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FLEXIBLE REINFORCED FIBROUS SHEETING

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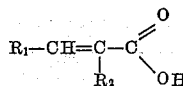
This invention relates to flexible non-woven fibrous sheeting reinforced with acidic copolymer to impart to the non-woven fibrous sheeting high internal bonding strength, resistance to delamination and splitting and to pressure-sensitive tape formed from the acidic copolymer reinforced sheeting. The invention also relates to a flexible non-woven fibrous reinforced sheeting in which the acidic copolymer is cross-linked with cations of a polyvalent metal which forms a basic metallic oxide.

Non-woven fibrous sheeting, as used for pressure-sensitive adhesive tape backing and the like, is composed of short fibers randomly arranged having a high degree of porosity and extremely low wet strength. In order to employ this type of sheeting as a backing for pressure-sensitive adhesive tape, the fibers must be impregnated with a material which is capable of holding the fibers together so as to impart to the sheeting a high degree of bonded strength. This bonded strength provides increased tensile strength and resistance to delamination and splitting. Also, the impregnant must be capable of imparting to the sheeting a high wet strength so that the fibers will hold together under all types of use and be capable of receiving a pressure-sensitive adhesive coating to form tape that can be stored for long periods of time without loss of bonding strength.

This invention provides an improved tape backing in which non-woven fibrous sheeting having low internal strength can be bonded internally and made usable by being impregnated with an acidic copolymer in which the acid portion is polymerized unsaturated monocarboxylic acid or acids. Sheetting impregnated with these acidic copolymers becomes a reinforced sheeting having a high tensile strength, resistance to delamination and splitting, and a high degree of flexibility. The invention also provides for reinforcement of non-woven fibrous sheeting by cross-linking the carboxyl groups present in the acidic portion of the impregnated copolymers with a polyvalent cation, either before impregnation or during the curing of the acidic copolymer which has impregnated the fibrous sheeting.

The acidic copolymers used to produce the improved impregnated non-woven fibrous sheeting of this invention are copolymers formed from the copolymerization of conjugated dienes and/or conjugated chloro-dienes having from 4 to about 10 carbon atoms; the vinyl compounds acrylonitrile, styrene, or esters of acrylic or methacrylic acids formed from aliphatic alcohols having from 1 to

about 10 carbon atoms, and ethylenically unsaturated monocarboxylic acids having the formula:



wherein one of the designations R_1 and R_2 represents a substituent selected from the group consisting of an alkyl radical containing 1 to about 4 carbon atoms, an aryl radical containing 6 to about 9 carbon atoms, a halogen and hydrogen, and the other designation represents hydrogen.

It has been found that advantageously high internal bonding and tensile strength are obtainable with acidic copolymers formed from about 60 to about 95 percent by weight of the conjugated diene, from about 1 to about 28 percent by weight of the vinyl compound, and from about 1.0 to about 40 percent by weight of the ethylenically unsaturated monocarboxylic acid. Internal bonding is a measure of the resistance to delamination and splitting whereas tensile strength, while not directly tied to resistance to delamination, is a measure of the ability of the sheeting impregnated with the acidic copolymer to withstand tensile pull without breaking.

The acidic copolymer impregnating composition discussed above can be prepared by emulsion polymerization by methods known to those skilled in the art of polymerization. Non-woven fibrous sheeting used as a backing for pressure-sensitive adhesive tape, such as Paterson Parchment Paper Co. XL-420 bleached flat paper of Brown Co. 301-M semi-bleached kraft crepe paper, is dipped in the aqueous emulsion of the copolymers formed as described above. Fibrous sheeting before impregnating has a very low wet strength due to the random arrangement of the fibers forming the sheeting. Also this random arrangement provides for a high degree of porosity because of the looseness of the fibers forming the sheeting. The paper typically used for impregnation is "30 basis weight paper" (i.e., the weight of a ream of paper having a sheet size of 24" by 36" and 480 sheets to the ream is 30 pounds).

The dipping of the sheets in the aqueous emulsion saturates the interstices of the fibrous sheeting with the acidic copolymer of the emulsion. This type of paper sheeting becomes quickly fully saturated and effects about 100-percent pick-up of the acidic copolymer. For example, if a sheet of non-woven paper, as heretofore described, weighing 5 grams is immersed in the emulsion and allowed to remain until it has reached full saturation, it picks up approximately 5 grams of solids from the emulsion. The fibrous sheeting or paper web is internally bonded by the bonding together of the fibers by polymer particles deposited in the web from the aqueous emulsion or dispersion during the dipping.

To produce a finished impregnated reinforced saturated paper, the paper is first pressed free of excess impregnating material, such as by passing it through a squeeze roller arrangement. The paper is then further treated

by drying it to remove excess water and desirably bringing about the curing of the acidic copolymer in the sheeting. It has been found that good results are obtained when the sheet is dried at a temperature between 125° and 200° F. The drying time required depends on such factors such as air circulation, drying temperature, and the degree of water to be removed from the paper. It has been found that, with 100% emulsion pick-up using 30 basis weight paper, a drying time of about 5 to about 15 minutes at a temperature of from 125° to 175° F. gives excellent results. Also good results are obtained when lower percentages of pick-up of copolymer are effected, for example, 60 to less than 100 percent by weight of the paper impregnated.

It is apparent to one skilled in the art that by controlling the percentage of pick-up various degrees of internal bonded strength can be produced. For example, by lowering the percentage pick-up of the emulsion there is formed a sheeting having a lower degree of internal bonding. In this way, the internal bonded strength of the sheeting can be varied so that any desired internal strength can be produced. A reinforced sheeting may be made which has the desired internal bonding necessary to meet a particular specification. Non-woven fibrous sheeting so reinforced can be substituted for expensive woven fabric material.

The finished dried impregnated reinforced paper of this invention is internally bonded with acidic copolymer to the extent of from about 30 to about 60 percent by weight of the reinforced sheeting. The amount of acidic copolymer taken into the interstices of the fibrous sheeting depends on the type of material being impregnated and the degree of pick-up as heretofore described. For a 100 percent pick-up of the aqueous emulsion, the dried impregnated sheeting contains about 30 percent by weight of the acidic copolymer when the emulsion contains about 50 percent dry copolymer.

The internal bonding strength of the non-woven fibrous material can also be enhanced by the inclusion in the emulsion of polyvalent cations which form inorganic bases, oxides or hydroxides; organic bases or sodium aluminate. The polyvalent cations react with acidic groups of the copolymer and thus cross-link acidic groups in different chains. This cross-linking, it has been found, can be advantageously accomplished without the use of high drying or curing temperatures.

The internally bonded product produced from the impregnation of non-woven fibers presents many advantages over products previously known and used in the art of impregnating. It has been found that the inclusion of an acid portion in the polymer chain provides an effective reinforcing agent whereas copolymer of otherwise the same composition but not having this acid portion therein had heretofore been found unusable and more expensive polymers were found necessary for the desired results. Additionally, cross-linking the acidic polymer, in accordance with this invention, produces a superior reinforcing agent.

It has also been found that the acidic copolymer reinforced sheeting of this invention retains high internal bonding strength after prolonged exposure at temperatures above 250° F. and below -20° F. Tape bases formed from the impregnated sheeting described above provide a tape backing surface which does not, for many applications, require a tie-coating compound for holding pressure-sensitive adhesive to the tape. Also, release coatings are easily applied and are held firmly to the tape backing of this invention. Rolls of pressure-sensitive adhesive tape made with the reinforced impregnated backing paper set forth in this invention may be stored for long periods of

time without loss of efficiency in tape usage, tensile or internal bonded strength.

The improved impregnated sheeting of this invention, while making excellent tape backing for pressure-sensitive adhesive tapes and the like, has also found utility as a backing for other materials such as sandpaper, waterproof wrapping paper, reinforced non-woven fabric material, and the like.

The acidic copolymer useful in this invention can be prepared conveniently by the polymerization of monomeric materials, in the proportions set forth herein, comprising at least one conjugated diene, low molecular hydrocarbon having from 4 to about 10 carbon atoms, such as butadiene, isoprene and a conjugated chlorodiene having 4 to about 10 carbon atoms such as chloroprene and the like; a vinyl compound, such as acrylonitrile, styrene, or esters of acrylic acid or methacrylic acid formed from aliphatic alcohols having from 1 to about 10 carbon atoms, and with an ethylenically unsaturated monocarboxylic acid. Exemplary of such aliphatic alcohols are methyl, ethyl, butyl, 2-ethylhexyl, octyl and decyl alcohols and the like. Exemplary of such conjugated dienes suitable for use in any of the foregoing described methods involving carboxyl-containing diene polymers include the butadiene-1,3 hydrocarbons such as butadiene-1,3 itself; 2-methyl butadiene-1,3 (isoprene); 2,3-dimethyl butadiene-1,3; 2-neopentyl butadiene-1,3; and other hydrocarbon homologs of butadiene-1,3 and in addition the substituted dienes such as 2-chlorobutadiene-1,3; 2,5-dimethylhexadiene-3,4; the straight chain conjugated pentadienes such as piperylene; the straight and branch-chain conjugated hexadienes and others. In general, dienes containing more than 10 carbon atoms polymerize very slowly, if at all, in present polymerization systems and it is therefore preferred to employ a diene having 10 carbon atoms or less, while dienes having from 4 to 6 carbon atoms have particularly advantageous reaction rates and polymerization characteristics and are much preferred. Exemplary olefinically unsaturated monocarboxylic acids include crotonic acid, alpha-chlorocrotonic acid, isocrotonic or cis-2-butenic acid, hydrosorbic acid, cinnamic acid, m-chlorocinnamic acid, p-chlorocinnamic acid, acrylic acid, alpha-chloracrylic acid, methacrylic acid, ethacrylic acid, vinyl thiophenic acid, alpha-furyl acrylic acid, vinyl furoic acid, p-vinylbenzoic acid, vinyl-naphthoic acid and other polymerizable monoolefinically unsaturated monocarboxylic acids; alpha-isopropenyl acrylic acid, alpha-styryl acrylic acid (2-carboxy-4-phenyl-1,3-butadiene), sorbic acid, alpha-methyl sorbic acid, alpha-ethyl sorbic acid, alpha-chlorosorbic acid, alpha-bromosorbic acid, beta-chlorosorbic acid, alpha-, beta- or gamma-epsilon-dimethyl sorbic acid, 2,4-heptadienoic acid, 2,4-hexadienoic acid, 2,4-pentadienoic acid, alpha-vinyl cinnamic acid, alpha- and beta- vinyl acrylic acids, and other polymerizable poly-olefinically unsaturated monocarboxylic acids.

It is to be understood that the polymerization heretofore described is conducted under such conditions that the ethylenically unsaturated monocarboxylic acid is introduced into the polymer chain, and not under conditions such that the acid undergoes substantial homopolymerization. If the polymerization reaction is allowed to proceed to approximately 100 percent completion, then the ratios of the monomers charged represents the ratio of the polymerized constituents in the polymer chain. By acidic copolymer is meant a copolymer containing carboxyl groups in the polymer chain.

The copolymerization of unsaturated monocarboxylic acids of low molecular weight with non-acidic conjugated dienevinyl monomers is advantageously effected by emul-

sification of the monomers in an acid aqueous medium using emulsifiers stable therein. Suitable emulsifiers include the ethers and esters of polyglycols with aliphatic acids having from 10 to 20 carbon atoms; alkyl sulfonates or sulfates and alkylaryl sulfonates where the alkyl group contains from 10 to 20 carbon atoms, alkylaryl polyether sulfates or sulfated monoglycerides and similar emulsifiers that will occur to those skilled in the art. A particularly effective type of emulsifier has been found to be the amine salts of alkylaryl sulfonates. The polymerization may also include small amounts of stabilizers known to the art. The polymerization reaction may be promoted by the addition of free-radical yielding catalysts such as the alkali persulfates, percarbonates, perborates and the like, organic peracids, such as benzoyl peroxide, acetyl peroxide, and the like, alkyl peroxides such as di-t-butyl peroxide and organic hydroperoxides, such as diisopropylbenzene hydroperoxide. The polymerization mass may also contain small amounts of the sulphydryl-group-containing compounds termed "modifiers" in the synthetic rubber industry, such as alkylmercaptans containing from about 10 to 22 carbon atoms, e.g., n-dodecyl mercaptan, the commercially available mixed tertiary mercaptans containing from 12 to 16 carbon atoms, thiophenol, alpha- or beta-thionaphthol and the like. The polymerization can be effected within a wide range of temperatures; for example, within the range from about 5° C. to about 70° C. The above method conveniently results in the formation of polymer in the form of a latex or suspension of small drops or globules.

The polymerization described above is advantageously effected using an anionic or non-ionic emulsifier in the event that it is desired to neutralize or make alkaline, such as to a pH of about 7 or above, such as up to about 11, the resulting emulsion with a monovalent base without coagulation. Such neutralization results in salt formation by reaction or condensation of the cation of the monovalent base with the carboxylic acid groups of the polymer. Since some latices tend to thicken or swell, probably due to water imbibition, at high pH values, it is frequently desirable to add only enough base to raise the pH of the latex to a value in the lower portion of the alkaline range, generally below about 9. The neutralization may be effected with a volatile or thermally unstable monovalent base, such as ammonia, ethylamine, ethanolamine, morpholine, polymethylbenzyl ammonium hydroxide and the like or a fixed alkali such as NaOH and the like so that, during the drying or curing operation following deposition of the acidic copolymer, the cations of the monovalent base combined with the carboxylic acid groups of the acidic polymer are substantially completely replaced with the polyvalent cations of the cation producing compound incorporated in the aqueous emulsion.

As brought out briefly above, carboxylic acid groups in the polymer may be advantageously cross-linked with polyvalent cations to effect a bridging of carboxylic acid groups in different copolymer chains so that increased strength of internal bonding of the polymer mass is produced. It is believed that this increase in strength results from the formation of salt bridges or cross-links between acidic portions of the individual chains of the copolymers and the consequent interweaving of the mat of fibrous material impregnating sheeting.

Cross-linking of the carboxyl groups in the acidic copolymer with polyvalent metal cations or compounds can be effected in various ways. Thus, the free carboxyl group may react with an appropriate compound of the polyvalent metal, such as an oxide; or a salt of the carboxyl group with a monovalent cation, such as the am-

monium salt, may metathetically react with a salt of the polyvalent metal. Cross-linking to some degree may take place prior to impregnation, but it is felt that the substantial portion of the cross-linking takes place after impregnation when the impregnated sheeting is being dried or cured at elevated temperatures. It has been found that the use of salts, basic oxides, and hydroxides of polyvalent metals, such as zinc, lead, calcium, magnesium, tin, iron, nickel, cobalt, sodium aluminate or organic base and the like, provides cross-linking cations which accomplish a curing of the acidic copolymer to enhance the internal bonding of the fibers in the sheeting without the use of sulfur or sulfur-bearing accelerators or other compounds normally employed in conventional rubber vulcanization systems.

Particularly effective results are also obtained with compounds of polyvalent metals which form strongly basic oxides, such as the readily available and relatively inexpensive bivalent alkaline earth metals, calcium, barium, and magnesium (metals of the group II A of the periodic table) and zinc. Soluble salts such as nitrates, chlorides, acetates, formates and the like, can be employed where the condensation is effected after the sheeting has been impregnated by subjecting the sheeting to a normal drying operation. As stated above, basic metallic oxides can be employed with alkaline latices, the cross-linking or condensation being effected in subsequent operations such as drying or curing. Typical polyvalent cations formed from polyfunctional organic bases are ethylene diamine, tri-ethylene tetramine, tetra ethylene pentamine and the like. The amount of the oxide required for efficient curing obviously varies with the curing agent itself, its fineness and compatibility with the polymer and with the carboxyl content of the polymer. Useful results are obtained when the amount of oxide is equal to the amount chemically equivalent to the carboxyl content of the polymer.

It has been found that about 1.5 to about 5 parts by weight of a sodium aluminate or a polyvalent cation-containing compound or compounds, such as zinc oxide, calcium hydroxide and the like, for each 100 parts of acidic copolymer having about 3 to about 7 percent by weight acid when added to the emulsion produce a cross-linked impregnated non-woven fibrous sheeting with improved internal bonded strength in which a major portion of the carboxyl groups are effectively cross-linked or condensed. Other polyvalent cation producing compounds heretofore described can be used, the amount of compound depending on the amount of acid in the polymer chain and the ratio of the equivalent weight of the compound and the acid constituent.

As those skilled in the art will understand, other methods than those heretofore described may be employed to obtain the emulsion of the acidic copolymer useful in this invention. One such method is to prepare the ester form of the desired polymer, such as by polymerizing a butadiene and an alkyl or aryl ester of an acrylic acid in an alkaline system, and then partially hydrolyzing or saponifying the ester form of the polymer to the free acid form or to the salt form.

The following examples will serve to further illustrate the present invention:

Example I

An aqueous solution consisting of 100 parts of water, an emulsifying agent (4 parts of a sodium salt of an alkylaryl sulfonate), a chelating agent (0.02 part of ethylenediaminetetraacetic acid) and a peroxygen type of catalyst (0.5 part of potassium persulfate) was first placed in the reaction vessel. (Unless otherwise noted, all references to parts or percentages in these examples

refer to parts or percent by weight.) A modifier (0.8 part of mixed tertiary C₁₂ to C₁₆ mercaptans) was then placed in the reaction vessel, followed by 20 parts of acrylonitrile and then 5 parts of methacrylic acid. Small amounts of the ingredients previously charged to the reaction vessel and adhering to the walls of the charging equipment were flushed into the reaction vessel with 100 parts of water, making a total of 200 parts of water. As rapidly as possible thereafter, 75 parts of liquid butadiene was added to the reaction vessel, which was purged to remove air. The reaction vessel was brought to 50° C., the reaction mixture being agitated so as to form an emulsion. When the polymerization reaction had reached approximately 100 percent conversion the agitation was stopped and the unreacted monomers and some water were then removed by vacuum stripping. This produced an emulsion having a solids content of 42.4 percent referred to the weight of total dry solids (based on the total weight of the emulsion). Concentrated (28 percent) ammonium hydroxide was added to the emulsion until a pH of about 7.5 was reached. The neutralized emulsion of the acidic copolymer was stabilized by the addition, with stirring, of 2.0 parts, referred to 100 parts of dry solids, of a potassium salt of a rosin acid. To the emulsion was then added 1.0 part of antioxidant (polyalkyl polyphenol) and 1.0 part of a melamine-formaldehyde resin. This neutralized and stabilized aqueous emulsion of an acidic copolymer (75 percent by weight butadiene, 20 percent by weight acrylonitrile, and 5 percent by weight methacrylic acid) was then ready for use as an impregnating emulsion.

Several emulsions were prepared, in the manner set forth above, containing butadiene, acrylonitrile and methacrylic acid. A highly absorbent strip of non-woven fibrous sheeting (Paterson XL 420, 30 basis weight) was submerged in each emulsion. Each sheet of paper was submerged for a period of about 1 minute until it was completely saturated with the particular emulsion. The impregnated paper was then removed from the emulsion and stripped of excess emulsion by passing the sheets through squeeze rolls maintained under light pressure. After squeeze rolling, the paper was dried at a temperature between 140° and 170° F. for a period of about 10 minutes. Each impregnated reinforced paper was then subjected to a series of tests to determine the degree of internal bonding and tensile strength and elongation produced by the impregnation.

Tests for the internal bonding strength (resistance to delamination) were conducted by taking a sample 1 in. by 8 in. of the impregnated sheeting and sealing a piece of heat-sensitive adhesive cloth-backed tape to the front and back surfaces of the sample. The two pieces of cloth-backed tape were placed in the jaws of a tensile machine and the test sample was separated from the two pieces of cloth-backed tape at the rate of 12 inches per minute, thereby placing a strain on the internal bonding of the paper. The force was continued until the maximum force was reached at which point the delamination was recorded as ounces per inch of width.

Tests for tensile strength of the impregnated paper were conducted by taking a 1 in. by 8 in. sample of the impregnated paper and placing the ends thereof in the jaws of a standard tensile testing machine. The tensile strength was recorded by stretching the paper at the rate of 12 inches per minute and the pounds per inch of width at which the sample failed were recorded as the tensile strength of the sample. In like manner, the percentage of elongation was measured by recording the percentage of elongation which took place before failure of the sample.

The following tables set forth the various acidic butadiene-acrylonitrile copolymers used to impregnate the various papers and the degree of internal bonding and tensile strength and elongation produced by each impregnation:

TABLE I

Physical characteristics and properties of non-woven fibrous tape backing¹ impregnated with an acidic copolymer consisting essentially of butadiene, acrylonitrile, and methacrylic acid

[Composition of Copolymer²]

Butadiene, Wt. Percent	Acrylonitrile, Wt. Percent	Methacrylic Acid, Wt. Percent	Tensile Strength, Mach. Dir., ³ lb./in. width	Elongation, Mach. Dir. Percent	Delamination Occurred at oz./in. width
79	20	1.0	11.4	10.0	48.0
79	20	1.0	14.2	15.8	44.8
79	20	1.0	11.4	10.0	48.0
75	24	1.0	16.3	12.5	41.6
78	20	2.0	12.3	18.4	46.4
78	20	2.0	15.6	10.0	43.2
75	23	2.0	17.2	9.2	41.6
77	20	3.0	15.2	13.3	43.2
77	20	3.0	15.6	10.8	42.4
77	20	3.0	15.0	25.0	52.8
77	20	3.0	16.6	10.0	44.8
77	20	3.0	16.6	10.0	41.6
77	22	3.0	17.8	9.2	44.8
76	20	4.0	16.6	23.3	52.8
75	20	5.0	16.4	11.7	54.5
75	20	5.0	17.9	11.7	46.5
75	20	5.0	17.1	15.8	54.4
75	20	5.0	17.6	14.2	49.6
75	20	5.0	18.2	21.6	48.0
94	1	5.0	13.5	9.2	46.4
73	20	7.0	16.6	18.7	46.4
73	20	7.0	18.0	10.8	47.4
92	1	7.0	16.1	10.0	49.6
89	1	10.0	17.3	10.0	46.4
74	12	14.0	16.8	11.7	41.4
74	8	18.0	19.7	9.2	51.0
74	4	22.0	22.9	7.5	54.2
60	1	39.0	18.2	5.6	54.5
80	20	-----	12.2	8.3	21.8
80	20	-----	11.3	8.3	21.3
80	20	-----	11.4	10.0	17.6

¹ 30 lb. basis weight bleached flat backing paper. Paterson XL 420, 480 sheets to the ream, size 24" x 36".

² Based on dry weight of the elastomer solids.

³ In the machine direction of the paper.

Several emulsions of acidic copolymer were prepared in accordance with the method set forth above, except that a semi-bleached kraft crepe paper of 30 lb. basis weight (480 sheets per ream, sheet size 24" x 36", Brown Company 301-M) was impregnated with the aqueous emulsion.

TABLE II

Physical characteristics and properties of non-woven fibrous tape backing¹ impregnated with an acidic copolymer consisting essentially of butadiene, acrylonitrile, and methacrylic acid

[Composition of the Copolymer²]

Butadiene, Wt. Percent	Acrylonitrile, Wt. Percent	Methacrylic Acid, Wt. Percent	Tensile Strength, Mach. Dir., ³ lb./in. width	Elongation, Mach. Dir. Percent	Delamination Occurred at oz./in. width
73	20	7	26.1	22.5	60.5
75	20	5	22.8	25.8	49.6

¹ 30 lb. basis weight semi-bleached kraft crepe paper. Brown Company 301-M, 480 sheets per ream, sheet size 24" x 36".

² Based on dry weight of the elastomer solids.

³ In the machine direction of the paper.

The data set forth in Tables I and II clearly illustrate the improvement of internal bonding strength produced in non-woven fibrous papers impregnated with the acidic copolymer of this invention over papers impregnated with copolymers not having an acidic group therein. It is to be particularly noted that both the tensile strength and the resistance to delamination of the impregnated papers of this invention are substantially higher and consequently provide a sheeting having more uses and the ability to perform in a better and more efficient manner.

Substitution of methyl methacrylate in place of acrylo-

nitrile in the above acidic copolymer produces similar results.

Each of the papers impregnated with acidic copolymer, when coated with a pressure-sensitive adhesive to form an adhesive tape, stripped from a base without splitting or delamination, and, after periods of storage in

Example II

In the manner described in Example I, several emulsions of acidic copolymers of various monomers were prepared and non-woven fibrous papers impregnated with the various emulsions with the results shown in the following tables:

TABLE III

Physical characteristics and properties of non-woven fibrous tape backing¹ impregnated with an acidic copolymer consisting essentially of isoprene or chloroprene, acrylonitrile or styrene, and methacrylic acid

[Composition of the Copolymer²]

Isoprene, Wt. Percent	Chloroprene, Wt. Percent	Acrylonitrile, Wt. Percent	Styrene, Wt. Percent	Methacrylic Acid, Wt. Percent	Tensile Strength, MD, ³ lb./in. width	Elong., Percent MD ³	Delamination, oz./in. width
75	-----	20	-----	5	17.2	10.0	43.2
-----	75	20	-----	5	17.6	11.7	52.8
-----	75	-----	20	5	18.9	10.0	49.6

¹ 30 lb. basis weight bleached flat backing paper. Paterson XL 420, 480 sheets per ream, size 24" x 36".

² Based on dry weight of the elastomer solids.

³ In the machine direction of the paper.

TABLE IV

Physical characteristics and properties of non-woven fibrous tape backing¹ impregnated with an acidic copolymer consisting essentially of butadiene, acrylonitrile, styrene, and methacrylic acid

[Composition of Copolymer²]

Butadiene, Wt. Percent	Acrylonitrile, Wt. Percent	Styrene, Wt. Percent	Methacrylic Acid, Wt. Percent	Tensile Strength, Mach. Dir., ³ lb./in. width	Elong., Mach. Dir., ³ Percent	Delamination Occurred at oz./in. width
75	20	-----	5	15.8	13.3	60.0
75	15	5	5	15.5	20.0	56.8
75	10	10	5	15.3	20.8	56.0
75	5	15	5	16.6	15.0	52.8
75	-----	20	5	15.9	13.3	54.0
80	-----	20	-----	9.9	5.0	22.4
72	-----	28	-----	10.5	5.8	24.0

¹ 30 lb. basis weight bleached flat backing paper. Paterson XL 420, 480 sheets per ream, size 24" x 36".

² Based on dry weight of the elastomer solids.

³ In the machine direction of the paper.

TABLE V

Physical characteristics and properties of non-woven fibrous tape backing¹ impregnated with an acidic copolymer consisting essentially of butadiene, acrylonitrile and sorbic acid, acrylic acid, or cinnamic acid

[Composition of Copolymer²]

Butadiene, Wt. Percent	Acrylonitrile, Wt. Percent	Sorbic Acid, Wt. Percent	Acrylic Acid, Wt. Percent	Cinnamic Acid, Wt. Percent	Tensile Strength, MD ³ lb./in. w.	Elong., Percent MD ³	Delamination, oz./in. w.
75	20	5	-----	-----	16.3	11.7	40.0
75	20	-----	5	-----	16.0	11.7	40.0
75	20	-----	-----	5	13.1	12.5	41.6

¹ 30 lb. basis weight bleached flat backing paper. Paterson XL 420, 480 sheets per ream, size 24" x 36".

² Based on dry weight of the elastomer solids.

³ In the machine direction of the paper.

rolled form, maintained the same quality and improved tensile and internal bonding strength.

As in Example I, the above papers impregnated with 75 an acidic copolymer show an improved degree of in-

ternal bonding strength and tensile strength over papers impregnated with copolymers not having acid groups therein.

Each of the papers impregnated with the above acidic copolymers, when coated with a pressure-sensitive adhesive to form an adhesive tape, strips from a base without splitting or delamination, and do not deteriorate after long periods of storage in rolled form.

The results given in both Examples I and II show the high degree of internal bonding strength and tensile strength produced in non-woven fibrous sheeting by impregnation with an acidic copolymer having a monocarboxylic acid portion. It has also been found that non-woven fibrous sheeting impregnated with the acidic copolymer in which the acid constituent (carboxyl group) is cross-linked with polyvalent cations provides an improved reinforced sheeting having high internal bonding strength and tensile strength. This cross-linking is accomplished without the use of sulfur-bearing accelerators or other compounds of a type normally employed in conventional rubber curing processes.

The following example serves to illustrate the improved impregnated sheeting in which a major portion of the acid groups are cross-linked:

Example III

Acidic copolymer emulsions were prepared in accordance with the procedure set forth in Example I, containing 3.5 parts of zinc oxide per 100 parts of acidic copolymer thoroughly mixed throughout. Table VI sets forth a comparison of the internal bonding strength, elongation, and tensile strength of paper impregnated with each type of emulsion.

TABLE VI

Physical characteristics and properties of non-woven fibrous tape backing¹ impregnated with an acidic copolymer consisting essentially of butadiene, acrylonitrile, and methacrylic acid in the ratio of 73:20:7, and having added 3.5 parts of zinc oxide per 100 parts of copolymer, as compared with acidic copolymer without zinc oxide

Zinc Oxide p.p.h.	Tensile Strength, Mach. Dir., ² lb./in. width	Elongation, Mach. Dir., ² percent	Delamina- tion Oc- curred at oz./in. width
-----	14.8	4.2	46.4
-----	14.0	3.8	52.8
-----	11.3	3.5	41.6
3.5	21.6	4.2	52.0
3.5	19.5	4.2	46.4
3.5	18.8	4.7	43.2

¹ 30 lb. basis weight bleached flat backing paper. Paterson XL 420, 480 sheets per ream, size 24" x 36".

² In the machine direction of the paper.

Acidic copolymer emulsions of varying monomer composition were prepared in accordance with the procedure given in Example I, except that 2.0 parts of sodium aluminate per 100 parts of copolymer were thoroughly mixed throughout some of the aqueous emulsions. Table VII sets forth the weight ratios of the constituents forming the acid copolymer, the degree of internal bonding strength and tensile strength produced in each impregnated paper using the cation-containing emulsion, and a comparison with papers impregnated with acidic copolymers not employing cation cross-linking made as set forth in Example I.

TABLE VII

Physical characteristics and properties of non-woven fibrous tape backing¹ impregnated with an acidic copolymer consisting essentially of butadiene, acrylonitrile, and methacrylic acid, and having added 2.0 parts of sodium aluminate per 100 parts of copolymer, as compared with acidic copolymer without sodium aluminate

BD/AN/MAA Ratio	Sodium Aluminate p.p.h.	Tensile Strength, Mach. Dir., lb./in. width	Elong., Mach. Dir., percent	Delamina- tion Oc- curred at oz./in. width
73:20:7	-----	19.7	8.3	44.6
73:20:7	-----	14.9	9.2	48.0
75:20:5	-----	16.9	11.7	46.4
73:20:7	2.0	23.7	7.5	54.4
73:20:7	2.0	21.3	7.5	52.8
75:20:5	2.0	24.0	7.5	59.2

¹ 30 lb. basis weight bleached flat backing paper. Paterson XL-420, 480 sheets per ream, size 24" x 36".

² In the machine direction of the paper.

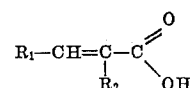
The above results clearly show that paper impregnated with emulsions, in which cross-linking of the acid portion of the polymer chains with sodium aluminate, has increased tensile strength over papers impregnated with copolymers which are not cross-linked.

Papers impregnated with the cross-linked acidic copolymer, when used as backing for pressure-sensitive adhesive tape, exhibit high internal bonding strength and resistance to splitting and delamination when stripped from a base surface. Also, storage in rolled form for extended periods of time causes no deterioration of the strength of these papers.

Although the present invention has been described with particularity with reference to preferred embodiments and various modifications thereof, it will be obvious to those skilled in the art, after understanding the invention, that various changes and other modifications may be made therein without departing from the spirit and scope of the invention and the appended claims should therefore be interpreted to cover such changes and modification.

We claim:

1. A flexible non-woven fibrous reinforced sheeting having high degree of internal bonding throughout the interstices of the fibers comprising a thin web of fibrous sheeting internally bonded by the bonding together of the fibers by polymer particles deposited in the web from an aqueous emulsion of an acidic copolymer, said copolymer forming about 30 to about 60 percent by weight of the internally bonded sheeting and consisting essentially of a copolymer of from about 60 to about 95 percent by weight of at least one polymerizable conjugated diene compound selected from the class consisting of conjugated dienes and conjugated chloro-dienes having from 4 to about 10 carbon atoms; from about 1 to about 30 percent by weight of at least one polymerizable vinyl compound selected from the group consisting of acrylonitrile, styrene, esters of acrylic and methacrylic acids formed from aliphatic alcohols having from 1 to about 10 carbon atoms; and from about 1 to about 40 percent by weight of at least one polymerizable ethylenically unsaturated monocarboxylic acid having the formula:



- wherein one of the designations R₁ and R₂ represents a substituent selected from the group consisting of an alkyl radical containing 1 to about 4 carbon atoms, an aryl radical containing 6 to about 9 carbon atoms, a halogen and hydrogen and the other designation represents hydrogen.

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2. The flexible non-woven reinforced fibrous sheeting claimed in claim 1 in which the ethylenically unsaturated monocarboxylic acid is sorbic acid.

3. The flexible non-woven fibrous reinforced sheeting claimed in claim 1 in which the ethylenically unsaturated monocarboxylic acid is acrylic acid.

4. The flexible non-woven fibrous reinforced sheeting claimed in claim 1 in which the ethylenically unsaturated monocarboxylic acid is cinnamic acid.

5. The flexible non-woven fibrous reinforced sheeting claimed in claim 1 in which the vinyl compound is styrene.

6. The flexible non-woven fibrous reinforced sheeting claimed in claim 1 in which the vinyl compound is acrylonitrile.

7. The flexible non-woven fibrous reinforced sheeting claimed in claim 1 in which the vinyl compound is methyl methacrylate.

8. The flexible non-woven fibrous reinforced sheeting as claimed in claim 1 in which conjugated diene compound is butadiene.

9. The flexible non-woven fibrous reinforced sheeting as claimed in claim 1 in which conjugated diene compound is isoprene.

10. The flexible non-woven fibrous reinforced sheeting as claimed in claim 1 in which conjugated chloro-diene compound is chloroprene.

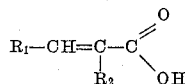
11. A flexible non-woven fibrous reinforced sheeting having a high degree of internal bonding throughout the interstices of the fiber comprising a thin web of fibrous sheeting, said sheeting internally bonded by the bonding together of the fibers by polymer particles deposited in the web from an aqueous emulsion of a copolymer, said copolymer forming about 30 to about 60 percent by weight of the internally bonded sheeting and consisting essentially of a copolymer having from about 60 to about 95 percent by weight of butadiene; from about 1 to about 30 percent by weight of at least one polymerizable vinyl compound selected from the group consisting of acrylonitrile, styrene and methyl methacrylate; and from about 1 to about 40 percent by weight of ethylenically unsaturated monocarboxylic acid selected from the group consisting of methacrylic acid, acrylic acid, sorbic acid and cinnamic acid.

12. The flexible non-woven fibrous reinforced sheeting claimed in claim 11 in which the vinyl compound is acrylonitrile and the ethylenically unsaturated monocarboxylic acid is methacrylic acid.

13. A flexible non-woven fibrous reinforced sheeting

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having high degree of internal bonding throughout the interstices of the fibers comprising a thin web of fibrous sheeting internally bonded by the bonding together of the fibers by polymer particles deposited in the web from an aqueous emulsion of an acidic copolymer, said copolymer forming about 30 to about 60 percent by weight of the internally bonded sheeting and consisting essentially of a copolymer of from about 60 to about 59 percent by weight of at least one polymerizable conjugated diene compound selected from the group consisting of conjugated dienes and conjugated chloro-dienes having from 4 to about 10 carbon atoms; from about 1 to about 28 percent by weight of at least one polymerizable vinyl compound selected from the group consisting of acrylonitrile, styrene, esters of acrylic and methacrylic acids formed from aliphatic alcohols having from 1 to about 10 carbon atoms; and from about 1 to about 40 percent by weight of at least one polymerizable ethylenically unsaturated monocarboxylic acid having the formula:



wherein one of the designations R_1 and R_2 represents a substituent selected from the group consisting of an alkyl radical containing 1 to about 4 carbon atoms, an aryl radical containing 6 to about 9 carbon atoms, a halogen and hydrogen and the other designation represents hydrogen; and at least a major portion of the carboxylic groups of the acidic copolymer cross-linked with polyvalent cations.

14. The flexible non-woven fibrous reinforced sheeting claimed in claim 13 in which at least a major portion of the carboxylic groups of said acidic copolymer is cross-linked with a cation formed from zinc oxide.

15. The flexible non-woven fibrous reinforced sheeting claimed in claim 13 in which at least a major portion of the carboxylic groups of said acidic copolymer is cross-linked with sodium aluminate.

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