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COPOLYMERS OF CONJUGATED DIOLEFINS AND PARTIAL ESTERS OF UNSATURATED POLYBASIC ACIDS

Robert R. Brown and George F. Schmidt, Dover, Del., assignors to Standard Brands Chemical Industries, Inc., Dover, Del., a corporation of Delaware

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This invention relates to latex compositions of certain conjugated diolefinic copolymers exhibiting enhanced fiber bonding properties and improved unified non-woven fibrous articles such as fiborus webs or mats internally bonded, with said conjugated diolefinic copolymers.

More particularly, the invention relates to latices of copolymers comprising conjugated diolefins and partial esters of unsaturated polybasic acids, and to flexible non-woven fibrous sheeting, such as paper, non-woven fabrics, and the like, containing these copolymers. In a more specific aspect, this invention relates to impregnated paper backing sheets suitable for fabrication into pressure-sensitive adhesive tapes and the tapes so produced, such sheets being characterized by unexpected development of unusually high wet strength and a high resistance to delamination of the paper backing in combination with other desirable properties.

Heretofore, both natural and synthetic polymer latices have been used in impregnation or saturation of non-woven fibrous materials to convert these materials into useful articles by bonding of the fibers to provide internal strength and develop other specific properties, such as wet strength. The term "non-woven fibrous materials" as used herein, refers to a mat, web or sheet of fibers which has been laid down by mechanical, pneumatic, electrical, or vacuum means, or otherwise deposited. The typically open, highly porous, and unbonded structure of webs or mats made of such fibrous materials inherently has little or no resistance to delamination, splitting and tearing. In many applications of bonded, non-woven fibrous materials, it is essential that the internal bond strength be highly developed in order to avoid splitting or delamination of the fiber structure when subjected to the stresses of normal use. The internal bond strength should also be retained after storage under normal conditions. In addition, the ability of such impregnated or saturated fibrous masses to tolerate pigmentation with retention of high internal bond strength; to exhibit good elongation characteristics, resistance to oils and solvents, and non-discoloration are often necessary or desirable properties for the many end-product forms of such fibrous materials.

Heretofore, various general purpose synthetic copolymer latices have been applied as bonding agents for unification of non-woven fibrous sheeting. One example of such application has been the saturation of paper backing for pressure-sensitive adhesive tapes. In practice, however, the copolymers heretofore employed have had limitations as impregnants. For example, it has been customary to substantially completely saturate the sheeting with latex impregnant to achieve satisfactory internal bond strength and thus improve delamination resistance. In practice, such saturation generally involved about 50 to 100 percent impregnation (expressed as percentage by weight of dry latex solids to weight of dry fiber). While this practice resulted in the satisfactory improvement of internal bond strength, it was also found that use of said saturants resulted with the concomitant disadvantage of a stiffening effect with a lack of conformability in the sheeting being impregnated. The disadvantage of stiffness in sheeting which should be conformable to uneven surfaces is readily apparent. In contrast, the present invention provides high internal bond strength; with lower copolymer latex content and without the accompanying undesirable effect of stiffness.

In accordance with the present invention, it has been found unexpectedly that non-woven fibrous articles having highly improved internal bond strength are obtained by unifying the fibrous materials with latices comprising copolymers of conjugated diolefins with certain partial esters of unsaturated polybasic acids. It has also been found that utilization of the latices of this invention provide an impregnant composition for saturating fibrous materials wherein resulting product has the characteristics of improved tensile strength (wet and dry), elongation, edge tear, as well as the above-mentioned resistance to delamination.

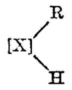
The copolymers particularly suitable for use in the unifying compositions of this invention are prepared from monomeric materials at least predominantly comprising one or more aliphatic conjugated dienes and, preferably, one or more ethylenically unsaturated monomers copolymerizable with the diene. As used herein, the term "ethylenically unasturated monomers" includes copolymerizable monoolefinic monomers and is to be construed as excluding conjugated dienes, but may include other polyolefinic monomers.

The monomeric aliphatic conjugated dienes suitable for use include the butadiene-1,3 hydrocarbons such as butadiene-1,3 itself; 2-methyl butadiene-1,3 (isoprene); 2,3-dimethyl butadiene-1,3; piperylene; 2-neopentyl butadiene-1,3; and other hydrocarbon homologs of butadiene-1,3. In addition, the substituted dienes, such as 2-chloro butadiene-1,3; 2-cyano butadiene-1,3; the straight chain conjugated pentadienes; the straight chain and branch chain conjugated hexadienes, and the like, are found suitable. In general, dienes containing more than 10 carbon atoms polymerize very slowly, if at all, in the present polymerization systems; consequently, it is preferred to employ a diene having ten carbon atoms or less. Dienes having from 4 to 6 carbon atoms have particularly advantageous reaction rates and polymerization characteristics and, therefore, are preferred. The butadiene-1,3 hydrocarbons, and butadiene-1,3, in particular, are preferred.

In addition to the two essential types of monomers (that is, the conjugated dienes and the partial ester of an unsaturated polybasic acid), the monomer mixture to be polymerized may also contain one or more interpolymerizable monoolefinic monomeric materials. The monoolefinic monomer, which together with the aliphatic conjugated diene constitutes a major portion of the monomeric material for directly preparing the copolymers useful in the latices of this invention, may be any such monomer which is copolymerizable with the diene. Such monoolefinic monomers are well known in the art and are indicated by typical monomers set forth below. In particular, the monoolefinic monomer is characterized as one which contains an activated carbon-to-carbon double bond, that is, a monomer containing an olefinic double bond which readily functions in an addition polymerization reaction because of the olefinic double bond being present in the monomer molecule either in the alpha-beta position with respect to a stronger polar or functional group, such as nitrile, carboxylic ester, halogen, keto, amide, and other such groups well known in the art as activating groups, or because it is adjacent to a terminal methylene group, that is, $CH_2=C<$. Among the monoolefinic monomers copolymerizable with the dienes in aqueous dispersion and characterized by the presence of such groups are the aliphatic unsaturated nitriles, such as the lower molecular weight nitriles, acrylonitrile, alpha-chloro acrylonitrile, methacrylonitrile, ethacrylonitrile; the low molecular weight alcohol esters of acrylic and substituted acrylic acids, such as methyl methacrylate, methyl acrylate, methyl ethacrylate, butyl methacrylate, isobutyl dichloro acrylate, and other acrylic esters of alcohols, preferably having from one to six carbon atoms; styrenes, such as styrene itself, halo, cyano, alkyl, aryl, and other substituted styrenes, for example vinyl toluene, alpha methyl styrene, alpha chloro styrene, p-cyano styrene, p-phenyl styrene; other polymerizable vinyl compounds, such as vinyl naphthalene, vinyl pyridine, vinyl ethers and ketones; and other compounds such as vinylidene chloride.

It is preferred to employ copolymerizable monoolefinic monomers selected from the group consisting of nitriles, styrenes, and lower molecular weight alcohol esters of acrylic and alpha-substituted acrylic acids.

The partial esters of unsaturated polybasic acids employed in this invention may be prepared from unsaturated acids having two or more carboxylic groups or the anhydrides thereof. Preferably the partial esters employed are the "half esters" or monoesters prepared from unsaturated acids containing two carboxylic groups. The monoesters of dibasic acids which are suitably employed have the structural formula:



wherein X represents the acid residue of a dibasic acid having from 4 to 8 carbon atoms and preferably from 4 to 5 carbon atoms and R represents an alkyl radical having from 1 to 2 and most preferably 1 carbon atom, and wherein the R group may be substituted on either of the carboxylic groups of the acid residue. Non-limiting examples of the acids suitable for use include fumaric, maleic, glutaconic, citraconic, itaconic, mesaconic, aconitic, and the like, with fumaric, maleic, and itaconic acids being preferred. It will be appreciated that as used herein the term "unsaturated polybasic acid" includes in addition to the acids exemplified above, dimers, trimers and like condensation products of unsaturated monocarboxylic acids having two or more carboxyl groups, e.g., dimers and trimers of methacrylic acid.

In accordance with this invention, the R group is advantageously an alkyl radical of two carbon atoms and preferably one carbon atom, inasmuch as partial esters containing a greater number of carbon atoms in the alcohol portion thereof do not exhibit the enhanced fiber bonding properties of the partial esters of this invention. For reasons of economy and ease of preparation, as well as for the above reasons set forth, the monomethyl ester of itaconic acid is preferred. This monoester is prepared simply by refluxing methanol with itaconic acid in the presence of small amounts of an esterification catalyst, such as sulfuric acid, paratoluene sulfonic acid, cation exchange resins containing sulfonic acid groups, and the like.

The unexpectedly high internal bond strength is advantageously obtainable with a relatively small content of partial ester of an unsaturated polybasic acid in the diene copolymer and effective amounts may be as low as about 0.5 percent by weight based on the total monomer charge. On the other hand, the partial ester content in the copolymer may be much higher, if desired. For example, suitable polymers have been prepared containing as high as about 20 percent by weight of such partial ester content based on the total monomer charge. For many applications, however, little is to be gained above about 10 percent by weight of partial ester based on the total monomer charge.

In accordance with this invention, it is also contemplated to utilize the copolymer latices herein described in admixture with other copolymers, such as diene-nitrile and diene-styrene copolymers and other copolymers containing carboxyl groups derived from monocarboxylic acids such as diene-nitrile-methacrylic acid, diene-styrene-methacrylic acid copolymers. In the case of such blends, due to the high internal bond strength developed by the diene-partial ester copolymers, substantial amounts of the other copolymers, e.g., up to about half of the mixture, may be utilized without undue decrease in the development of this property in the impregnated fibers.

In certain applications such as unified paper backing for pressure-sensitive adhesive tape or other flexible nonwoven unified sheeting, it is particularly desirable to enhance the elongation properties of the article. In accordance with this invention, therefore, it has been found possible to provide such desirable elongation in combination with adequate tensile strength and excellent internal bond strength by the inclusion in the monomer mixture of relatively small quantities of a strength imparting monomeric material such as acrylic and substituted acrylic acid and other copolymerizable ethylenically unsaturated monocarboxylic acids, such as crotonic acid, alpha-chlorocrotonic acid, hydrosorbic acid, cinnamic acid, m-chlorocinnamic acid, p-chlorocinnamic acid, acrylic acid, alpha-chloroacrylic acid, methacrylic acid, ethacrylic acid, vinyl thiophenic acid, alphafuryl acrylic acid, vinyl furoic acid, p-vinylbenzoic acid, vinyl-naphthoic acid, 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-chloro sorbic acid, alpha-bromo sorbic acid, beta-chloro sorbic 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, and alpha- and beta-vinyl acrylic acids.

Generally, small amounts of the monocarboxylic acids (about 0.5 percent) are effective for this purpose and, advantageosuly, the amount need be no more than about 5 percent by weight of the total monomer mixture and their use in the invention is not dependent on any particular diene content or the presence of a nitrile in the copolymer.

The synthetic copolymer latices utilized in this invention are also advantageously compatible with various resins used in compounding, such as wet strength resins well known to those skilled in the art, for example, melamine-formaldehyde. Also, in many instances in the preparation of unified paper backings for adhesive tapes, sandpaper backing, masking tape, printing tape, waterproof wrapping paper, and the like, the impregnated material is subjected to temperatures encountered in drying and in subsequent heat treatment. Such procedures are advantageous in the various applications of the present invention in that the internal bond strengths developed are usually enhanced rather than impaired.

The amounts of monoolefinic and diolefinic monomeric materials advantageously may vary within very wide limits. Thus, the invention provides for the preparation of copolymers from monomeric mixtures of from about 20 to about 90 percent by weight of the conjugated diene and from about 10 to about 75 percent by weight of the total monomer charge of one or more of the monoolefinic monomers, the combined weight of these two monomeric materials being a major portion of the total monomeric mixture. As mentioned, the partial ester of an unsaturated polybasic acid employed in the direct emulsion copolymerization of the copolymer economically constitutes from about 0.5 to about 20 or more percent by weight of the monomer charged since it has been found that the major advantages of this invention can be achieved with such amounts. It is a distinct advantage of the invention that the fiber bonding properties of the copolymers are obtainable with relatively small quantities of partial esters of unsaturated polybasic acid.

The copolymerization of the copolymers is advantageously effected by emulsification of the monomers in an acid aqueous medium using emulsifiers which are 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 alkaryl sulfonates where the alkyl group contains from 10 to 20 carbon atoms; alkaryl 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 sodium salts of alkaryl sulfonates. The polymerization system may also include small amounts of stabilizers also known to the art. If desired, the polymerization reaction may be promoted by the addition of free radical yielding initiators such as the alkali persulfates, percarbonates, perborates, and the like; organic peroxides, such as benzoyl peroxide, acetyl peroxide and the like; alkyl peroxides such as di-t-butyl peroxide; and organic hydroperoxide such as di-isopropyl benzene hydroperoxide. Redox systems of initiation may be employed utilizing the above-mentioned substances with suitable reducing agents well known in the art. The monomeric reaction mixture may also contain small amounts of the sulfhydryl-group-containing compounds termed modifiers in the synthetic rubber industry such as alkyl mercaptans containing from about 10 to 22 carbon atoms, for example, 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 of from 40° to about 175° F. The above method conveniently results in the formation of polymer in the form of a latex or suspension of small drops or globules.

It may be desirable to introduce the partial ester, preferably, the monoester of an unsaturated dibasic acid, to the remaining monomer mixture gradually during the course of the polymerization reaction rather than in a single charge prior to the time of initiation in order to provide greater homogeneity of the composition of the polymer chain with respect to the amount and distribution of the carboxylic acid groups. The synthetic latex thus prepared is ready for use as a non-woven fibrous material saturant or impregnant without the necessity of neutralization. Alternatively, the polymerization may also be effected using well-known anionic or nonionic emulsifiers followed by neutralizing or alkalizing of the latex, for example with ammonium hydroxide, to pH 7 or above without coagulation and with retention of the enhanced adhesiveness and fiber bonding property.

It is advantageous, in terms of ease of copolymerization and for the development of the highest internal bond strengths to select certain ranges (expressed as percent by weight of the monomer mixture) for the diene and preferred monoolefinic monomers charged to the mixture of monomeric materials for said polymerization. For instance, nitriles such as acrylonitrile when copolymerized in amounts of from about 10 to about 45 percent, preferably about 15 to about 35 percent, with at least about 50 percent of the diene provide high internal bond in the impregnated fibers with excellent oil and solvent resistance. With styrene and substituted styrenes, amounts of from about 10 to about 75 percent, preferably about 15 to about 70 percent, may advantageously be used. It is to be understood, however, that lesser quantities of any of these preferred monomers may be present when more than one is utilized. In general, the larger the total amount of such monoolefinic monomers, the greater the increase in plastic properties and decrease in elastomeric properties of the copolymer with development of high tensile strength and lower elongation. Thus, with various combinations of the monoolefinic monomers, unique combinations of properties may be imparted to the fibrous articles impregnated with these copolymers while producing internal bond strength heretofore unobtainable with either general or special purpose synthetic latices which do not contain the monoester of an unsaturated polybasic acid in the polymer.

As stated above, one of the outstanding advantages obtained in the unification of non-woven fibrous articles with the partial ester-containing diene copolymer latices is the unusually high internal bond developed. For instance, paper saturated with such copolymers at about 50 to about 100 percent saturation (or pickup) level exhibited internal bond strength measured by resistance to delamination as high as 50 percent greater than those obtained with copolymer saturants employing modifying monomers known to the art. In practical application, a major advantage of the invention is the ability to use a lower degree of saturation of the fibers, for example 50 percent pickup, while still obtaining internal bond strength comparable to those obtainable with higher total saturation, that is 95 to 100 percent pickup, with butadiene-nitrile and butadiene-styrene latex saturants containing no partial esters of unsaturated polybasic acids.

In addition to this improvement, the copolymer latices employed in this invention permit the development of unique combinations of properties with the high internal bond strength which are not obtainable with the ordinary synthetic latices when used as saturants. Among those which have not heretofore been mentioned are the retention of high internal bond strength with pigmentation, high elongation with retention of internal bond strength and tensile strength, resistance to oils, solvents and discoloration on exposure ultraviolet light, and in some tape applications, the avoidance of a tie or primer coat for securing the pressure-sensitive adhesives to bonded fibrous backing, depending on the particular copolymer employed.

The fibrous masses may have a suitable copolymer content imparted by impregnation, such as dip saturation of preformed webs or sheets or by beater addition of an aqueous dispersion of copolymer directly to the fibers prior to formation of any web or sheeting. In these processes, the copolymer is deposited from an aqueous dispersion onto the fibers and within the interstices of the open porous web or sheeting.

The dispersions for impregnation may be acid, that is, they may be used after acid polymerization without neutralization or, if desired, they may be neutralized prior to impregnation of the fibrous articles while still retaining the enhanced adhesiveness and fiber binder properties. Where the carboxylic acid groups are formed from, or introduced into, the preformed copolymer, the copolymerization of the diene and the comonomer is effected in an acidic aqueous medium. The pH employed in the preparation of the latices is preferably from about 2 to 5. To provide a finished, internally bonded saturated web or sheeting, the material is freed of excess saturant usually by passing through squeeze rolls or the like, and it is then subjected to a drying operation.

In general, the polymer content on a dry solids basis may be from about 30 percent to about 60 percent by weight of the dry unified web or sheeting. For a particular polymer, the internal bond strength varies with polymer content. This corresponds approximately to 40 to 150 percent saturation or pickup (based on the dry weight of the fibrous material before impregnation).

It is also advantageous in the practice of the invention to subject the unified fibrous article to heat treatment for short periods of time at elevated temperatures, such as from about above 150° F. up to about 400° F., the time of heat treatment preferably decreasing with increasing temperatures. This enhances the internal bond strength of the article.

The copolymer latices of the invention are further illustrated in the following examples and their application to unified paper backings, e.g., creped masking tape base, rope tape stock, low-tensile flatback base, etc., The backings being internally bonded with the copolymers deposited from aqueous dispersions. It is to be understood, however, that the invention has application to various fibrous masses, webs, flexible and rigid sheeting, and other fibrous articles which are customarily internally bonded, including non-woven textile fabrics made with fibers such as cotton, rayon, nylon, polyester, and other natural and synthetic fibers. Accordingly, the examples are not to be construed as a limitation of the invention but merely illustrative of specific embodiments. Unless otherwise noted, all references to parts or percentages in these examples refer to parts or percent by weight.

Example I

An aqueous solution consisting of 150 parts of water, an emulsifying agent (4 parts of sodium salt of dodecyl benzene sulfonate), a chelating agent (0.04 part of ethylene diamine tetra acetic acid), a peroxygen type initiator (0.1 part of potassium persulfate), and a modified (0.9 part n-dodecyl mercaptan) was placed in a reaction vessel along with 65 parts of butadiene, 20.1 parts of acrylonitrile, 12 parts of styrene and 2.9 parts of monomethyl itaconate. The reaction vessel was initially brought to 125° F. and then raised to 160° F. after 4 hours; the reaction mixture being agitated so as to form an emulsion. After 7.5 hours, i.e., after the polymerization reaction had reached approximately 95 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 total solids content of 42–45 percent expressed in weight of dry solids based on the total weight of the emulsion. It was observed that no appreciable floc was formed, either during polymerization or stripping and concentrating. Concentrated (28 percent) ammonium hydroxide was added to the emulsion until a pH of about 8.5 was reached. To the latex was then added, 1.0 part of a non-staining antioxidant (a polyalkyl polyphenol) referred to 100 parts of dry solids.

Example II

Various half ester-containing copolymer latices were prepared in the manner set forth in Example I with variations in the monoolefinic monomer utilized in the copolymer. The composition of each of the copolymers is indicated in the following table in terms of percentage by weight of the various monomers charged.

Sheets of creped masking tape base (Duracel 301M) were submerged in each of the copolymer latices. Each sheet was dipped for a period sufficient to obtain complete saturation of the tape base with the latex. The impregnated sheets were then withdrawn from the latex and excess latex removed by passing the sheets through squeeze rolls maintained under light pressure. After squeeze rolling, the impregnated paper was dried at a temperature of about 220° F. for a period of about 5 minutes to produce a paper having a polymer content of 75 percent on a dry basis of the weight of the untreated masking tape base. This paper was cured for about one minute at about 375° F. The paper sheets were then subjected to a series of tests to determine the tensile strength (both wet and dry), internal bond strength represented as delamination resistance, and elongation properties developed by the impregnation with the particular copolymer. As indicated, comparison tests were performed utilizing synthetic latex saturants containing equivalent amounts (based on carboxyl content) of monomethyl itaconate, itaconic acid, and methacrylic acid. As further indicated, the polymer types included commercial butadiene-acrylonitrile copolymers with two different compositions, and butadiene-styrene copolymers. The copolymers employed in the comparisons were prepared by well-known methods of emulsion polymerization. The description of the polymerization recipes employed in each of the tests performed on polymers referred to, "Nitrile," "Styrene" and "Low-Acid Nitrile" polymers, is set forth below in tabular form.

DESCRIPTION OF POLYMERIZATION RECIPE

NITRILE POLYMERS

Monomers	Variation		
	MMI	IA	MAA
Butadiene	75	75	75
Acrylonitrile	20	22.7	22
Itaconic Acid		2.3	
Monomethyl Itaconate	5.0		
Methacrylic Acid			3.0

The following other ingredients are identical in all three recipes.

Water	150
Emulsifier [1]	4.0
Sequestrene AA [2]	0.04
Potassium Persulfate	0.1
Sulfole [3]	0.6

STYRENE POLYMERS

Monomers	Variation		
	MMI	IA	MAA
Butadiene	75	75	75
Styrene	20	22.7	22
Itaconic Acid		2.3	
Monomethyl Itaconate	5		
Methacrylic Acid			3

The following other ingredients are identical in all three recipes.

Water	150
Emulsifier [1]	4.0
Sequestrene AA [2]	0.04
Potassium Persulfate	0.1
Sulfole [3]	0.6

LOW-ACID NITRILE POLYMERS

Monomers	Variation		
	MMI	IA	MAA
Butadiene	65	65	65
Acrylonitrile	20.1	21.7	21.3
Styrene	12	12	12
Itaconic Acid		1.3	
Monomethyl Itaconate	2.9		
Methacrylic Acid			1.7

The following other ingredients are identical in all three recipes.

Water	150
Emulsifier [1]	4.0
Sequestrene AA [2]	0.04
Potassium Persulfate	0.1
Sulfole [3]	0.9

[1] Emulsifier—Sodium salt of dodecyl benzene sulfonate.
[2] Sequestrene AA—Ethylene diamine tetraacetic acid.
[3] Sulfole—Tertiary dodecyl mercaptan.

Internal bond tests: Internal bond strength is determined by measurement of resistance to delamination of the polymer impregnated sheets. The test is identified as the Permacel Tape Corporation Ply Adhesion Test. Such tests were conducted by taking sample sheets and sealing heat sensitive adhesive cloth backed tape to the front and back surfaces of the sample. The sample was reduced to 1 inch by 8 inches in size and placed in the jaws of a tensile machine. By operation of the machine, the two outer pieces of cloth backed tape were pulled apart at the rate of 12 inches per minute and the splitting or delamination of the impregnated paper sheet took place. The force required to continue the failure of the sheet by splitting or delamination was measured on a tensile testing machine (a Thwing-Albert Tensile machine with a recording device) and this measured force was reported as the internal bond strength of the saturated paper in ounces per inch of width of test sample.

Tests for tensile strength of the impregnated paper were conducted by taking 1 inch by 8 inch samples 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 in the machine direction of the paper and the pounds per inch of width at which the sample failed in tension were recorded as the tensile strength of the sample. In like manner, the percentage elongation was measured by recording the percentage of elongation which took place before failure of the sample, the elongation being measured in the machine direction (MD) and cross direction (CD) of the paper sheet.

In the following tables, the results of the tests of the above properties of the impregnated paper sheets are recorded. The composition of the copolymer saturant is indicated in the percentage by weight of the total monomer charge.

The following abbreviations are provided for simplifying tabular identification of the particular monomer employed:

AN=acrylonitrile
BD=butadiene
IA=itaconic acid
MAA=methacrylic acid
MMI=monomethyl itaconate
MBI=monobutyl itaconate
MMM=monomethyl maleate

TABLE 1.—PHYSICAL PROPERTIES OF CREPE MASKING TAPE BASE IMPREGNATED WITH VARIOUS CARBOXYLIC-CONTAINING COPOLYMERS

[75% pickup; cured 1 minute at 375° F.]

	Reactive Carboxylic Monomer		
	MMI	IA	MAA
Nitrile Polymer:			
MD Tensile (lbs./inch)	16.7	16.3	14.2
MD Elongation (percent)	22	22	22
Delamination Resistance (oz./inch)	78	70	53
MD Wet Tensile (lbs./inch)	11.3	8.7	8.2
MD Wet Elongation (percent)	25	28	25
Styrene Polymer:			
MD Tensile (lbs./inch)	18.4	15.6	13.1
MD Elongation (percent)	22	22	20
Delamination Resistance (oz./inch)	70	62	43
MD Wet Tensile (lbs./inch)	12.5	9.3	5.0
MD Wet Elongation (percent)	27	25	23
Low-Acid Nitrile Polymer:			
MD Tensile (lbs./inch)	13.1	13.6	13.5
MD Elongation (percent)	25	23	27
Delamination Resistance (oz./inch)	72	69	56
MD Wet Tensile (lbs./inch)	8.2	7.6	5.4
MD Wet Elongation (percent)	27	27	23

From the foregoing data, it is readily apparent that in all cases delamination resistance of the paper impregnated with the monomethyl itaconate-containing copolymers was highly superior to that developed by the copolymers employing itaconic acid or methacrylic acid, even where a lower weight percent of the active carboxylic monomer was employed. The copolymers employing the monomethyl itaconate were vastly superior in delamination resistance as well as wet tensile strength.

Example III

The advantage of the invention which permits development of good delamination resistance as well as wet tensile strength is further illustrated in Table 2 below. The latices of the copolymers of butadiene-acrylonitrile and butadiene-styrene prepared in Example II with the addition of monomethyl itaconate, itaconic acid, or methacrylic acid were again employed for purpose of comparison. Sheets of rope tape stock were impregnated and dried with the latices in the manner above-described so as to obtain 80 percent weight of dry latex solids based on the weight of dry untreated paper. The samples were then subjected to the tests for delamination resistance, elongation and tensile strength with the following results:

TABLE 2.—PHYSICAL PROPERTIES OF ROPE TAPE STOCK BACKINGS

[80% pickup; cured one minute at 375° F.]

	Reactive Carboxylic Monomer		
	MMI	IA	MAA
Nitrile Polymer:			
MD Tensile (lbs./inch)	41.1	40.0	34.8
MD Elongation (percent)	12	10	10
Delamination Resistance (oz./inch)	78	64	59
MD Wet Tensile (lbs./inch)	27.0	24.1	19.2
CD Wet Elongation (percent)	15	15	12
Styrene Polymer:			
MD Tensile (lbs./inch)	40.5	36.2	30.9
MD Elongation (percent)	9	9	9
Delamination Resistance (oz./inch)	69	46	50
MD Wet Tensile (lbs./inch)	17.5	20.6	17.5
MD Wet Elongation (percent)	12	15	13
Low-Acid Nitrile Polymer:			
MD Tensile (lbs./inch)	32.7	34.6	32.2
MD Elongation (percent)	10	13	12
Delamination Resistance (oz./inch)	78	64	69
MD Wet Tensile (lbs./inch)	23.5	22.5	18.5
MD Wet Elongation (percent)	15	13	12

It is evident from the above data that, with the same number of equivalents of carboxyl groups, i.e., derived from monomethyl itaconate, itaconic acid, and methacrylic acid, the monomethyl itaconate provides excellent physical properties in comparison with the other reactive carboxylic monomers. This is amply illustrated by the impressive increase in delamination resistance and wet strength values.

Example IV

The superior elongation characteristics of the copolymer latices prepared in Example II when used in base papers made with a low degree of fiber bonding is shown in Table 3.

TABLE 3.—PHYSICAL PROPERTIES EMPLOYING LOW TENSILE FLAT BACK BASE PAPER*

[50% pickup; cured 1 minute at 375° F.]

	Reactive Carboxylic Monomer		
	MMI	IA	MAA
Nitrile Polymer:			
MD Tensile (lbs./inch)	13.3	12.0	13.1
CD Tensile (lbs./inch)	7.4	7.1	7.2
MD Elongation (percent)	15	10	10
CD Elongation (percent)	23	20	20
Delamination Resistance (oz./inch)	50	42	34
Styrene Polymer:			
MD Tensile (lbs./inch)	14.0	12.4	11.2
CD Tensile (lbs./inch)	8.2	7.1	6.2
MD Elongation (percent)	10	10	9
CD Elongation (percent)	20	17	12
Delamination Resistance (oz./inch)	50	32	32
Low-Acid Nitrile Polymer:			
MD Tensile (lbs./inch)	11.5	11.4	11.5
CD Tensile (lbs./inch)	6.7	6.7	6.6
MD Elongation (percent)	17	15	13
CD Elongation (percent)	28	25	23
Delamination Resistance (oz./inch)	53	34	34

*28 lb./ream (500 sheets, 24-inch x 36-inch per ream).

Example V

The development of improved edge tear in rope base sheets employing latices comprising monomethyl itaconate in comparison with itaconic acid and methacrylic acid in butadiene-acrylonitrile copolymers is demonstrated in Table 4 below. The copolymer latices were prepared according to Example II except the polymers containing itaconic acid or monomethyl itaconate each contain the same number of equivalents of carboxyl groups while the methacrylic acid variation does not; it containing considerably greater amounts (5:3).

TABLE 4

	75/20/5 BD/AN/MMI	75/22.7/2.3 BD/AN/IA	75/20/5 BD/AN/MAA
MD Tensile (lbs./inch)	45.7	45.0	45.5
MD Elongation (percent)	7.5	7.5	7.5
CD Elmendorf (grs.)	183	170	179
Delamination Resistance (oz./inch)	69	61	56
CD Edge Tear* (lbs.)	44.0	33.7	37.0
Delamination—No Cure (oz./inch)	58	43	43

*Finch Edge Tear Test-(Tappi) Standard Method T470m-54.

From the foregoing data, the advantages emanating from the use of the copolymer latices of this invention are apparent. This is evidenced by the above improvement in edge tear as well as the accompanying improvement in delamination resistance with no decrease in the other properties.

Example VI

A series of experiments was effected in an effort to illustrate the superiority of the use of monomethyl itaconate polymers over monobutyl itaconate. The compositions of the polymers and the base papers employed are set forth below, along with the comparative data resulting from such experiments.

TABLE 5.—PROPERTIES OF MONOBUTYL ITACONATE POLYMERS

[In a creped masking tape base, containing some wet strength resin; 100% pickup and cured 1 minute at 190° C.]

	75/20/5 BD/AN/MMI	75/20/5 BD/AN/MBI
MD Tensile (lbs./inch)	21.0	20.2
CD Elmendorf (grs.)	85	101
Delamination Resistance (oz./inch)	67	59
MD Wet Tensile (lbs./inch)	15.6	11.3
CD Edge Tear (lbs.)	26.7	25.6
Delamination—Uncured (oz./inch)	61	48
[In rope paper, 90% pickup; cured 1 minute at 400° F.]		
MD Tensile (lbs./inch)	39.0	30.3
CD Elmendorf (grs.)	232	188
Delamination Resistance (oz./inch)	80	64
CD Edge Tear (lbs.)	40.5	35.0

The superiority in wet tensile, bonding strength especially in the uncured state, etc., of the monomethyl itaconate is evident from a comparison of the properties outlined above.

Example VII

A series of experiments was effected in order to illustrate the operability of the monoesters of maleic acid in the latices of this invention. The compositions of the polymers and the base papers employed are set forth below in tabular form. The results are compared with monomethyl itaconate-containing latices.

TABLE 6.—PROPERTIES OF MONOESTERS OF MALEIC ACID

[In creped masking tape base; 100% pickup cured 3 minutes at 175° C.]

	75/20/5 BD/AN/MMI	75/20/5 BD/AN/MMM
MD Tensile (lbs./inch)	19.7	19.0
MD Elongation (percent)	22	20
CD Elmendorf (grs.)	83	85
Delamination Resistance (oz./inch)	93	88
MD Wet Tensile (lbs./inch)	10.3	8.9
MD Wet Elongation (percent)	22	18
CD Edge Tear (lbs.)	33.2	28.5
Delamination—Uncured (oz./inch)	62	62

It will be apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, and therefore it is not intended to be limited except as indicated in the appended claims.

What is claimed is:

1. An impregnating composition characterized by enhanced adhesiveness and fiber-bonding properties, comprising a stable latex consisting essentially of an aqueous dispersion of a copolymer prepared by emulsion polymerization in an aqueous acid medium of a monomeric mixture containing about 20 to about 84.5 percent by weight of butadiene-1,3, from about 0.5 to about 20 percent by weight of monomethyl itaconate, and a balance of from about 10 to about 75 percent by weight of at least one monoolefinic monomer copolymerizable with said butadiene and selected from the group consisting of nitriles, styrenes and lower molecular weight alcohol esters of acrylic or alpha-substituted acrylic acids; the monomeric mixture containing at least about 50 percent by weight of said butadiene when the monoolefinic monomer is a nitrile.

2. The composition of claim 1, in which the copolymer is prepared from a monomeric mixture containing from about 50 to about 75 percent by weight of butadiene-1,3, from about 0.5 to about 10 percent by weight of monomethyl itaconate, and the balance being from about 15 to about 35 percent by weight of acrylonitrile.

3. The composition of claim 1, in which the copolymer is prepared from a monomeric mixture containing from about 20 to about 75 percent by weight of butadiene-1,3, from about 0.5 to about 10 percent by weight of monomethyl itaconate and the balance being from about 15 to about 70 percent by weight of styrene.

4. A fibrous article comprising a non-woven fibrous mass with high resistance to delamination, said mass being internally bonded with from 30 to 60 percent by weight of an impregnating composition comprising a copolymer prepared by emulsion polymerization of a monomeric mixture containing from about 20 to about 84.5 percent by weight of an aliphatic conjugated diene having from four to ten carbon atoms, from about 0.5 to about 20 percent by weight of a partial alkyl ester of itaconic acid, the alkyl portion of the ester containing from 1 to 2 carbon atoms and a balance of from about 10 to about 75 percent by weight of at least one monoolefinic monomer selected from the group consisting of nitriles, styrenes and lower molecular weight alcohol esters of acrylic or alpha-substituted acrylic acids; the monomeric mixture containing at least about 50 percent by weight of said diene when the monoolefinic monomer is a nitrile.

5. The fibrous article of claim 4, in which the copolymer is prepared from a monomeric mixture containing from about 50 to about 75 percent by weight of butadiene-1,3, from about 0.5 to about 10 percent by weight of monomethyl itaconate and a balance of from about 15 to about 35 percent by weight of acrylonitrile.

6. The fibrous article of claim 4, in which the copolymer is prepared from a monomeric mixture containing from about 20 to about 75 percent by weight of butadiene-1,3, from about 0.5 to about 10 percent by weight of monomethyl itaconate and a balance of from about 15 to about 70 percent by weight of styrene.

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GEORGE F. LESMES, *Primary Examiner.*

JOHN T. GOOLKASIAN, *Assistant Examiner.*

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Disclaimer

3,422,050.—*Robert R. Brown*, and *George F. Schmidt*, Dover, Del. COPOLYMERS OF CONJUGATED DIOLEFINS AND PARTIAL ESTERS OF UNSATURATED POLYBASIC ACIDS. Patent dated Jan. 14, 1969. Disclaimer filed Mar. 31, 1971, by the assignee, *Standard Brands Chemical Industries, Inc.*

Hereby enters this disclaimer to claims 1 and 2 of said patent.

[*Official Gazette June 15, 1971.*]