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IMPREGNATED WEB AND METHOD AND COMPOSITION FOR MAKING SAME

Paul M. Goodloe, Gorham, and Louis P. MacKinnon, Berlin, N.H., assignors to Brown Company, Berlin, N.H., a corporation of Maine

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This invention relates to the impregnation of paper to produce products having high tear strength and high wet strength and to a method and impregnating composition for making the same and pertains more specifically to the impregnation of webs made of naturally-occurring cellulosic papermaking fibers, particularly wood pulp fibers, to provide products generally useful for sandpaper backing, pressure-sensitive-tape backing, book-cover stock and the like.

It has hitherto been proposed to impregnate fibrous webs with synthetic polymeric material to provide products useful as tape backings or sandpaper backings. However, the use of natural rubber for impregnating fibrous webs has generally produced unsatisfactory results because of the tackiness of the resulting impregnated product and because of the difficulty of obtaining sufficient impregnation of ordinary paper on account of the large particle size of natural latex. While synthetic rubbery polymers which are of relatively small particle size have been widely used as impregnants for this purpose, they tend to be more expensive than natural rubber, a disadvantage which is particularly noticeable because the cost of the impregnant usually far exceeds the cost of the fibrous web. Furthermore, it has proved to be exceedingly difficult to obtain all of the desired physical properties simultaneously using a synthetic rubber impregnant. For example, it is generally possible to obtain a product of the type described having high wet strength only at a great sacrifice of tear strength.

One object of the present invention is to provide for the impregnation of cellulosic fibrous webs to produce a non-tacky sheet having both high wet strength and high tear strength.

Another object is to provide a method and composition for the impregnation of cellulosic fibrous webs, especially paper webs, to produce non-tacky sheet material suitable for use as sandpaper backing, pressure-sensitive-tape backing, book-cover stock, and the like.

Other and further objects will be apparent from the description which follows.

It has now been discovered that an impregnating composition comprising natural rubber latex in which is dispersed a relatively small proportion of colloidal styrene polymer particles together with a heat-advancing phenolic resin can be employed to impregnate ordinary paper which can then be dried and cured by heating for a relatively short time at a moderate temperature to produce a product which is not only non-tacky, but also possessed of high wet strength and high tear strength simultaneously—a unique combination of desirable physical properties for this type of product. The product possesses in addition the characteristic of forming a firm bond with conventional pressure-sensitive adhesives, which have a natural rubber base, without the interposition of a primer coat. Surprisingly enough, the extent of impregnation is entirely satisfactory even with papers of high compactness despite the fact that one of the ingredients of the impregnating composition, natural latex, has a large particle size which has hitherto made it impossible to obtain adequate impregnation of ordinary wood-pulp paper.

Any ordinary paper made of wood pulp cellulosic fibers may be employed as the base stock in the present invention, including all of the conventional forms of

paper made by any of the usual papermaking processes. Any of the conventional wood pulps may be used for the paper including soda pulp, sulfite pulp, sulfate (kraft) pulp, and semi-chemical pulp. For most purposes kraft paper having a basis weight of 20 to 60 pounds (24 x 36 x 480) is the most desirable base stock. Compactness (defined as basis weight in pounds divided by caliper in mils multiplied by ten) of the paper may vary from 35 to a maximum of 70. It will be appreciated, of course, that the lower the compactness the more easily the paper can be impregnated because of the larger amount of free space present.

The natural rubber latex employed in the impregnating composition may be any of the usual natural rubber latices, although for most purposes centrifuged latex is preferred because of its more uniform properties. It is believed that the uniform large average particle size of centrifuged natural rubber latex, more than 80% by weight of the particles of which have a diameter upwards of 1000 Angstrom units, together with the very low content of non-rubber solids (less than 1.5% by weight) of the natural latex account for the high wet strength of the finished product.

The styrene polymer particles are usually and preferably supplied in the form of a latex which may be mixed with the natural rubber latex in any conventional manner with moderate stirring without coagulation or precipitation. Such latices of non-film-forming styrene polymer particles may be made by any conventional anionic emulsion polymerization procedure which produces an alkaline latex, the polymer particles being of colloidal dimensions having a maximum average diameter of two microns. The relative quantities of styrene polymer particles and of natural rubber present in the impregnating composition may vary over a considerable range, from 5% by weight of styrene polymer based on the weight of the rubber solids to as much as 33% by weight. Best results are usually obtained by employing mixtures containing from 8% to 14%, by weight of the rubber solids, of polystyrene latex solids.

The third essential ingredient of the composition employed for impregnating the fibrous webs is a heat-advancing phenolic resin such as a phenol-formaldehyde resin or a resorcinol-formaldehyde resin. Among suitable resin solutions or dispersions are those made by combining, under alkaline conditions phenol and formaldehyde at a molar ratio from about 1:1 to 1:2 by weight, the condensation being stopped at a point where the resin remains readily soluble or dispersible in water, in which form it is known as a "resole." In the case of resins containing an amount of formaldehyde near the lower end of the range, a material such as hexamethylenetetramine may be added if desired. In the case of resins containing an amount of formaldehyde near the upper end of the range or of resins condensed to an extent slightly beyond the optimum, the addition of a small amount of alkali such as sodium hydroxide may be desirable to improve dispersibility of the resin in water. The solids content of the resin solution or dispersion is usually high, upwards of 60% by weight as supplied, and the solids content of the mixed composition as used for impregnating is usually from 20% to 40% by weight, although higher concentrations up to 50% by weight or more may be used in some cases. The amount of phenolic resin in the composition may vary over a considerable range, from about 1.5% to 15% by weight of the rubber.

Any of the conventional compounding ingredients—such as antioxidants, accelerators, vulcanizing agents, dyes, pigments, etc.—may also be included in the composition.

The mixture of aqueous dispersions which forms the impregnating composition of the present invention, containing natural rubber latex, particles of polystyrene dis-

persed therein and a heat-advancing water-dispersible phenolic resin, may be used for impregnating the paper web in any conventional fashion. One of the most convenient impregnating procedures is that known as tub impregnation in which the web is advanced continuously into and out of a body of the aqueous composition contained in a suitable tub or container, the web being urged beneath the surface of the body by means of suitable rollers or guides, following which it is passed between a pair of squeeze rollers to remove excess impregnating composition. The speed of travel of the web and the pressure between the squeeze rollers is adjusted so as to provide for a pickup such that the impregnated web contains from 10% to 100%, by weight of the paper fibers, of the solids from the impregnating composition. The impregnated web is then dried either in hot air or on steam-heated drying drums and is cured by heating to a moderately elevated temperature, of the order of 250°–350° F. for a short period of time, from about one-half minute to ten minutes. The precise time and temperature employed will depend, as is well known in the art, upon the relative proportions of natural rubber and phenolic resin in the composition, as well as upon the relative weight of impregnant and paper, higher temperatures usually requiring shorter times. The heating to obtain the desired cure may be carried out in the same fashion as the drying step; i.e., by heating either in hot air or preferably in contact with steam-heated drums.

The finished impregnated sheet product is found to have, even at high proportions of impregnant to fibers, a substantially non-tacky surface unlike similar webs impregnated with conventional natural rubber latex compositions. In addition, the finished product is found to have remarkably high wet strength in combination with high tear strength.

The following specific examples are intended to illustrate more clearly the nature of the invention, but not to act as a limitation on the scope thereof.

Example 1

The following composition was prepared, in which the parts are by weight of the solids present in the composition:

	Parts
Centrifuged natural rubber latex	87.5
Aqueous dispersion of finely divided polystyrene (Dow X580.6 latex)	12.5
Alkali condensed phenol-formaldehyde resin dispersible in water	2.0

The natural rubber latex contained approximately 1.5% by weight of the rubber of hydroquinonemonobenzylether as an antioxidant. The impregnating composition was prepared simply by mixing together the three ingredients in the order listed above to give a mixed aqueous dispersion containing approximately 30% total solids by weight.

The impregnating composition described above was employed in a conventional tub impregnator to saturate a kraft paper having a basis weight of 35.5 pounds (24 x 36 x 480) and a caliper of 0.0053 inch. The paper prior to saturation had the following properties:

Mullen, points	20
Gurley densometer, secs./400 cc. (1 ply, 5 oz. cylinder)	14.5
Tear (Elmendorf):	
MD [1]	122
CD [2]	134
Tensile, lb./0.5 in.:	
MD	6.6
CD	2.3
Wet tensile, lb./0.5 in., 0 min. soak:	
MD	0.31
CD	0.15
Stretch, percent at break:	
MD	1.4
CD	1.4

[1] Machine direction.
[2] Cross machine direction.

The saturator was operated so as to give four different levels of pickup on four different samples of the same paper. The impregnated paper samples were then dried and cured for two minutes at 320° F. in a circulating air oven. All samples were then conditioned by allowing them to stand at room temperature for twenty-four hours, after which their physical properties were measured with the following results:

	Percent solids, on wt. of paper fiber	Tensile, lb./in.		Percent stretch		Elmendorf tear		Gurley stiffness	
		MD	CD	MD	CD	MD	CD	MD	CD
A	84	25.7	11.3	2.5	8.3	150	234	7,630	3,920
B	69	25.5	11.3	2.5	8.0	148	219	5,700	3,740
C	50	24.5	10.4	2.5	8.3	144	215	4,550	2,500
D	29	21.1	8.8	2.0	6.3	138	186	1,420	356

All of the impregnated products were non-tacky and exhibited remarkably good bonding to conventional natural-rubber-base pressure-sensitive adhesives without the necessity for any priming coat.

Example 2

An impregnating composition was prepared as described in Example 1 above, except that the relative proportions of ingredients were as follows, in which the parts are by weight of solids:

	Parts
Natural rubber latex	90
Polystyrene dispersion	10
Water-dispersible phenol-aldehyde resin	2

Samples of the same kraft paper as described in Example 1 were saturated with the foregoing composition at four different levels of saturation, and the products were dried and cured as described in Example 1. The physical properties of the finished products were as follows:

	Percent solids, on wt. of paper fiber	Tensile, lb./in.		Percent stretch		Elmendorf tear		Gurley stiffness	
		MD	CD	MD	CD	MD	CD	MD	CD
A	86.0	25.9	12.1	2.5	8.0	183	235	9,250	4,630
B	70.0	26.2	11.0	2.5	7.0	164	232	6,050	4,800
C	49.0	24.0	11.0	2.0	7.3	146	220	4,270	2,670
D	29.6	21.7	9.4	2.0	6.0	146	190	1,950	356

The products exhibited the same good bonding to pressure-sensitive adhesives as did those of Example 1.

Example 3

An impregnating composition was prepared as described in Example 1 having the following composition, in which the parts are by weight of solids:

	Parts
Natural latex	92.5
Aqueous polystyrene dispersion	7.5
Water-dispersible phenol-aldehyde resin	2.0

Samples of the same kraft paper as described in Example 1 above were saturated at four different levels of saturation, dried, and cured as described in Example 1, with the following results:

	Percent solids, on wt. of paper fiber	Tensile, lb./in.		Percent stretch		Elmendorf tear		Gurley stiffness	
		MD	CD	MD	CD	MD	CD	MD	CD
A	85.0	25.7	11.3	2.5	7.0	168	245	7,900	4,180
B	70.5	25.0	11.5	2.3	7.3	154	242	5,500	3,380
C	50.0	28.0	10.5	2.2	7.3	167	230	6,400	2,310
D	29.4	21.1	9.1	2.0	5.3	154	212	1,600	710

Example 4

An impregnating composition was prepared as described

in Example 1 having the following composition, in which the parts are by weight of solids:

	Parts
Natural rubber	95.0
Aqueous polystyrene dispersion	5.0
Water-dispersible phenol-aldehyde resin	2.0

Samples of the same kraft paper as described in Example 1 above were saturated at four different levels of saturation, dried, and cured as described in Example 1, with the following results:

	Percent solids, on wt. of paper fiber	Tensile, lb./in.		Percent stretch		Elmendorf tear		Gurley stiffness	
		MD	CD	MD	CD	MD	CD	MD	CD
A	85.0	26.2	12.5	3.0	8.3	179	242	7,500	4,800
B	69.0	25.1	11.9	2.8	8.5	187	231	6,600	3,556
C	48.2	23.3	10.3	2.3	8.0	167	250	5,080	3,380
D	30.0	20.4	9.5	2.0	6.0	154	209	1,420	445

The wet tensile strength (MD) was determined for those samples of the foregoing products in which the total solids of the impregnating composition was approximately 50% by weight of the weight of the paper fibers, with the following results:

Example	Wet tensile, MD, lb./in.	Wet tensile,[1] percent of dry tensile
1-C	6.8	27.7
2-C	6.3	26.2
3-C	4.6	16.4
4-C	6.4	27.4

[1] Soaked two hours in water at room temperature.

Example 5

The composition of Example 2 above was employed to saturate a creped kraft paper having a basis weight of 30.1 pounds (24 x 36 x 480) and a caliper of 0.0084 inch. The paper prior to impregnation had the following physical properties:

Mullen, points	16
Gurley densometer, secs./400 cc. (2 ply, 20 oz. cylinder)	3
Tear (Elmendorf):	
MD	90
CD	115
Tensile, lb./0.5":	
MD	5.24
CD	2.68
Stretch, percent:	
MD	11.2
CD	3.1
Wet tensile, lb./0.5":	
MD	0.47

The impregnation was carried out at three different levels of saturation for three different samples, which were dried and cured for two minutes at 320° F. The physical properties of the finished product were as follows:

	Percent solids, on wt. of paper fiber	Tensile, lb./in.		Percent stretch		Wet tensile,[1] lb./in. MD	Elmendorf tear	
		MD	CD	MD	CD		MD	CD
A	91	17.3	14.5	14.0	6.3	6.2	180	220
B	70	15.3	14.1	14.1	6.6	4.1	182	218
C	50	14.1	13.7	13.0	5.0	3.9	179	190

[1] Soaked two hours in water at room temperature.

Example 6

The impregnating composition described in Example 3 above was employed to impregnate the kraft paper of Example 5, the product being dried and cured for two minutes at 320° F. The products at three different levels of saturation had the following properties:

	Percent solids, on wt. of paper fiber	Tensile, lb./in.		Percent stretch		Wet tensile,[1] lb./in. MD	Elmendorf tear	
		MD	CD	MD	CD		MD	CD
A	90	16.7	15.6	13.0	7.0	5.4	199	221
B	70	15.8	13.4	12.6	5.0	4.9	180	195
C	51	14.8	14.3	11.3	5.6	5.2	175	195

[1] Soaked two hours in water at room temperature.

Example 7

The paper described in Example 1 was saturated on a commercial saturator with the impregnating composition described in Example 2. The pickup was 51.5% by weight of solids based on the weight of the paper fibers at a speed of 150 feet per minute. The impregnated paper was dried in a conventional festoon drier with loops approximately six feet long. The cure was carried out for ninety seconds at 300°–320° F. The finished product exhibited no tackiness and had the following physical properties.

Tensile:		
MD	lb./in.	27.4
CD	lb./in.	12.4
Stretch at break:		
MD	percent	4.5
CD	do	11.1
Elmendorf tear:		
MD	gms.	148
CD	gms.	208
Gurley stiffness:		
MD	mg.	5502
CD	mg.	2390
Wet tensile[1]:		
MD	lb./in.	15.5

[1] Soaked two hours in water at room temperature.

Although specific embodiments of the invention have been described herein, it is not intended to limit the invention solely thereto, but to include all of the obvious variations and modifications within the spirit and scope of the appended claims.

What is claimed is:

1. An impregnating composition comprising natural rubber latex having dispersed therein from 5% to 33% by weight, based on the weight of rubber solids, of styrene polymer particles and from 1.5% to 5%, by weight of the rubber, of a heat-advancing alkali-condensed phenolic resole.

2. An impregnating composition comprising natural rubber latex having dispersed therein from 8% to 14% by weight, based on the weight of rubber solids, of colloidal polystyrene particles and from 1.5% to 5%, by weight of the rubber, of heat-advancing alkali-condensed phenol-aldehyde resole.

3. A non-tacky impregnated sheet comprising a web of naturally-occurring cellulosic papermaking fibers and from 10% to 100%, by weight of the fibers, of a cured impregnant comprising natural rubber, from 5% to 33% by weight, based on the weight of the rubber, of styrene polymer particles dispersed in said rubber, and from 1.5% to 5%, by weight of the rubber, of an alkali-condensed thermoset phenolic resin.

4. A non-tacky impregnated sheet having high tear strength and high wet strength comprising a web of wood pulp paper and from 10% to 100%, by weight of the paper, of a cured impregnant comprising natural rubber, from 5% to 33% by weight, based on the weight of the rubber, of styrene polymer particles dispersed in said rubber, and from 1.5% to 5%, by weight of the rubber, of an alkali-condensed thermoset phenolic resin.

5. A non-tacky impregnated sheet having high tear strength and high wet strength comprising a web of wood pulp paper and from 30% to 60%, by weight of the paper, of a cured impregnant comprising natural rubber, from 8% to 14% by weight, based on the weight of the rubber, of colloidal polystyrene particles dispersed in said rubber, and from 1.5% to 5%, by weight of the rubber, of alkali-condensed thermoset phenol-aldehyde resin.

6. The method of making sheet material which comprises impregnating a web of wood pulp fibers with a composition comprising natural rubber latex having dispersed therein from 5% to 33% by weight, based on the weight of rubber solids, of colloidal styrene polymer particles, and from 1.5% to 5%, by weight of the rubber, of a heat-advancing alkali-condensed phenolic resole, the amount of the solids of said composition present in the impregnated web being from 10% to 100% by weight of the fibers, drying the impregnated web, and heating the impregnated web to cure said composition.

7. The method of making sheet material having high tear strength and high wet strength which comprises impregnating a web of wood pulp paper with a composition comprising natural rubber latex having dispersed therein from 8% to 14% by weight, based on the weight of rubber solids, of colloidal polystyrene particles, and from 1.5% to 5%, by weight of the rubber, of heat-advancing

alkali-condensed phenol-aldehyde resole, the amount of the solids of said composition present in the paper being from 10% to 100% by weight of the paper, drying the impregnated paper, and heating the impregnated paper to cure the composition.

8. The method of making non-tacky sheet material having high tear strength and high wet strength which comprises impregnating a web of wood pulp paper with a composition comprising natural rubber latex having dispersed therein from 8% to 14% by weight, based on the weight of rubber solids, of colloidal polystyrene particles, and from 1.5% to 5%, by weight of the rubber, of heat-advancing alkali-condensed phenol-aldehyde resole, the amount of the solids of said composition being from 30% to 60% by weight of the paper, drying the impregnated paper, and heating the impregnated paper to cure the composition.

References Cited in the file of this patent

UNITED STATES PATENTS

2,410,078	Kellgren	Oct. 29, 1946
2,601,597	Daniel et al.	June 24, 1952
2,708,645	Norman	May 17, 1955
2,723,207	Hall et al.	Nov. 8, 1955