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3,188,233

NONWOVEN FABRIC PREPARED FROM BUTYL RUBBER LATEX

Kenneth W. Powers, Nixon, and William P. Cain, Linden, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware
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The present invention deals with forming improved nonwoven fabrics. More particularly, it deals with utilizing a butyl rubber latex as a binder while obtaining good strength and durability characteristics in the nonwoven fabric product.

Nonwovens 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 unique nature of nonwoven 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, nonwoven fabrics derive their ultimate strength, drape, etc. largely from the binder system. For example, nonwoven fabrics employing conventional polyvinylacetate as a binder have good tensile properties although they are quite stiff and, thus, unsuitable for use in most wearing apparel.

It has recently been suggested that a latex of butyl rubber be used as a binder for nonwoven fabrics. In contrast to the stiffness of other binder systems, butyl rubber latex has been found to produce a product having good softness and drape characteristics, as well as satisfactory stability. However, the resulting nonwoven fabric has been found to have relatively poor characteristics of strength and durability, such as is measured by tensile and launderability tests.

In accordance with the present invention, means are taught whereby a nonwoven fabric is obtained which simultaneously offers the advantages of good drape and softness, while having excellent strength and durability. More specifically, in accordance with the present invention, the fiber batt is impregnated with a binder system comprising a latex (aqueous dispersion) of butyl rubber, casein, and a melamine-formaldehyde resin. The impregnated fibers, after being subjected to drying, exhibit the above desirable properties. That the present binder system yields such a desirable nonwoven fabric is surprising. As noted previously, the use of butyl latex alone gives a product of relatively poor strength and durability. While the addition of casein improves the strength properties, durability remains unsatisfactory. Moreover, the casein is soluble in water and thus readily tends to be leached from the fabric. Similarly, the use of butyl rubber latex and melamine-formaldehyde resin alone gives an unsuitable product since the melamine-formaldehyde resin is not compatible with butyl rubber. However, the use of all three components, i.e., butyl rubber, melamine-formaldehyde resin, and casein, provides the advantages of each material without incurring their disadvantages. The casein and melamine-formaldehyde resins inter-react. The casein serves to make the melamine-formaldehyde resin compatible with the butyl rubber, while the melamine-formaldehyde resin simultaneously insolubilizes the casein. The combination of a melamine-formaldehyde resin and casein solubilized in the butyl rubber serves to reinforce and increase the durability of the butyl rubber while the butyl rubber serves to plasticize and protect the resin phase.

In general, it is preferred to employ in aqueous dispersion containing all three components to impregnate

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the fiber batt. The combined weight of butyl rubber, casein, and melamine-formaldehyde resin broadly ranges from 5 to 70, preferably 10 to 50, weight percent of the dried nonwoven fabric. The butyl rubber solids generally comprise 4 to 60, preferably 8 to 40 weight percent of the fabric.

The term "butyl rubber" denotes copolymers of a major proportion, e.g., 85 to 99.5 weight percent of a C_4 to C_8 isooolefin 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 $0^\circ C.$ 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 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 C_4 to C_{10} aliphatic, may be emulsified with water, generally in the presence of a salt of a C_8 to C_{18} organic sulfate 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 nonionic 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 $200^\circ F.$ 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 2,595,797.

The melamine-formaldehyde resin employed in the present binder system may, during impregnation, be present in the form of a partially polymerized resin having a low molecular weight, e.g., 200 to 800, a more fully polymerized polymer, or simply in the form of the monomers (all polymerization taking place in situ). While the preferred melamine monomer is melamine itself, various other amino resin forming materials such as urea, alkylated melamines (i.e., methylated or butylated melamine), triazines (i.e., benzoguanamine) and substituted ureas (i.e., ethylene urea) can also be utilized. Melamine resins which have been modified to reduce chlorine retention are especially desirable. While it is preferred to use formaldehyde or its polymers as the second monomer, other water-soluble aldehydes, such as acetaldehyde or furfural, may be substituted wholly or in part for the formaldehyde.

In addition to the melamine-formaldehyde resin, catalysts suitable for promoting further polymerization during drying are also added. Thus the ultimate binder to be used for impregnation may contain 1 to 40 weight percent (based on dry resin weight) of catalyst such as ammonium salts, e.g., ammonium chloride, ammonium sulfate and ammonium nitrate, heavy metal halides such as zinc chloride, amine salts such as hydroxyalkylamine hydrochloride, etc., all of which are well known to promote the polymerization of the melamine-formaldehyde admixture.

In general, it is first necessary to prepare a water solution of casein by cooking it with ammonia or some other basic material, such as borax or sodium hydroxide. Ammonia is preferred since it will be given off during the

drying step. The solution of casein, e.g., 5 to 40% solution, preferably 10 to 30% solution, is then blended with the butyl rubber latex.

While it is preferred to dip the fiber batt in a latex containing all three ingredients, if desired each of the ingredients can be incorporated by individual steps. The butyl rubber solids will normally constitute 1 to 40, preferably 1 to 25, weight percent of the total mixture of binder components, including water, and will comprise 60 to 95 weight percent of the dry binder components. Best results are obtained when, on a solids basis, 5 to 35 parts by weight of casein and 2 to 35, especially 5 to 30 parts by weight of melamine-formaldehyde resin are employed per 100 parts by weight of butyl rubber solids. The molecular ratio of melamine to formaldehyde will generally vary from 1 to 5. The pH of the mixture used for impregnation may vary from 4 to 11, it preferably being 7.5 to 9, but suitable addition of alkaline materials such as sodium hydroxide.

The fiber batt can be any of a wide variety of materials, such as cotton, rayon, synthetic polyester fibers, nylon, acrylonitrile copolymers and hydrocarbon polymer fibers (e.g., polypropylene). It preferably is a cellulosic material such as cotton or rayon. Any of the conventional impregnating methods may be employed, such as padding, spraying, dipping and the like. After impregnation, the fiber batt is dried at elevated temperatures, preferably within the range of 130° to 250° F. The moisture is removed while further polymerization of melamine and formaldehyde takes place. Hot air drying for a period of 0.5 to 30 minutes is normally utilized. The dried batt is then cured for about 1 minute to 30 minutes at a temperature of 280° F. to 350° F.

A typical operation would involve the formation of a 20% aqueous solution of casein by cooking casein with an aqueous solution of ammonia. This is then blended with a butyl rubber latex containing about 50 weight percent rubbery solids. To this admixture is added a partially polymerized melamine-formaldehyde resin and a catalyst of ammonium chloride. The fiber batt, e.g., cotton fibers, is dipped through the binder latex at a temperature of about 30° to 150° F., and then passed through squeeze rollers so that 30 weight percent (based on dried nonwoven fabric) of solids has been added on. The impregnated fiber batt is then subjected to drying at a temperature of 170° F. by hot air drying. It is finally cured for 5 minutes at 300° F. A nonwoven fabric of good drape and softness, as well as improved strength and durability, is thus obtained.

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

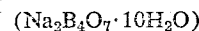
In all of the following examples, a typical butyl rubber latex, hereinafter referred to as "butyl rubber latex A" was employed. Butyl rubber latex A had the following inspection.

- (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 min. at 212° F.)—70–90
Molecular weight—200,000–400,000
- (2) Total solids: 53–55 weight percent (rubber solids 49.8–51.7 weight percent)
- (3) Specific gravity: 0.96 gr./cc. at 70° F.
- (4) pH: 5–6
- (5) Particle size:
0.5 micron (average)
0.05–1 micron (range)

In the following experiments a typical melamine-formaldehyde resin sold under the trade name of Aerotex Resin M-W by the American Cyanamid Company was employed. The melamine-formaldehyde resin was in the form of an 80% active aqueous solution of methylated mela-

mine-formaldehyde condensate having a molecular weight of the order of 400 to 700. A minor portion, e.g., 5%, of a metal halide catalyst was added to the adhesive formulation to catalyze polymerization of the resin.

The casein employed in the following examples was an aqueous solution of casein solubilized with borax. The casein solution was prepared by adding 100 parts by weight of casein to 387 parts by weight of water, heating and then adding 12 parts by weight of borax



and 1 part by weight of a fungicide preservative.

The designation "p.h.r." denotes parts per hundred of rubber based on parts by weight of solids. Thus, 20 p.h.r. of borated casein designates 20 weight parts of casein (not casein solution) per 100 weight parts of butyl rubber solid.

Similarly, the ratios set forth in the following Tables II and III are on the basis of parts by weight of solids to parts by weight of solids, and refer to the ingredient indicated rather than the solution of the ingredient employed.

EXAMPLE 1

The following experiments indicate the unsuitability of butyl latex alone, butyl latex with casein only, and butyl latex with melamine-formaldehyde resin only for obtaining good film properties. In all of the runs indicated in Table I, films approximately 25 mils thick were cast on a glass casting plate, allowed to dry overnight and then cured for 15 minutes at 298° F. Tensile strengths were measured on micro-dumbbells pulled at 5 inches per minute on an Instron tester at 73° F. and 45% R.H. (relative humidity).

Table I
PROPERTIES OF CAST FILMS

Film composition	Properties dry		Properties wet ¹	
	Tensile strength, p.s.i.	Elongation, percent	Tensile strength, p.s.i.	Elongation, percent
Butyl latex.....	26	>2,000	-----	-----
Butyl latex with 20 p.h.r. borated casein.....	200	470	14	>2,000
Butyl latex with 30 p.h.r. melamine-formaldehyde resin.....	(²)	(²)	(²)	(²)
Butyl latex with 30 p.h.r. melamine-formaldehyde resin and 20 p.h.r. borated casein.....	310	<100	185	<100

¹ After 30 minutes immersion in room temperature water.

² Separated on drying, leaving hard brittle resin layer and soft rubber layer. Resin layer cracks immediately on testing.

As shown by the data in Table I, a butyl rubber latex alone gives a film of low strength. A combination of butyl latex and casein exhibits poor wet strength properties whereas the poor compatibility of butyl latex and melamine-formaldehyde resin alone is evidenced by the separation of the film into two layers upon drying.

In contrast, the combination of butyl latex, melamine-formaldehyde resin, and casein exhibited both good wet and dry strength plus overall good compatibility. The above results indicate the necessity of employing a combination of all three ingredients in order to obtain a high-quality product.

EXAMPLES 2 AND 3

To further illustrate the necessity of employing the present three component system as a binder for nonwoven fabrics and to illustrate the superior results obtained thereby, the following experimental studies will be described.

Samples were prepared from the nonwoven fiber batts indicated in Tables II and III by "padding" the binder

into the batt by means of a washing machine wringer. The lower roll of the wringer was wrapped with cheesecloth and dipped into a trough containing the binder having the composition indicated. The batt was fed through the wringer; the binder was picked up by the bottom roll and carried into the nip to saturate the batt. Excess binder was squeezed from the batt and the amount of pick-up was controlled at about 40% by controlling the wringer pressure.

The resulting samples were air-dried and then cured for 15 minutes in a circulating air oven at 300° F.

One inch by six inch samples were cut from the batt (in both the machine and cross-machine directions for the carded batts) and the samples were tested on an Instron tester at a pull of 5 inches per minutes at 73° F. and 45% R.H.

Laundryability was evaluated by washing the samples in a top-loading home automatic washer (1959 Lady Kenmore) using a 15 minute normal wash cycle (30 minute overall cycle) with Wisk detergent and hot wash water at 160° F. Samples were washed with a normal wash load and dried in a home dryer. Properties of the washed samples were measured as for the original samples with laundryability being indicated as a percentage of breaking strength retained after washing.

Table II

PROPERTIES OF NONWOVENS
[5 denier, 2 oz./yd.², random rayon batt]

Binder	Butyl latex	90/10 butyl latex/M.F. resin	80/20 butyl latex/M.F. resin	60/40 butyl latex/M.F. resin	90/10 butyl latex/R.F. resin
Yield strength ¹	1.4	2.9	3.4	3.4	12.3
Breaking strength ²	5.8	8.5	8.8	8.1	24.1
Laundryability, percent breaking strength retained	59	75	79	82	85

¹ Lb. pull/in. width/solids-add-on at inflection point of stress-strain curve.

² Lb. pull/in. width/solids-add-on.

Table III

PROPERTIES OF NONWOVENS
[26 g./yd.² carded rayon batt]

Binder	Butyl latex	Butyl latex 20 p.h.r. casein	Butyl latex with 5 p.h.r. M.F. and 15 p.h.r. casein	Butyl latex with 10 p.h.r. M.F. and 20 p.h.r. casein	90/10 butyl latex/R.F. resin
Yield strength: ¹					
M	4.5	7.0	7.4	13	6.3
CM	0.35	1.9	1.3	2.3	0.8
Breaking strength: ²					
M	1.8	2.6	3.2	3.1	2.5
CM	0.16	0.26	0.56	0.71	0.42
Laundryability, percent breaking strength retained:					
M			72	96	70
CM			63	84	75

¹ Lb. pull/in. width at inflection point of stress-strain curve.

² Lb. pull/in. width/weight in grams of 1" x 6" sample.

³ Disintegrated.

⁴ Varies, disintegrated to 50% retention.

As shown particularly in Table II, butyl latex plus melamine-formaldehyde alone only moderately improves the tensile strength of a nonwoven fabric over that obtained by the use of butyl latex alone, and is not nearly as beneficial as butyl latex in combination with resorcinol formaldehyde. In contrast, Table III illustrates that the use of a combination of butyl latex, casein and melamine-formaldehyde offers a great improvement over the use of butyl latex alone and gives better results than the use of resorcinol formaldehyde. The good strength and laundryability obtained by the use of melamine-formaldehyde, casein and butyl latex, and the lack of a color problem is particularly noted. The use of casein alone with butyl latex does not yield as high strength as the 3-component blend and also is less desirable because it causes greater stiffness. Laundryability is also questionable

without the melamine-formaldehyde present. Some samples disintegrated completely on laundering whereas others retained about 50% of their strength. This is because wet strength of the butyl/casein binder is very low and the batt easily falls apart while wet. However, if it is handled gently enough while wet, it will regain a good portion of its strength upon redrying.

Various modifications may be made to the present invention. For example, other substances may be added to the binder system to exert further control over flexibility, or to add weight, color, stability towards aging, and the like.

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

What is claimed is:

1. A nonwoven fabric comprising a web of fibers impregnated with between about 5 and about 70 wt. percent of a heat cured binder consisting essentially of a rubbery copolymer of a major portion of a C₄ to C₈ isooolefin and a minor portion of a C₄ to C₁₄ multiolefin, between about 5 and about 35 parts, per 100 parts of rubbery copolymer, of casein, and between about 2 and about 35 parts, per 100 parts of rubbery copolymer, of a melamine-formaldehyde resin having a mole ratio of melamine to formaldehyde of between about 1:1 and about 5:1.

2. The nonwoven fabric of claim 1 which contains about 4 to 60 weight percent of rubbery copolymer based on dried nonwoven fabric.

3. The nonwoven fabric of claim 1 which contains, per 100 parts by weight of rubbery copolymer solids, 5 to 35 parts by weight (on a solids basis) of casein and 5 to 30 parts by weight (on a solids basis) of melamine-formaldehyde resin.

4. The nonwoven fabric of claim 1 wherein said fibers are cellulosic fibers.

5. The nonwoven fabric of claim 1 wherein the isooolefin is isobutylene and the multiolefin is isoprene.

6. The nonwoven fabric of claim 1 wherein the fabric is impregnated with between about 10 and about 50 wt. percent of binder.

7. A nonwoven fabric comprising a web of cellulosic

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fibers impregnated with between about 5 and about 70 wt. percent of a heat cured binder consisting essentially of a rubbery copolymer of 85 to 99.5 weight percent of a C₄ to C₈ isoolefin and 0.5 to 15 weight percent of a C₄ to C₁₄ multiolefin; and per 100 parts by weight of rubbery copolymer, 5 to 35 parts by weight of casein and 5 to 30 parts by weight of a melamine-formaldehyde resin having a mole ratio of melamine to formaldehyde of between about 1:1 and about 5:1.

8. The nonwoven fabric of claim 7 which contains about 4 to 60 weight percent of rubbery copolymer based on weight of dried nonwoven fabric.

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9. The nonwoven fabric of claim 7 wherein the isoolefin is isobutylene and the multiolefin is isoprene.

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WILLIAM D. MARTIN, *Primary Examiner*.

RICHARD D. NEVIUS, *Examiner*.