March 31, 1959 H. J. BARTH 2,880,186

COMPOSITIONS CONTAINING NATURAL RUBBER AND A CARBOXYL-CONTAINING DIENE POLYMER, A FILM THEREOF, AND METHOD OF MAKING SAME

Filed April 16, 1954

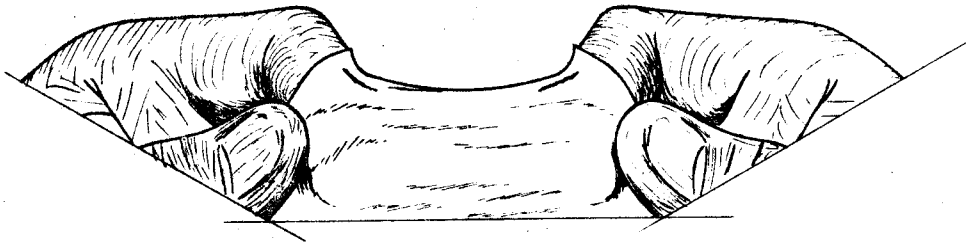


Fig. 2

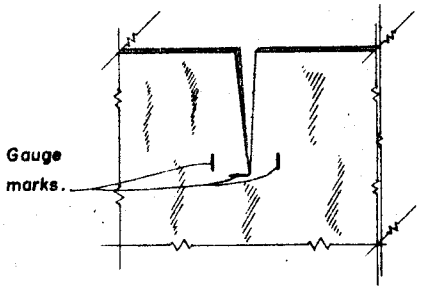



Fig. 1

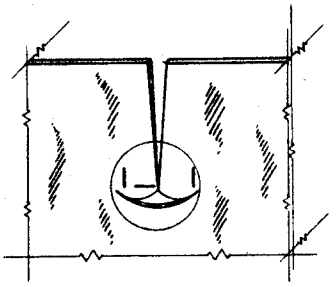


Fig. 3

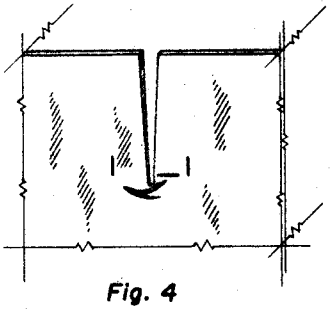


Fig. 4

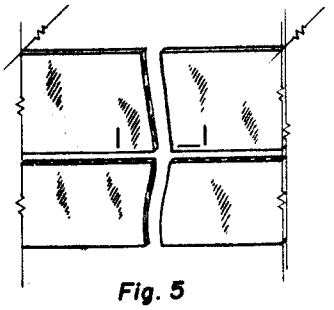


Fig. 5

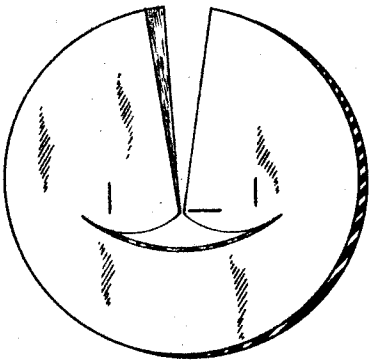


Fig. 6

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2,880,186

# COMPOSITIONS CONTAINING NATURAL RUBBER AND A CARBOXYL-CONTAINING DIENE POLYMER, A FILM THEREOF, AND METHOD OF MAKING SAME

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20 Claims. (Cl. 260—5)

The present invention relates to elastomeric materials or compounds and is particularly concerned with elastomeric material that can be employed to produce strong elastic films that have improved service life. Such films can be conveniently fabricated by depositing such elastomeric material on a form and curing the film so deposited.

The process of depositing natural rubber from latex on a shaped dipping form so as to form a shaped elastic film, band or sheet has been widely employed to produce a variety of useful products, such as gloves, tobacco pouches, overshoes, sheets, shower caps, girdles, baby pants and the like, commonly referred to as deposited latex products or dipped rubber goods.

These products have been satisfactory, as proven by customer acceptance, and have been made additionally attractive to the consuming public by many worthwhile improvements. In an endeavor to further improve these products, studies have been made of the factors influencing their durability or service life. Such studies have shown that tear resistance is a major factor in the service life of products that are frequently manually stretched or placed under considerable tension in use. Typical of such products are those used as garments, such as girdles or baby pants. Since such a garment is designed or selected to hug or confine the person of the wearer, it is unavoidably stretched a considerable amount during the act of putting it on or removing it. If the wearer carelessly or hurriedly imposes a high local stress by stretching the garment with a single thumb or finger or nicks or cuts the film with a sharp fingernail or ring, a line of tear under tension is initiated. Due to the inherent characteristics of a deposited natural rubber latex film, such a line of tear is propagated rapidly as a straight line. Since further propagation of this line of tear requires considerably less force than the force necessary to initiate the tear, the garment, under such conditions, is apt to split or tear for several inches and is thereby rendered useless. Attempts to overcome the low resistance to tear propagation of deposited natural rubber latex films by variations in compounding or by the use of fillers and the like have been unsuccessful or resulted in serious loss of elasticity. Moreover, as is well known, conventional methods used to reinforce milled rubber stocks, such as the addition of carbon black, do not impart effective tear resistance to deposited natural rubber latex films.

The problem of improving the resistance to tear propagation or initiation has been seriously hampered by the lack of satisfactory test methods. Methods analogous to those used for testing the tensile properties of films (such as by stretching a dumb-bell shaped specimen that has been nicked) give results that are contradictory to the simple test where a nicked sheet is pulled apart by hand. This lack of an adequate method has been subject of comment in the scientific literature (see, for example, articles discussing this situation by W. F. Busse in "Industrial and Engineering Chemistry," volume 26, page 1194 (1934) and B. L. Davis, "Transactions of the Institute of the Rubber Industry," volume 14, page 242 (1938)).



It has now been found that films having high resistance to tear propagation and/or initiation can be prepared from mixtures of natural rubber and polymeric material which contains polar functional groups that, in the deposited latex film, are cross linked, such as by a polyfunctional material of opposite polarity. In accordance with the present invention, mixed latices or emulsions of natural rubber and acidic vinyl polymers, which acidic polymers typically contain between about 0.01 to 0.1 acid equivalents per 100 parts of dry polymer, have been found to yield deposited latex films which, when the acid groups of the polymer are cross linked through a polyvalent ion or compound, have improved resistance to tear propagation and/or initiation and which are characterized by a tear pattern substantially different from that of a film produced from natural rubber latex. (The term "polymer" is used herein only for synthetically prepared materials and is not applied to the natural polymer obtained from trees or plants. The natural polymer is referred to herein as natural rubber.)

As stated above, when the film of deposited natural rubber latex is nicked and manually pulled apart, a generally straight line of tear propagates from the nick and continues unimpeded when moderate force or stress is applied and even continues to the opposite boundary of the film unless the stress is removed or relaxed. In contrast, when the deposited latex films of the present invention are similarly treated, the film is substantially "tear-proof" and little, if any, rupture occurs when moderate force is applied so as to cause an elongation equal to or even greater than that normally encountered in use; i.e., of the order of 200 to 300 percent elongation. When the film is further elongated by the application of increasingly greater force, the cut propagates or extends at the most a short distance as a straight line at the end of which is a small arcuate tear transverse to the straight line. (This behavior is referred to herein as "arcuate tear" for brevity.) Often the straight portion of the tear is insignificant in length, such as less than $\frac{1}{16}$ of an inch, and the nick or cut terminates virtually immediately in the arcuate tear. In general, no further tearing occurs when the original stress is continued or even when greater stress is applied. Although occasionally repetition of the arcuate tear occurs, there is no further propagation as a straight line. Consequently a nick or cut in films of the present invention does not spread or run under conditions of use and a garment made of such a film remains useful even though nicked, cut or torn. Additionally, it has been found empirically that films clearly exhibiting the arcuate tear characteristic resist manual initiation of a tear in the absence of a nick or cut to a considerably greater extent than do films exhibiting the unimpeded straight line tear characteristic. Service tests by typical wearers of deposited latex garments have confirmed this superiority.

This arcuate tear characteristic has been found to occur, in accordance with the present invention and explained more fully below, in films deposited from latex comprising natural rubber and acidic vinyl polymers blended in ratios generally in the range of about 2.5 to about 50 parts by weight of natural rubber to 1 part by weight of acidic polymer when the acidic groups of the polymer are properly cross-linked. It has been further found that such an arcuate tear characteristic is exhibited by films prepared by deposition of blends of natural rubber and a wide variety of carboxyl-containing vinyl copolymers in which the acidic polymer is cross-linked or condensed with a polybasic cation, such as the cation of a polyvalent metal. Additionally, it has been

found that alkaline natural rubber latices, e.g., ammoniated latices, are compatible with and form blends suitable for dipping with latices or emulsions of such acidic polymers when the latter are neutralized or made alkaline with a volatile monovalent base, such as ammonia. Effective compatibility and dipping characteristics have been found to result when the acidic vinyl polymer contains from about 0.01 to 0.1 acidic equivalents of carboxylic acid groups (—COOH groups) per 100 parts by weight of polymer with particularly advantageous results in the range of about 0.02 to about 0.08 acidic equivalent.

Suitable acidic vinyl polymers for use in the present invention include carboxyl-containing vinyl elastomers prepared from monomeric material comprising at least one polymerizable 1,3-diene monomer and at least one polymerizable monomer containing one or more functional groups, which groups are either free carboxylic acid groups or are convertible to salts of carboxyl groups with volatile monovalent bases. Suitable acidic vinyl polymers can also be prepared by the introduction of the proper amount of carboxylic acid groups, by known reactions, into vinyl polymers lacking these groups.

Acidic vinyl polymers useful in the present invention can be prepared conveniently by polymerization of monomeric material comprising at least one polymerizable 1,3-diene monomer, such as 1,3-butadiene, and an olefinically unsaturated carboxylic acid, such as methacrylic acid or maleic acid. Such polymerizations should be conducted under conditions such that the olefinically unsaturated carboxylic acid is introduced into the polymer and not under conditions such that the unsaturated carboxylic acid undergoes substantial homopolymerization.

The copolymerization of many unsaturated acids, such as acrylic acids of low molecular weight, with non-acidic vinyl monomers is advantageously effected by emulsification 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-radial 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 sulfhydryl-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 5° to 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 so that the resulting emulsion of acidic vinyl polymer can be neutralized or made alkaline, such as to a pH of about 7 or above, such as up to about 11, 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 so that, during the drying or curing operation following deposition of latex from the blended latices of acidic vinyl polymer and natural rubber described below, the cations of the monovalent base combined with the carboxylic acid groups of the acidic polymer are substantially completely replaced with the polyvalent cation of a compound incorporated in the blended latices before and/or during and/or after deposition. This substitution of a polyvalent cation for a monovalent cation results in cross-linking the acidic vinyl polymer and is believed to be the basis of the unusual characteristics of the film so produced.



After neutralization of the acidic vinyl polymer with the monovalent base, the resulting latex may be stabilized, such by adding a small amount of lauryl sulfate. The neutralized acidic vinyl polymer latex is then blended, such as by stirring or agitating, with an alkaline latex of natural rubber. Such compositions are referred to herein as blended latex or latex blends. Suitable natural rubber latices are commercial latices having dry rubber solids contents, based on 100 parts by weight of latex, of between about 30 to 70 weight percent, and preferably in the upper portion of this range. Such latices may be produced by known methods and stabilized in the alkaline range by a volatile monovalent base of the type described above, such as ammonia. Those skilled in the art will understand that care should be employed in the preparation and blending of the two types of latices so that the pH of the resulting blend is not in a region where either latex is unstable in the compounded state. As will be described more fully below, suitably compounded blended latices of natural rubber and acidic vinyl polymer can be used for the preparation of films in the form of shaped articles by depositing one or more layers of such a blended latex on a shaped dipping form of the type disclosed in U.S. Patent 2,015,632, issued September 24, 1935, to A. N. Spanel.

As brought out briefly above, carboxylic acid groups in the polymer are condensed, either during or after deposition of a film from the blended latex of natural rubber and acidic vinyl polymer, with a polyacidic cation or basic radical, typically a cation of a polyvalent metal that forms a basic oxide or a polyamine, such as diethylene triamine. Such condensation results in a considerable increase in the strength and tear resistance of the film and is believed to result from the formation of salt bridges or cross-links between individual chains of the acidic polymer and a consequent interweaving of natural rubber with the structure so formed.

Condensation of the carboxyl groups in the acidic polymer in the blended latex 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 ammonium salt, may metathetically react with a salt of the polyvalent metal. The condensation may be effected at the time of deposition of the latex on the dipping form by coating the dipping form with a salt of the polyvalent metal prior to immersing the dipping form in a bath of latex. The salt may be deposited on the dipping form by spraying, brushing or dipping the form in a solution, such as an aqueous, acetone or alcohol solution, of a salt, such as a nitrate or chloride, of the polyvalent metal. Preferably, the solvent in the salt solution is dried prior to immersion in the bath of latex to minimize contamination of the bath and to effect a uniform deposit. This method has the advantage that the salt on the form acts

like a coagulant and produces a thick deposit of latex. The process can be repeated if a greater thickness of latex is desired.

Alternatively, the latex blend may be deposited on the form and thereafter treated with a solution of the polyvalent salt. This operation provides for the condensation of the deposited film and additionally acts like a coagulant in the event that further deposition is effected. In still another method, the blended latex which is deposited on the form contains a compound of the polyvalent metal which is unreactive with the carboxyl groups at the time of deposition but which is reactive under the conditions of drying and curing, such as heating to 150 to 250° F. For example, an oxide of a polyvalent salt, such as zinc oxide, can be incorporated in blended latex containing acidic polymer neutralized with ammonia, prior to deposition of the latex. On drying, the zinc oxide condenses with the carboxyl groups of the polymer with the elimination of ammonia and water. Standard curing agents, such as elemental sulfur, can be incorporated in either the natural latex or the latex of the acidic polymer or in the blended latex prior to deposition if desired.

Compounds of various polyvalent metals may be used in the method described above including compounds of tin, iron, lead, nickel, cobalt and the like. However, particularly effective results are 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 IIA 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 at the time of deposition or by treating a deposited film. Any convenient concentration of salt can be employed in such solutions.

As stated above, basic metallic oxides can be employed with alkaline latices, the condensation being effected in subsequent operations such as drying or curing. 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 at least equal to the amount chemically equivalent to the carboxyl content of the polymer.

In accordance with a preferred method, a finely ground oxide of a polyvalent metal of the type referred to above is incorporated or compounded in the natural rubber latex, prior to blending with the neutralized latex of the acidic vinyl polymer, together with an adequate amount of sulfur to vulcanize the natural rubber and with other known compounding ingredients, such as accelerators. Metal oxides useful for this purpose are those which are unchanged at the pH of the natural rubber latex or the blend and which are so insoluble that they furnish insufficient ions to cause coagulation. A particular advantageous oxide is zinc oxide. The compounded natural rubber latex is then blended with a neutralized latex of acidic vinyl polymer, as described above. Alternatively, the polyvalent metal oxide and other compounding ingredients can be added in whole or in part to the neutralized latex of the acidic polymer or to the blended latex. The blended latex can conveniently be deposited on a shaped dipping form by coating such a form with a solution of a salt of a polyvalent metal, such as an acetone solution of calcium nitrate, either before or after the first dip into the blended latex. The solvent may be allowed to evaporate before dipping the coated form into the blended latex. When the coated dipping form is dipped into the blended latex, the salt on the form quickly produces a thick deposit of blended latex on the dipping form. The film so formed is then dried and cured or an additional thickness of latex deposited by repeating the process. The polyvalent salt used to produce the blended latex deposit is effective in curing the neutralized acidic polymer by condensation of the polyvalent metal cation with the carboxylic acid group by a cation exchange reaction, thus adding to the curing effect of the basic polyvalent metal oxide compounded in the blended latex.

As those skilled in the art will understand, other methods than that described above may be employed to obtain the emulsion of the acidic vinyl polymer 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 by hydrolyzing or saponifying the ester form of the polymer to the free acid form or to the salt form.

For another example, polymers or copolymers of one or more alkyl acrylates, such as methyl or ethyl acrylate, may be partially hydrolzyed to yield useful carboxyl containing polymers before or after deposition of a film. Additionally, known techniques of hydrolysis can be employed to obtain the desired form of the polymer from polymers which contain non-acidic groups that hydrolyze to acidic groups, such as acid chlorides, amides, or nitriles. For example, a polymer prepared from monomers comprising 50 percent or more of a butadiene and at least about one percent of one or more olefinically unsaturated nitriles, such as acrylonitrile or methacrylonitrile, can be treated to hydrolyze all or a part of the nitrile groups.

Another method of preparing carboxyl-containing polymers useful in the present invention comprises reacting a carboxylating or carboxyl-supplying agent such as maleic acid or a mercaptocarboxylic acid, such as thioglycollic acid or the anhydride thereof, with a vinyl polymer not containing carboxyl groups, such as one prepared from monomeric material comprising an open chain, aliphatic conjugated diene preferably in the presence of a peroxygen catalyst. This method may also be employed to introduce additional carboxyl groups in a vinyl polymer containing an insufficient number of such groups.

The open-chain, aliphatic 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; 1- or 2-cyanobutadiene-1,3; 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.

In polymerizations which directly produce the acidic polymer, it is preferred to employ one or more olefinically unsaturated carboxylic acids containing at least one activated olefinic carbon-to-carbon double bond, that is, an acidic monomer containing a polymerizable olefinic double bond which readily functions in an addition polymerization reaction. Such activation is typically present when an olefinic double bond is present in the monomer molecule either in the alpha-beta position with respect to the carboxyl group or attached to a terminal methylene grouping, thus:



(a)

or



(b)

In the alpha-beta unsaturated carboxylic acids (*a*), the close proximity of the strongly polar carboxyl group to

the double-bonded carbon atoms has a strong activating influence rendering the substances containing this structure very readily polymerizable. Likewise, when an olefinic double bond is present which is attached to a terminal methylene grouping (*b*), the double-bonded carbon atoms readily enter into polymerization reactions because of the accessibility of the double bond. Acids in which the olefinic bond is not alpha-beta, such as beta-gamma olefinically unsaturated acids, can be employed where their interpolymerization is not too greatly retarded, as is frequently the case. However, some acids of this tye are polymerizable under the proper conditions, such as temperature, type and concentration of catalyst.

In general, typical carboxylic acids from which the acidic polymers referred to herein are formed can be represented by the formula R—CH=CY—(Z)$_x$—COOH in which R is preferably hydrogen, but can be carboxyl, a carboxylic ester, alkyl or alkenyl, Y is hydrogen, halogen, cyano, sulfo, alkyl, aryl, thienyl or furyl, *x* is zero or any whole number and generally no more than 3, and Z is a methylene or a substituted methylene group or an allyl, arylene, thienylene or furylene divalent cyclic radical, which groups can be substituted by alkyl or aryl groups. Exemplary olefinically unsaturated carboxylic acids include crotonic acid, alpha-chlorocrotonic acid, isocrotinic or cis-2-butenoic 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, vinylnaphthoic 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-hepthdienoic 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; maleic acid, fumaric acid, hydromuconic acid, glutaconic acid, itaconic acid, beta-(p-carboxyphenyl) acrylic acid and other polymerizable monoolefinically unsaturated polycarboxylic acids; 2,4-pentadiendioic-1,3 acid, muconic acid and other polymerizable polyolefinically unsaturated polycarboxylic acids.

Other polymerizable ethylenically unsaturated compounds such as styrene, vinyl toluene, vinyl naphthalene, alkyl acrylates, alkyl alk-acrylates, vinylidene chloride, and the like, may be interpolymerized with an unsaturated acid, partially in place of the diene hydrocarbons in the processes referred to above. Terpolymers having desirable properties, such as oil-resistance can be produced by the interpolymerization of minor amounts, such as from 5 to 45 weight percent, of polymerizable ethylenically unsaturated compounds, such as acrylonitrile or methacrylonitrile, with a diene hydrocarbon or its halogenated derivative, such as butadiene or chloro-butadiene, and an unsaturated carboxylic acid such as methacrylic acid. Additionally, the use of a third monomer often produces a more rapid and/or uniform polymerization and frequently results in a product having a more uniform disposition of the carboxyl groups.

The proportions of the monomers in the polymerization of the acidic polymer (e.g., the diene and olefinically-unsaturated carboxylic acid) can be varied over a considerable range in accordance with desired variations in the properties of the film, without loss of high tear resistance. However, the number of acid groups introduced by the same weight percent of unsaturated acid monomer will vary with the molecular weight and number of carboxyl groups in the monomer. Different acidic vinyl polymers having the same carboxyl content, based on 100 parts by weight of the polymer, can be produced from different percentages of unsaturated acid monomers of different molecular weights and/or relative carboxyl content. This is true not only of the polymerization processes referred to above but also applies where different percentages of the various carboxylating agents having different molecular weight and/or carboxyl content are employed in the carboxyl introducing processes referred to above. Since the carboxyl group (—COOH) is the functional group which results in cross-linking, it is obvious that the evaluation of acidic polymers should be made on a basis directly proportional to or equal to the carboxyl content. Accordingly a convenient measure of the number of carboxylic acid groups referred to a fixed quantity of total polymer has been adopted herein and is referred to as "acid equivalents per 100 parts by weight of acidic polymer" or Equiv./100 AP. This measure has been calculated as the number of carboxyl groups per 100 AP or by dividing the total weight of —COOH groups per 100 AP by 45, based on 100 parts by weight of total monomers charged to the polymerization system.

Acidic vinyl polymers prepared by interpolymerization of as little as one weight percent of methacrylic acid (0.01 Equiv./100 AP) with other vinyl monomers have been found to contain sufficient carboxyl groups so that the films made from blends thereof with natural rubber latex, after cross-linking by polyvalent metal cations, show high tear resistance and characteristic arcuate tears. Within the scope of present information, the upper limit of the carboxyl content in the acidic polymer appears to be controlled by the practical consideration of compatibility of the neutralized acidic vinyl polymer latex and the natural latex or by the coagulation of the acidic polymer on neutralization. Attempts to blend latices of neutralized acidic polymers containing more than 0.1 Equiv./100 AP (e.g., polymers prepared from 1,3 butadiene, acrylonitrile and more than 10 percent by weight, based on 100 parts by weight of total monomers, of methacrylic acid) have resulted in coagulation or such excessive thickening upon neutralization or blending with natural rubber latex that the production of a dipped film was not feasible. However, except as limited by compatibility of the two types of latices, properly proportioned blends of natural rubber latex and latices of various acidic polymers of high carboxyl content, such as up to 0.1 Equiv./100 AP, have produced films having high tear resistance and characteristic arcuate tear.

In the drawings:

Figure 1 illustrates a film cut and marked for manual testing of its tear characteristics;

Figure 2 illustrates the method of manually pulling apart the film illustrated in Fig. 1;

Figure 3 illustrates the arcuate tear typical of films of the present invention;

Figure 4 illustrates the type of tear characteristic of natural rubber latex films;

Figure 5 illustrates a double arcuate tear occasionally found in films of the present invention; and

Figure 6 is an enlarged view of the tear in Figure 3.

In order to illustrate the present invention but not to be construed as a limitation thereof, the following examples are given. The values of the modulus at 300 percent elongation, ultimate gum tensile strength and elongation at break referred to in the examples or reported in the tables were measured by well known standard methods. The "machine tear" was measured by the method and apparatus set forth in A.S.T.M. tear test D 624–4 except that a modified "crescent" speciment was used. Such a modified "crescent" specimen is prepared from a die made by modifying "Die B," referred to in the method, so that the concave side of the crescent is angular rather than rounded at the bottom; i.e., the sides extend until they intersect at an angle of approximately 90°. The modified specimen is referred to as an angle tear test specimen and is used in the rubber industry.

The "tear characteristics" were measured by a manual

test. In this test, a cut about 1 inch long is made by a sharp pair of scissors in the upper straight horizontal edge of the film to be tested, the cut being perpendicular to the upper edge (see Figure 1 of the drawing). A gauge mark is made in ink ¼ of an inch laterally from the bottom of the cut on each side of the cut and the bottom of the cut marked in ink. The film is then grasped in both hands, with both thumbs on the same side of the film, the balls of the thumbs being placed close (within about ¼ inch) to the bottom of the cut; i.e., the cut is between the two thumbs. The index finger of each hand is curled and the first joint placed behind the ball of the thumb on the corresponding hand. Each thumb and index finger is pressed tightly together and the hands are pulled rapidly and forcibly apart with a uniform and rolling motion of the wrists so that the thumbs move outwardly more rapidly than the fingers. Under these conditions, the sides of the cut are pulled apart so that they are almost in the same straight line (see Figure 2). Pulling is continued until partial rupture or tearing of the film occurs. The pulling operation is effected in less than one to two seconds. The amount of elongation referred to below is evaluated from a measurement of the distance between gauge marks. The tension on the film is then quickly relaxed before complete rupture of the film occurs so that the characteristics of the tear can be noted, as well as the distance 'earing has propogated with reference to the marked bottom of the cut. However, natural rubber films generally split completely across the film before tension could be relaxed.

In some instances, a "comparison" manual tear test was made. In such a test, two films are placed together so that their upper horizontal edges match, are cut together and pulled apart together without displacement relative to each other, as described immediately above.

## EXAMPLE I

An aqueous solution consisting of 100 parts of water, an emulsifying agent (4 parts of an amine salt of an alkylaryl sulfonate), a chelating agent (0.05 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 (0.5 part of mixed tertiary $C_{12}$ to $C_{16}$ mercaptans) was then placed in the reaction vessel, followed by 20 parts of acrylonitrile and then 7 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, 73 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 70 percent conversion, 0.4 part of a shortstopping agent (2,5-di-tert-butylhydroquinone), in a 25 percent aqueous dispersion acidified to a pH of about 4, was injected into the reaction mixture. The latex emulsion was agitated for approximately one-half hour to insure complete admixture of the shortstopping agent and termination of the polymerization reaction. Unreacted monomers and some water were then removed by vacuum stripping. This produced a latex having a solids content of 42.4 percent referred to the weight of total dry solids based on the total weight of the latex or emulsion). Concentrated (28 percent) ammonium hydroxide was added to the latex until a pH of about 7.5 was reached. The neutralized latex of the acidic polymer was stabilized by the addition, with stirring, of ½ part, referred to 100 parts of dry solids, of a 25 percent solution of commercial grade mixed sodium salts of the sulfate monoesters of lauryl and myristyl alcohols, and 1 part of sodium silicate, which was dissolved in a small amount of water. This neutralized and stabilized latex of the acidic polymer was then ready for blending with natural latex compounded as described immediately below.

An alkaline natural rubber latex, having a solids content of 64 percent and an alkalinity, calculated as $NH_3$, of 0.7 percent, was compounded with 2 parts by weight of elemental sulfur, 2 parts by weight of zinc oxide and 5 parts by weight of titanium dioxide per 100 parts of dry rubber, together with standard amounts of antioxidant, accelerator and stabilizer. As is common practice, soluble compounding ingredients were added as concentrated solutions while insoluble ingredients were dispersed, by standard methods, in water at about 50 percent solids and added to the latex.

A compounded latex blend was prepared by slowly adding, with stirring, the neutralized and stabilized acidic polymer latex to the compounded natural latex in relative amounts such that the dry solids in the resulting blend were in the ratio of 15 parts of neutralized acidic polymer solids to 85 parts of natural latex solids. Sufficient water was added to reduce the total solids content to about 50 percent.

A clean stainless steel plate held in a vertical position was then slowly dipped into a bath of the compounded latex blend, then removed slowly so as to deposit a thin and uniform layer of latex compound on the plate. The plate with the deposited compounded latex film thereon was thereafter dipped into a bath consisting of a 50 percent solution of calcium nitrate tetrahydrate in acetone. The plate was allowed to remain or dwell in the bath of calcium nitrate solution for a brief period of the order of 15 seconds and thereafter removed slowly and uniformly. The solvent in the calcium solution was allowed to evaporate by air drying. The plate with deposited compounded latex film and deposited calcium nitrate was then dipped into the original bath of the latex where it was allowed to remain for about one minute. The plate and adhering latex film was dipped again in the bath of calcium nitrate solution, removed from this bath and dried for about two hours at 150° F., cured in air for about 30 minutes at 230° F. and cured and leached in water at 210° F. for about 20 minutes. The film so prepared was then stripped from the plate and air dried at about 150° for a period of about 3 hours. This method is referred to herein as dipping with salt solution or coagulant dipping.

The film prepared as described above and designated as 213 B was subjected to the manual tear test. No propagation of the cut was observed when the portion of the test film adjacent the cut was evenly elongated about 2.5 times its original length (between gauge marks) and an elongation of about 4.5 times its original length was necessary to initiate substantial and measurable tear. The time for complete elongation was about 1 second. The tear, once initiated, propagated less than 1/32 inch as a straight line and thereafter terminated in an arcuate tear concavely transverse to the straight line and approximately symmetrical with respect thereto. The arcuate tear was approximately 5/16 of an inch end to end. This tear is illustrated in Figures 3 and 6 of the drawing.

For comparison, a 100 percent natural rubber latex film, (AN–415), was prepared by the same method as that described above except for the addition of the acidic polymer. When subjected to the manual tear test, this film tore easily at an elongation of about 2 times its original length. Immediately thereafter the cut propagated completely across the width of the film. This type of tear is illustrated in Figure 4 of the drawing.

A comparison manual tear test was made using blended latex test film 213 B and 100 percent rubber latex film AN–415. The blended latex film behaved as described above except for formation of a second arcuate tear 5/8

of an inch end to end, as illustrated in Figure 5, whereas the 100 percent natural rubber latex film ripped or "popped" across the complete width of the test film, about 3 inches. A repetition of the test done as rapidly as possible (i.e., by jerking) gave substantially the same results. These tests showed that the film prepared in accordance with the present invention was substantially "tearproof" when compared with films prepared from 100 percent natural rubber latex.

An additional blend of compounded natural latex and neutralized acidic polymer latex was made in the proportion, based on dry weight of total solids, of 80:20. Film 213 C, prepared from this blend, showed arcuate tear characteristics and tore less than 1/32 of an inch as a straight line and ended in an arcuate tear 1/8 of an inch from end to end at an elongation of 3 times its original distance between gauge marks. The film showed no substantial rupture at lower elongations than that noted.

Two additional series, 202 and 205, of blended latices and films having the compositions noted in Table I were prepared as described above. The properties of these films are listed in Table I.

The data in Table I indicates that borderline arcuate tear characteristics occur from 2.5 to 5 weight percent and at 30 weight percent of the acidic polymer. In the range 7 to 27.5 weight percent of the acidic polymer, the films consistently and unmistakably had high tear resistance and gave arcuate tear properties by the manual tear test.

As can be seen by a comparison of columns 7 and 8 of Table I, machine "angle tear" test data do not correlate with the tear characteristics of the films.

## EXAMPLE II

A natural rubber latex having a dry rubber solids content of 64 percent and an $NH_3$ content of 0.7 percent, was compounded in a similar manner to that described in Example I, but using 1.0 part each of zinc oxide and sulfur instead of the 2.0 parts of each of these ingredients used in Example I.

This compounded natural latex was blended in various proportions with a neutralized acidic polymer latex prepared from butadiene (70 percent), acrylonitrile (20 percent) and methacrylic acid (7 percent), the preparation of the polymer and the blending being essentially in accordance with the methods described in Example I. Films were prepared from these blended and compounded latices both using the dipping technique described in Example I (dipping with salt solution) and using the same technique except for the steps involving the use of the calcium nitrate solution (dipping without salt solution). The results of testing the films so prepared and data on the composition of the blends are set forth in Table II.

All of the films stated in Table II to have arcuate tear characteristics (films 110–C, –D, –E and –F and 92–B, –C, and –D) exhibited similar behavior to that described in Example I in connection with films 213–B and –C (i.e., the stated films resisted tear propagation to a far greater extent than natural rubber).

The data in Table II (*a*) prove that arcuate tear characteristics occur in films made from latex blends having low concentrations (4 to 10 percent) of the acidic polymer. In none of the films exhibiting arcuate tear 110–C, –D, –E, and –F), did the cut propagate or continue for more than 1/8 of an inch in the manual tear test and no arcuate tear larger than 3/8 of an inch from end to end was observed. Elongations of from 3 to 8 times the original distance between gauge marks were necessary to initiate tear in all of these films.

The data in Table II (*b*) show that the arcuate tear charatceristic is obtained when deposition of the blended latex is effected without the aid of a metallic salt deposit.

As can be seen by comparing Table I and Table II, the use of lesser amounts of zinc oxide and sulfur in the films reported in Table II generally produced films that had lower moduli and were more easily stretched than the films reported in Table I, without any sacrifice in the ultimate tensile strength of the films.

## EXAMPLE III

A number of latices were prepared from monomer charges consisting of butadiene (70 percent), acrylonitrile (20 percent) and methacrylic acid (7 percent), using a polymerization technique similar to that described in Example I. However, the amount of potassium persulfate employed was reduced to either 0.025 or 0.050 part by weight and from 1 or 2 parts by weight of mercaptan modifier was used, since such amounts of catalyst and modifier had been found to produce acidic polymers having desirably low 300 percent moduli (i.e., less than 1000 p.s.i.) without disadvantageous reduction of the ultimate gum tensile strength. Indeed such "low modulus" polymers typically have ultimate tensile strengths that are four

*Table I.—Tear characteristics and properties of films deposited from blends of natural rubber latex and the latex of a neutralized butadiene (70%), acrylonitrile (20%) and methacrylic acid (7%) polymer* [1]

| Film No. | Composition of Blended Latex [2] | | Modulus at 300% Elongation, p.s.i. | Ultimate Gum Tensile Strength, p.s.i. | Elongation at break, percent | Tear Properties | |
|---|---|---|---|---|---|---|---|
| | Natural Rubber, percent | BD/AN/MAA Polymer, percent | | | | Machine "Tear," lbs./in. | Manual Test, Type of Tear |
| AN-415 | 100 | 0 | [3] 341 | [3] 4,800 | [3] 850 | [3] 219 | Straight line. |
| 202-H | 97.5 | 2.5 | 217 | 3,400 | 975 | 300 | Unidirectional arcuate.[4] |
| 202-G | 95 | 5 | 237 | 3,925 | 995 | 398 | Do. |
| 202-F | 92.5 | 7.5 | 270 | 3,530 | 960 | 371 | Arcuate. |
| 202-E | 90 | 10 | 300 | 3,525 | 918 | 390 | Do. |
| 213-B | 85 | 15 | 367 | 3,265 | 875 | 354 | Do. |
| 205-A | 80 | 20 | [5] 522 | [5] 3,030 | [5] 798 | 280 | Do. |
| 205-B | 77.5 | 22.5 | 662 | 3,095 | 735 | 232 | Do. |
| 205-C | 75 | 25 | 619 | 2,700 | 725 | 217 | Do. |
| 205-D | 72.5 | 27.5 | 762 | 2,525 | 625 | 215 | Do. |
| 205-E | 70 | 30 | 850 | 2,340 | 560 | 208 | Variable arcuate.[6] |
| 216-D | 0 | 100 | 1,490 | 3,350 | 440 | 151 | Straight line. |

[1] Based on weight percent of monomer charge.
[2] Based on dry weight of elastomer solids; BD = butadiene; AN = acrylonitrile; MAA = methacrylic acid.
[3] Properties determined on aged film.
[4] Arcuate tear in the direction of dipping, straight tear transverse to direction of dipping.
[5] Averaged with properties of 213 series.
[6] Gave straight line tear on 50% trials.
All films were between 0.022 to 0.031 inch thick.

*Table II.—Tear characteristics and properties of films deposited from blends of natural rubber latex and the latex of a neutralized butadiene (73%), acrylonitrile (20%) and methacrylic acid (7%) polymer [1] using "low modulus" compounding formula*

| Film No. | Composition of Blended Latex [2] | | Modulus at 300% Elongation p.s.i. | Ultimate Gum Tensile Strength, p.s.i. | Elongation at break percent | Tear Properties | |
|---|---|---|---|---|---|---|---|
| | Natural Rubber, Percent | BD/AN/MAA Polymer, Percent | | | | Machine "Tear," lbs./in. | Manuel Test, Type of Tear |
| **(a) DIPPING WITH SALT SOLUTION** | | | | | | | |
| 110-A | 100 | 0 | 200 | 3,850 | 900 | 355 | Straight line. |
| 110-B | 98 | 2 | 200 | 4,220 | 935 | 392 | Do. |
| 110-C | 96 | 4 | 208 | 3,685 | 900 | 375 | Arcuate tear. |
| 110-D | 94 | 6 | 225 | 3,830 | 900 | 390 | Do. |
| 110-E | 92 | 8 | 283 | 4,042 | 900 | 380 | Do. |
| 110-F | 90 | 10 | 250 | 3,525 | 875 | 368 | Do. |
| **(b) DIPPING WITHOUT SALT SOLUTION** | | | | | | | |
| 92-A | 100 | 0 | 150 | 4,317 | 883 | 300 | Straight line. |
| 92-B | 95 | 5 | 150 | 4,417 | 917 | 400 | Arcuate tear. |
| 92-C | 90 | 10 | 225 | 4,683 | 900 | 437 | Do. |
| 92-D | 85 | 15 | 280 | 4,183 | 883 | ---------- | Do. |

[1] Based on weight percent of monomer charge.
[2] Based on dry weight of elastomer solids; BD=butadiene; AN=acrylonitrile; MAA=methacrylic acid.
All films were between 0.019 to 0.026 inch thick.

times or more the 300 percent modulus. (This polymerization method is referred to herein as the "low modulus" polymerization recipe and includes the use, based on 100 moles of total monomeric material, from about 0.01 to 0.05 oxidation equivalent of a peroxygen type of catalyst and an amount of modifier equivalent to about 0.01 to 1 mole of primary dodecyl mercaptan.) These latices were mixed into a single batch and were neutralized with ammonium hydroxide as described in Example I.

The neutralized "low-modulus" acidic polymer latex thus produced was blended, in the proportions stated in Table III, with ammoniated natural rubber latex compounded as described in Example II. Films, prepared by dipping with salt solution as described in Example I, were evaluated both with machine and manual tear tests. The results of these evaluations are given in Table III.

As shown in Table III, tear-resistance, as indicated by the arcuate tear characteristic, was obtained over the range of just above 2 weight percent to 30 weight percent of the acidic polymer. It is to be noted that the "low-modulus" acidic polymer increased the 300 percent modulus of natural rubber only 21 p.s.i. when present in a 10 weight percent concentration whereas an acidic polymer prepared by a conventional polymerization recipe increased the 300 percent modulus of natural rubber by 83 p.s.i. at the same concentration of acidic polymer, a 50 p.s.i. increase being observed even when low amounts of zinc oxide and sulfur were used. (Compare 202-E, Table I and 110-F, Table II with 185-D, Table III.) The advantage of the "low-modulus" acidic polymer was even greater at 20 weight percent of acidic polymer (compare 205-A, Table I with 185-E, Table III). The advantage of a relatively low 300 percent modulus was achieved without loss in tear-resistance, the arcuate tears produced by manual tests being generally no larger, and frequently smaller in the 185 (Table III) series than in the series reported in Table I.

The films prepared from the "low-modulus" acidic polymer (185 series) were manually tested three weeks after their initial tests in order to evaluate the permanence of

*Table III.—Tear characteristics and other properties of films deposited from blends of natural rubber latex and the latex of a neutralized "low modulus" butadiene, acrylonitrile, methacrylic acid polymer* [1]

| Film No. | Composition of Blended Latex (2) | | Modulus at 300% Elongation, p.s.i. | Ultimate Gum Tensile Strength, p.s.i. | Elongation at Break Percent | Tear Properties | |
|---|---|---|---|---|---|---|---|
| | Natural Rubber, Percent | BD/AN/MAA Polymer, Percent | | | | Machine "Tear", lbs./in. | Manual Test, Type of Tear |
| 185-A | 100 | 0 | 192 | 4,560 | 950 | 315 | Straight line. |
| 185-B | 97.5 | 2.5 | 192 | 4,435 | 950 | 465 | Arcuate. |
| 185-C | 95 | 5 | 200 | 4,020 | 940 | 388 | Do. |
| 185-D | 90 | 10 | 213 | 3,640 | 925 | 340 | Do. |
| 185-E | 80 | 20 | 242 | 3,200 | 950 | 235 | Do. |
| 185-F | 75 | 25 | 268 | 3,120 | 900 | 245 | Do. |
| 185-G | 72.5 | 27.5 | 233 | 2,810 | 875 | 198 | Do. |
| 185-H | 70 | 30 | 242 | 2,790 | 865 | 203 | Do. |

[1] Butadiene (BD) 73%, acrylonitrile (AN) 20% methacrylic acid (MAA) 7%, based on weight percent in monomer charge.

the arcuate tear characteristic. Films 185–C to 185–H, inclusive (5 to 30 weight percent of acidic polymer) gave as good results in the second test as in the first test. Film 185–B showed an arcuate tear characteristic on the second test that was inferior to that shown in the first test but still did not tear in a straight line, thus indicating moderate tear-resistance.

Additional films were prepared, using substantially the same technique and acidic polymer of the same composition as that described in connection with the 185 series above. Films from blended latices of 65:35, 60:40, 25:75 and 10:90 (natural rubber:acidic polymer) all had little, if any, tear-resistance and showed straight line tear when manually tested.

## EXAMPLE IV

A number of latices of acidic polymers made from monomer charges containing varying percentages of butadiene, acrylonitrile, and methacrylic acid were prepared and neutralized according to the the method described in Example I, using 0.05 part of potassium persulfate as catalyst and either 0.5 or 1.0 part of dodecyl mercaptan as modifier (as in Example II). After the neutralized acidic polymer latices were blended with varying amounts of natural rubber latex compounded as described in Example II, films were deposited from the blended latices using the "dipping with salt solution" method, all as described in Example I. The resulting films were evaluated using the manual tear test method with the results set forth in Table IV.

*Table IV.—Tear-resistant films from blends of natural rubber latex and latex of acidic polymers having varying amounts of butadiene, acrylonitrile and methacrylic acid*

| Film No. | Composition of Polymer [1] | | | Composition [2] of Natural Rubber/Acidic Polymer Blends which showed Arcuate Tear [3] |
|---|---|---|---|---|
| | BD | AN | MAA | |
| 37–E–12–12D–E | 70 | 20 | 1 | 98/2; 97/3; 85/15. |
| 37–B–283A, B | 78 | 20 | 2 | 98/2; 97/3; 85/15. |
| 363–A, B | 67 | 30 | 3 | 97/3; 85/15. |
| 37–A–284A, B | 77 | 20 | 3 | 98/2; 97/3; 85/15. |
| 282–B | 65 | 30 | 5 | 85/15. |
| 37–F–237–1A, B, C | 75 | 20 | 5 | 98/2; 95/5; 85/15; 70/30. |
| 222–3A, B | 85 | 10 | 5 | 95/5; 85/15. |
| 223–2A, B | 83 | 10 | 7 | 95/5; 85–15. |
| 227–2A, B, D | 73 | 20 | 7 | 97/3; 95/5; 85/15. |
| 260–B | 63 | 30 | 7 | 85/15. |
| 259–B | 60 | 30 | 10 | 85/15. |
| 237–2A, B | 70 | 20 | 10 | 95/5; 85/15. |
| | 80 | 10 | 10 | Polymer latex gelled after neutralization. |
| | 60 | 20 | 20 | Polymer latex coagulated when neutralized. |
| | 50 | 20 | 30 | Polymer latex gelled after polymerization. |

[1] Based on weight percent of monomer charge, BD=butadiene, AN=acrylonitrile, MAA=methacrylic acid.
[2] Based on weight percent of dry elastomer solids.
[3] As measured by manual tear test.

Films from blended latex containing a 5 percent methacrylic acid polymer were prepared, using blended latices containing from 2 to 30 weight percent of acidic polymer (237–1 series in Table IV) and were found to be tear-resistant and to have arcuate tear characteristics in each instance. As further shown in Table IV, acidic polymers prepared from as little as 1 or as much as 10 percent of methacrylic acid were tear-resistant and showed arcuate tear with the manual tear test. It was assumed that the 85:15 (natural rubber:acidic polymer) blend was adequate evidence to establish that the 2.5 to 30 weight percent range previously found effective also applied in testing new acidic polymers. Additional evaluations at 97:3 and 98:2 weight percent showed that a number of acidic polymers yielded blended latices of the stated compositions which were tear-resistant and had arcuate tear characteristics and confirmed the utility of the lower portion of the effective range.



## EXAMPLE V

A number of latices of acidic polymers made from monomer charges containing various monomers were prepared, neutralized, and blended with compounded natural rubber latex as described in Example IV. Films were prepared from these blended latices and evaluated by the manual tear test, with the results set forth in Table V. Films 248–1A, 248–2B and 234–B in Table V were prepared in the same manner except that the acidic polymers for 248–1A and 248–2B were polymerized using 0.1 and 0.15 part of potassium persulfate, respectively; the acidic polymer for 234–B was polymerized by starting with 2 parts of methacrylic acid and adding increments of 0.4 part of methacrylic acid at every five percent increment of conversion up to 70 percent conversion.

As can be seen from inspection of the data in Table V, variation of the type of monomer varied the elastic properties of the films; however films having high tear-resistance and showing the arcuate tear characteristic were produced from blended latices whose compositions fell within the range of 2.5 to 30 weight percent of acidic polymer previously found effective.

## EXAMPLE VI

A blend of 92.5 weight percent of natural rubber latex and 7.5 weight percent of a neutralized acidic polymer polymerized from 73 percent butadiene, 20 percent acrylonitrile and 7 percent of methacrylic acid was prepared as described in Example IV. Films were deposited from this blended latex by the method described in Example I using the following solutions instead of calcium nitrate tetrahydrate in acetone:

(*a*) 20 percent solution of barium chloride in water.
(*b*) 30 percent solution of stannic chloride in water.
(*c*) 30 percent solution of sodium chloride in water.

The film prepared using solutions (*a*) and (*b*) gave films having tear-resistance and showing arcuate tear characteristics. The barium chloride solution (*a*) produced a film having better resistance to initiation or propagation of tear than did a film produced from the calcium nitrate solution used as a control. However, the stannic chloride solution (*b*) gave a film inferior in tear-resistance to the film produced from calcium nitrate solution.

The film produced using the sodium chloride solution (*c*) had poor tear-resistance and tore in a straight line.

*Table V.—Tear-resistant films from blends of natural rubber latex and latex of acidic polymers made from various monomers*

| Film No. | Composition of Polymer [1] | | | | | Composition [2] of Natural Rubber/Acidic Polymer Blends which showed Arcuate Tear [3] | Properties of film from 85/15 Blend | | |
|---|---|---|---|---|---|---|---|---|---|
| | BD | AN | MAA | Stated Monomer | Percent | | Mod. at 300% Elong., p.s.i. | Ult. Gum Tensile, p.s.i. | Elong. at Break, Percent |
| 248-1A, 2A | 73 | 0 | 7 | Styrene | 20 | 95/5; 85/15 | 300 | 2,400 | 785 |
| 255-1A, B | 0 | 20 | 7 | Isoprene | 73 | 95/5; 85/15 | 300 | 2,275 | 775 |
| 296-B, C | 0 | 20 | 7 | Chloroprene | 73 | 85/15; 70/30 | 208 | 3,300 | 875 |
| 300-A, B | 76.5 | 20 | 0 | Maleic acid | 3.5 | 98/2; 97/3; 85/15 | 200 | 1,800 | 725 |
| 302-A, B | 76.5 | 20 | 0 | Fumaric acid | 3.5 | 98/2; 97/3; 85/15 | 261 | 2,495 | 765 |
| 303-B | 73 | 20 | 0 | Crotonic acid | 7 | 85/15 | 233 | 2,010 | 725 |
| 234-B | 90 | 0 | 10 | | | 85/15 | 275 | 3,240 | 835 |
| 21-A, B | 73 | 20 | 0 | Cinnamic acid | 7 | 85/15 | 267 | 2,100 | 760 |
| 21-D, E | 68 | 20 | 0 | do | 12 | 85/15 | 267 | 1,750 | 700 |
| 29-A, B | 74.2 | 20 | 0 | Acrylic acid | 5.8 | 97/3; 85/15 | 219 | 3,150 | 910 |

[1] Based on weight percent of monomer charge, BD=butadiene, AN=acrylonitrile, MAA=methacrylic acid.
[2] Based on weight percent or dry elastomer solids.
[3] As measured by manual tear test.

## EXAMPLE VII

A blended and compounded latex was prepared which contained 63 parts of natural rubber latex (62.5 percent solids), 30 parts of neoprene latex (Dupont 601–A, a 62.5 percent solids latex of polymerized 2-chloro-1,3-butadiene), 7 parts of an acidic vinyl polymer (a 39.7 percent solids latex made from 73 parts of butadiene, 20 parts of acrylonitrile and 7 parts of methacrylic acid using a similar polymerization recipe to that described in Example III), 2 parts of zinc oxide, 5 parts of titanium dioxide and 1 part of sulfur, together with a standard small amount of accelerator, as described in Example I. A film was prepared from this latex, using the technique of dipping without salt solution described in Example II.

The film so prepared had a 300 percent modulus of 150 p.s.i., an ultimate tensile strength of 3500 p.s.i. and an elongation at break of 1000 percent. When tested manually, the film had excellent tear-resistance and exhibited the arcuate tear characteristic.

Films identically prepared except for the use of the following parts of natural rubber latex/acidic vinyl polymer/neoprene had excellent tear-resistance and showed the arcuate tear characteristic:

90/10/0; 81/9/10; 72/8/20

All of these films had oil-resistance superior to that of 100 percent natural rubber films; those made from the higher amounts of neoprene having considerably improved oil-resistance.

As demonstrated in the above examples, latices containing mixtures of natural rubber and a wide variety of acidic vinyl polymers made from polymerizable olefinically unsaturated carboxylic acids can be employed to produce unsupported films of extensive utility because of the tear-resistance of the film. Service tests indicate that shaped articles, such as girdles, baby pants and the like, made of such films have tear-resistance which is an order of magnitude better than that observed in similar articles made entirely of natural rubber. So great is the difference that films made in accordance with the present invention are substantially "tearproof" when compared to natural rubber films. A minor portion of the natural rubber in the blended latex can be replaced with a synthetic polymer so selected that the film has particularly advantageous properties, such as oil-resistance, in addition to high tear-resistance.

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 modifications.

I claim as my invention:

1. A deposited latex film having a high resistance to tear comprising a mixture of natural rubber and carboxyl-containing copolymer prepared from a 1,3 conjugated diene, the carboxyl content of said copolymer being from about 0.01 to 0.1 acid equivalent by weight of combined —COOH per 100 parts by weight of dry copolymer, said mixture containing about 70 to 98 parts by weight of natural rubber and about 2 to 30 parts by weight of said carboxyl-containing copolymer, at least a major portion of the carboxyl groups of said copolymer having been cross-linked with polyacidic cations selected from the group consisting of cations of metals that form basic oxides and of polyamines, said film having the property that a cut propagates at the most for a short distance and along a straight line at the end of which is a small arcuate tear transverse to said straight line.

2. The deposited latex film of claim 1 in which said carboxyl-containing copolymer is prepared from monomeric material comprising at least three copolymerizable monomers at least one of which imparts oil resistance to the polymer selected from the group consisting of chlorine substituted 1,3-diene hydrocarbons and low molecular weight polymerizable olefinically unsaturated nitriles.

3. The deposited latex film of claim 1 in which said carboxyl-containing copolymer is prepared from monomeric material comprising from about 5 to 40 weight percent of acrylonitrile.

4. The deposited latex film of claim 1 in which said carboxyl-containing copolymer is prepared from monomeric material comprising at least one polymerizable monovinyl aromatic hydrocarbon.

5. The deposited latex film of claim 1 in which said carboxyl-containing copolymer is prepared from monomeric material the major portion of which consists of at least one polymerizable 1,3-diene hydrocarbon having from 4 to about 10 carbon atoms.

6. The deposited latex film of claim 1 in which said carboxyl-containing copolymer is prepared from monomeric material comprising from about 50 to 90 weight percent of 1,3-butadiene.

7. The deposited latex film of claim 1 in which said carboxyl-containing copolymer is prepared from monomeric material comprising at least one polymerizable alpha-beta olefinically unsaturated carboxylic acid.

8. The deposited latex film of claim 1 in which said carboxyl-containing coplymer is prepared from monomeric material comprising from about 1 to 10 weight percent of methacrylic acid.

9. The deposited latex film of claim 1 in which said polyacidic cation is that of zinc.

10. The deposited latex film of claim 1 in which said polyacidic cation is that of a metal in group IIA of the periodic table.

11. The deposited latex film of claim 1 in which said polyacidic cation is that of calcium.

12. A stable latex suitable for producing a deposited latex film that has high resistance to tear comprising an aqueous suspension of natural rubber and the salt of a volatile base of a monovalent cation with carboxyl-containing copolymer prepared from a 1,3 conjugated diene, the carboxyl content of said copolymer being from about 0.01 to 0.1 acid equivalent by weight of combined —COOH per 100 parts by weight of dry copolymer, the ratio of the dry weight of the natural rubber to that of said carboxyl-containing copolymer being in the range of about 2.5:1 to 50:1.

13. The latex of claim 12 intimately admixed with fine particles of a basic polyvalent metal oxide that is so insoluble in water that it furnishes insufficient ions to coagulate said latex.

14. The latex of claim 13 in which the polyvalent metal oxide is zinc oxide.

15. An elastic film prepared by deposition from an aqueous blend of natural rubber, a carboxyl-containing copolymer prepared from a 1,3 conjugated diene and compatible with said natural rubber, the carboxyl content of said copolymer being from about 0.01 to 0.1 acid equivalent by weight of combined —COOH per 100 parts by weight of dry copolymer, and vulcanizing materials for said natural rubber, the ratio of the dry weight of said natural rubber to the dry weight of said carboxyl-containing copolymer being in the range of about 2.5:1 to 50:1, the major portion of the carboxyl groups in said carboxyl-containing copolymer having been cross linked with cations of a polyvalent metal that forms a basic oxide, said film having the property that it is substantially "tear-proof" when compared with a film similarly prepared from natural rubber without said carboxyl-containing copolymer.

16. An unsupported elastic film having a high resistance to tear comprising a vulcanized mixture of natural rubber and from 2 to 30 percent by weight, referred to 100 parts by weight of all elastomeric material present, of a carboxyl-containing copolymer prepared from between about 50 to 90 weight percent of 1,3-butadiene, about 5 to 40 weight percent of acrylonitrile and about 1 to 10 percent of methacrylic acid, the major portion of the carboxyl groups of said copolymer having been cross linked with cations of a polyvalent metal that forms a basic oxide.

17. The method of preparing a deposited latex film that has high resistance to tear which comprises the steps of depositing on a form a film of aqueous latex blend comprising natural rubber latex made alkaline with a volatile base of a monovalent cation and latex of a carboxyl-containing copolymer prepared from a 1,3 conjugated diene made alkaline with a volatile base of a monovalent cation and compatible with said natural rubber latex, the carboxyl content of said copolymer being from about 0.01 to 0.1 acid equivalent by weight of combined —COOH per 100 parts by weight of dry copolymer, removing said film from said form and at least partially curing said film by cross-linking acid groups of said carboxyl-containing copolymer with polyacidic cations selected from the group consisting of cations of metals that form basic oxides and of polyamines.

18. The method of claim 17 in which said form is coated with a soluble salt of a polyvalent metal that forms a basic oxide.

19. The method of claim 17 in which the film of said blend on said form is treated with a solution comprising said polyacidic cation, said polyacidic cation reacting with said carboxyl-containing copolymer during subsequent curing.

20. An elastic film comprising a gum cured mixture of vulcanized natural rubber and the cross-linked product of a polyacidic cation and a carboxyl-containing copolymer prepared from a 1,3 conjugated diene, the carboxyl content of said copolymer being from about 0.01 to 0.1 acid equivalent by weight of combined —COOH per 100 parts by weight of dry copolymer, said polyacidic cation being selected from the group consisting of cations of metals that form basic oxides and of polyamines, the ratio of the weight of said natural rubber to the weight of said carboxyl-containing copolymer being in the range of about 2.5:1 to 50:1, said film having the property that it is substantially "tear-proof" when compared with a film of similarly vulcanized natural rubber without said carboxyl-containing copolymer.

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