good tensile properties but are excessively stiff, as is evidenced by their bending length, e.g., greater than 4.9 inches. In contrast, butyl rubber latex A above gave good stiffness but somewhat poor tensile properties. The use of a combination of butyl latex and phenol-formaldehyde resin greatly improved the physical properties of the non-woven fabric without causing the fabric to be unduly stiff.

The data thus shows that the present invention gives a non-woven fabric of overall good physical properties.

EXAMPLE 2

A comparison was made between the use of a high unsaturation rubber latex, i.e., butadiene-acrylonitrile, and low unsaturation butyl rubber (butyl rubber latex A). The butadiene-acrylonitrile latex was characterized as follows:

BUTADIENE-ACRYLONITRILE LATEX

Butadiene/acrylonitrile ratio	55/45.
Solids, weight percent	40–45.
Stabilizer	Anionic.
pH	9.0.
Average particle size	2500 Angstroms.
Viscosity	20 cps.
Surface tension	25 dynes/cm.

In one run, the butadiene-acrylonitrile latex was mixed

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with a resorcinol-formaldehyde solution in accordance with the following recipe:

	Weight, percent
Butadiene-acrylonitrile latex solids	25
Resorcinol	1.9
Formaldehyde	1.2
Water	72

Butyl latex containing resorcinol formaldehyde was prepared in the same manner as indicated in Example 1.

A rayon batt was impregnated with each of the following binder systems: Butyl latex A alone, butyl latex A containing resorcinol-formaldehyde, acrylonitrile-butadiene latex alone, and acrylonitrile-butadiene latex containing resorcinol-formaldehyde, as prepared in the above-described manner. All binders were at a pH of 8 to 8.5. The physical properties of the non-woven rayon fabrics are indicated in Table II:

Table II

	Butyl	Butadiene-acrylonitrile	Butyl plus resorcinol-formaldehyde	Butadiene-acrylonitrile plus resorcinol-formaldehyde
Solids Add-on, Percent	33.3	31.0	34.0	38.7
Int. Tens. Mod./Solids Add-on, p.s.i./Percent/100	18,000	25,600	27,200	23,400
Yield Strength/Solids Add-on, lb./in./Percent/100	21.9	40.3	70.5	84.9
Breaking Strength/Solids Add-on, lb./in./Percent/100	38.9	73.6	140.0	147.2
Bending Length, in. (41.6° calc.)	3.0	2.8	3.9	5.2

Table II shows that incorporating resorcinol-formaldehyde resin in a high unsaturate rubber binder, i.e., acrylonitrile-butadiene, increases stiffness to a highly undesirable degree, and has some adverse effects on other physical properties, i.e., initial tensile modulus per solids added on. In contrast, the present invention gives a non-woven fabric of improved physical properties without a marked increase in stiffness.

EXAMPLE 3

To demonstrate the effect of aging the butyl latex, resorcinol-formaldehyde bath prior to bonding, the following series of tests were performed. A master batch of butyl rubber latex A and resorcinol-formaldehyde was prepared having the following composition:

	Weight percent
Latex solids (butyl rubber)	25
Resorcinol	1.9
Formaldehyde	1.2
Water	72

A non-woven cotton fabric was prepared by impregnating a cotton batt with portions of the master batch which had been aged for varying periods of time. In all runs, the pH of the bath was maintained at 8.0 to 8.5. The properties of the non-woven cotton fabrics formed are set forth in Table III.

Table III

	Butyl plus resorcinol-formaldehyde			
	Not Aged	Aged		
		2 hrs.	24 hrs.	48 hrs.
Solids Add-on, Percent	30.0	38.0	21.0	19.0
Int. Tens. Mod./Solids Add-on, p.s.i./Percent/100	2,400	3,700	14,700	27,000
Yield Strength/Solids Add-on, lb./in. Percent/100	13.9	21.9	60.1	63.8
Breaking Strength/Solids Add-on, lb./in./Percent/100	26.6	42.7	83.3	94.9
Bending Length, in.	3.1	3.2	3.8	4.1

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As shown by the above results, it is preferred to age the resorcinol-formaldehyde, butyl latex binder system for about 4 to 36, e.g., 24 hours, prior to application and drying in order to improve physical properties without causing undesirable stiffness, i.e., over a four inch bending length for a 7 oz./sq. yard non-woven fabric.

EXAMPLE 4

To demonstrate the effect of using a phenol-formaldehyde resin in a butyl latex binder system, the following formulations were prepared: a butyl rubber binder prepared by dilution of butyl rubber latex so as to contain 25% latex solids by weight, and a butyl rubber-phenol-formaldehyde resin containing 25% latex solids by weight plus 3% phenol-formaldehyde precondensate solids, plus 0.64% hexamethylenetetramine catalyst. The precondensate solids were obtained from a resin dispersion, indicating that the precondensation had proceeded to the extent of producing a water insoluble resin. In addition, a butyl rubber latex binder containing resorcinol-formaldehyde solution was prepared in accordance with the recipe given in Example 1 above. Non-woven fabrics were prepared by treating a unidirectional card web batt made of 0.84 oz./sq. yard 100% dulled viscose fiber, which had been lightly prebonded with 0.25% aqueous solution of carboxymethyl cellulose sodium salt. Batts were impregnated with each binder and oven-dried at 180° F. then cured at 320° F. for 3 minutes. The physical properties of the non-wovens made with each of the above binder systems are set forth in Table IV.

Table IV

Code No.	43	45	40
	Butyl	Butyl plus Phenol-formaldehyde	Butyl plus Resorcinol-formaldehyde
Solids Add-on, Percent	61	38	44
Initial Tensile Modulus/Solids Add-on, p.s.i./Percent/100	10,000	20,000	21,000
Yield Strength/Solids Add-on, lb./in. Percent/100	8.4	13.4	17.7
Breaking Strength/Solids Add-on, lb./in./Percent/100	14.7	26.3	33.0
Bending Length in	1.47	1.63	1.95

It is seen in the Table IV that the properties of the fabric bonded with the latex containing phenol-formaldehyde precondensate are very much more like those of the fabric bonded with latex containing resorcinol-formaldehyde solids than those of the fabric bonded with butyl latex alone. In particular, the effect of imparting greatly improved tensile properties without increasing the stiffness is to be noted.

Numerous modifications of the present invention will suggest themselves to those skilled in the art. For example, other substances may be added to the binder system to exert further control over the flexibility, or to add weight, color, stability toward aging, and the like.

Having described the present invention that which is sought to be protected is set forth in the following claims.

What is claimed is:

1. A method of forming a non-woven fibrous material of enhanced tensile property without excessive stiffness characteristics, which method comprises: contacting non-woven cellulosic fibers with a binder solution consisting essentially of an aqueous solution of from 10 to 35 wt. percent of a rubbery copolymer of from 85 to 99.5 wt. percent of a C₄ to C₈ isoolefin and from 0.5 to 15 wt. percent of a C₄ to C₁₄ multiolefin and a heat-hardenable phenolic-aldehyde resin having a molar ratio of the phenolic component to the aldehyde component of from 1:1 to 5:1, said solution having a pH of between 7.5 and 9.0 and having been aged for a period of time up to 72 hours prior to contacting with said fibers; and there-

after, drying said non-woven fibers so contacted at a temperature between 130° and 280° F. to remove moisture and to polymerize the resin, thereby providing a fibrous material containing from 10 to 50 wt. percent of said binder.

2. The process of claim 1 wherein said binder solution is aged from 4 to 36 hours prior to contacting the fibers with said solution.

3. The process of claim 1 wherein said phenolic aldehyde resin is of the resol type.

4. The process of claim 1 wherein the phenolic component of the said phenolic aldehyde resin is a polyhydric phenol having hydroxyl groups in a meta position.

5. A method of forming a non-woven fibrous material of enhanced tensile properties without excessive stiffness characteristics, which method comprises: impregnating a non-woven web of cellulosic fibers with a latex binder solution consisting essentially of from 10 to 35 wt. percent of rubbery copolymer of 85 to 99.5 wt. percent of a C₄ to C₈ isoolefin and 0.5 to 15 wt. percent of a C₄ to C₁₄ multiolefin, and a heat-hardenable phenolic formaldehyde resin of the resol type having a molar ratio of the phenolic component to formaldehyde of from 1:1 to 5:1, said solution having a resin concentration of between 0.1 and 0.8 total mole of phenol and formaldehyde per 100 parts of said rubbery copolymer and a pH of between 7.5 and 9.0 and having been aged for a period of time of from 4 to 36 hours prior to impregnation of the fibers; and thereafter, drying said impregnated fibers at a temperature between 130° and 280° F. to provide a fibrous material having from 10 to 50 wt. percent of said binder material.

6. The process of claim 5 wherein said cellulosic fibers are cotton fibers.

7. The process of claim 5 wherein said cellulosic fibers are regenerated cellulose fibers.

8. The process of claim 5 wherein said resin is a phenol formaldehyde resin.

9. The process of claim 5 wherein said resin is a resorcinol formaldehyde resin.

10. The process of claim 5 wherein said isoolefin is isobutylene and said multiolefin is isoprene.

11. A method of forming a non-woven fibrous material of enhanced tensile properties without excessive stiffness characteristics, which method comprises:

impregnating a non-woven web of cotton fibers with a latex binder solution consisting essentially of a rubbery copolymer of from 85.0 to 99.5 wt. percent of isobutylene and from 0.5 to 15 wt. percent of isoprene and a water soluble heat hardenable phenolic formaldehyde resin of the resol type having a molar ratio of the phenolic component to formaldehyde of from 1:1 to 5:1, said solution having a pH of between 7.5 and 9.0 and having been aged for a period of time of from 4 to 36 hours prior to impregnation of the fiber, and thereafter

drying said impregnated fibers in the absence of rubbery copolymer curatives at temperatures of from 130 to 280° F. for from 0.5 to 30 minutes to provide a fibrous material having from 10 to 40 wt. percent

of the rubbery copolymer and resin concentration of between 0.1 and 0.8 total mole of phenol and formaldehyde per 100 parts of the rubbery copolymer.

12. A non-woven fibrous material of enhanced tensile properties without excessive stiffness characteristics, which material comprises non-woven cellulosic fibers and from 10 to 50 wt. percent of a binder consisting essentially of a rubbery copolymer of from 85 to 99.5 wt. percent of a C₄ to C₈ isoolefin and from 0.5 to 15 wt. percent of a C₄ to C₁₄ multiolefin and a phenolic aldehyde resin having a molar ratio of the phenolic component to the aldehyde of from 1:1 to 5:1, said resin being present in a concentration of between 0.1 and 0.8 total mole of phenol and aldehyde per 100 parts of said rubbery copolymer; the said fibrous material having been heated at a temperature between 130° and 280° F.

13. The non-woven fibrous material of claim 12 wherein the phenolic component of the said phenolic aldehyde resin is a polyhydric phenol having hydroxy groups in a meta position.

14. The non-woven fibrous material of claim 12 wherein said resin is a phenol formaldehyde resin.

15. The non-woven fibrous material of claim 12 wherein said phenolic aldehyde resin is of the resol type.

16. The non-woven fibrous material of claim 12 wherein said resin is resorcinol-formaldehyde.

17. The non-woven fibrous material of claim 12 wherein said cellulosic fibers are cotton fibers.

18. The non-woven fibrous material of claim 12 wherein said cellulosic fibers are regenerated cellulose fibers.

19. The non-woven fibrous material of claim 12 wherein said isoolefin is isobutylene and said multiolefin is isoprene.

20. A non-woven fibrous material of enhanced tensile properties and without excessive stiffness characteristics, which material comprises a web of randomly disposed cotton fibers and from 15 to 25 wt. percent of a binder consisting essentially of a rubbery copolymer of from 85 to 99.5 wt. percent of isobutylene and from 0.5 to 15 wt. percent of isoprene and a phenolic formaldehyde resin of the resol type with the molar ratio of the phenolic component to formaldehyde in the resin being from 1:1 to 5:1, said resin being present in a concentration of between 0.1 and 0.8 total mole of phenol and formaldehyde per 100 parts of the rubbery copolymer, the said fibrous material having been heated at a temperature between 130° and 280° F.

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