ABSTRACT

Fire retardant polyurethane compositions having good tensile and tear strength are formed comprising a liquid, hydroxyl-terminated diene polymer, a low molecular weight reinforcing polyol, an isocyanate, a filler, a fire retardant compound, and a catalyst. The resulting compositions find particular application as thixotropic polyurethane adhesive compositions applied to the underside of the primary fabric backing of tufted carpet as either a laminating adhesive, a precoat adhesive or a unitary carpet backing.

1 Claim, No Drawings
FIELD OF THE INVENTION

The present invention relates to fire retardant polyurethane compositions which find particular application to carpets, and to the resulting carpet material. More particularly, the present invention is directed to fire retardant thixotropic polyurethane compositions which retain desired strength characteristics and which can be advantageously applied to carpets as a unitary backing, a precoat adhesive, or a laminating adhesive.

BACKGROUND OF THE INVENTION

The tufting method which is now generally employed for the manufacture of carpets comprises looping pile fibers of natural or synthetic material through a relatively inexpensive woven or non-woven textile base, known as the primary fabric backing material. Short loops of the long pile fibers are pushed through the primary fabric backing material such that one single continuous length of fiber constituting a complete row of pile in the carpet is formed. The elongated loops extending from the base (the top side) of the primary fabric backing material can remain connected or severed, depending on whether a loop pile or a cut pile carpet is desired. The loops on the bottom side of the carpet are not cut. These pile loops or tufts are not securely fastened in the tufting process. Without additional anchorage these fibers or the tufts can be pulled from the primary fabric or otherwise disarranged. Necessary anchorage is provided by applying an adhesive material in liquid form to the underside of the carpet. The adhesive applied to the underside of the carpet is accordingly of major importance to the quality and performance of the carpet. It retains the pile fibers or tufts in place, secures the individual fibers of the yarn, and controls dimensional stability.

Without additional backing material applied to the adhesive material on the underside of the carpet, the carpet is said to have a unitary backing. Carpets having a unitary backing are used principally as commercial carpeting. If a sponge like material (or foam) is applied after the adhesive material is applied, the adhesive coating is referred to as a precoat composition. Uncured foam material can be applied directly to the precoated carpet back and cured in place, or it can be cured as a separate sheet and then laminated to the back of the carpet by means of the precoat or use of another adhesive. The precoat provides good tuft lock, while the foam material, such as polyvinyl chloride or styrene butadiene copolymer, serves as a cushion back for the carpet.

For the standard double back carpets the adhesive layer is referred to as a laminating adhesive. After the laminating adhesive is applied to the underside of the primary fabric backing material of a double back carpet, a further backing layer of secondary fabric material, known as the scrim, is applied to the coated underside of the carpet. The scrim serves to improve dimensional stability, appearance of the carpet and also to enhance tuft lock, i.e., the strength with which the fibers are retained in the primary fabric backing. The laminating adhesive for double back carpets serves not only to anchor the pile fibers or tufts, but also to adhere the scrim to the carpet. Conventionally, in the process of making double back tufted carpets the laminating adhesive is applied in liquid form to the underside of the carpet and the scrim is applied to the same side while the laminating adhesive is still wet and uncured. The carpet is then passed through an oven to dry and cure the laminating adhesive.

When reference is made herein to carpets, it will be understood that any fabric like sheet material is contemplated, whether tufted, woven, knitted, felted, cemented or otherwise, and that the fabric can be a carpet, rug, mat, floor covering, floor tile, wall covering or the like. The primary fabric is normally a material such as jute, burlap or polypropylene. The scrim or secondary fabric can consist of natural and/or synthetic materials, such as jute, hessian, burlap, nylon, polypropylene and the like. The pile fibers can also be natural or synthetic materials, such as wool, polyacrylate, cellulose acetate, polyester, nylon, polyacrylonitrile, polypropylene and the like, as well as mixtures of such materials.

Styrene butadiene rubber latex and carboxylated styrene butadiene rubber latex of the type commonly employed as a laminating adhesive have several known disadvantages. Such adhesive requires a long cure time at relatively high temperatures (e.g., 300°F for 8 to 10 minutes) and this means that large expensive curing ovens must be employed. With certain heat sensitive fibers that require lower curing temperatures, even longer curing times are necessary. Carboxylated styrene-buta diene latex adhesive may have a strong odor of ammonia associated with it and sometimes finished carpets have a heavy and unpleasant odor of styrene. In addition, carboxylated butadiene-styrene polymer adhesives can contain some residual unsaturation which tends to cause unsatisfactory aging characteristics, resulting in a loss of flexibility. In fact, polymerization which occurs as a result of such residual unsaturation has caused the backing of carpets and rugs to become stiff after only a few years. Another disadvantage of carboxylated styrene butadiene rubber latex adhesive is the required method of application. In general, a pan coater consisting of a latex pan, one or two adjustable doctor or striker bars, one or two variable speed coater rolls and one or two adjustable tension rolls are required for the application of such adhesive.

These require a fairly high degree of operator skill and attention to achieve a proper degree of penetration of adhesive into tufts. It is important that the adhesive employed for carpets not migrate past the primary backing fabric to the face or top side of the carpet since this migration can cause the yarn to become stiff and render the final carpet unacceptable. If the settings are not correct for the particular type of yarn used rejects become quite high. Quality of the finished carpet thus becomes highly dependent on operator skill and conscientiousness and increased expenses are incurred from the fact that several employees are required to operate the equipment. Another disadvantage is the poor green strength of carboxylated styrene butadiene rubber latex adhesive. If effective adhesion does not occur until near the end of a curing cycle the chances of delamination of any scrim applied are greater and product waste increases greatly.

The advent of certain synthetic materials in the carpet industry which permit a carpet to be used both indoors and outdoors has given rise to further problems
in connection with the manufacture of carpet material. Polypropylene is a relatively cheap material which in most respects is quite satisfactory for use as the pile fiber, the primary fabric backing material, and the scrim, or the secondary fabric substrate, of a carpet. However, polypropylene presents an adhesion problem since latex compositions normally employed in carpet manufacture do not adhere well to the surface of polypropylene. Carpets prepared from polypropylene have been subject to delamination of the scrim or secondary fabric substrate. In order to overcome this problem attempts have been made to employ multiple intervening adhesive layers, resulting in increased production costs.

Polyurethane compositions have been suggested for carpet backing applications. While polyurethane compositions overcome substantial disadvantages associated with styrene butadiene rubber latex and carboxylated styrene butadiene rubber latex, it has been difficult to render polyurethane compositions fire retardant. The use of fire retardant compounds in polyurethane compositions has been restricted to low levels due to (a) poor compatibility and (b) loss in strength when conventional polyethers, polyesters, polyacetates, and polyacrylates are incorporated into such compositions. The compatibility problem and problems arising from loss of strength have been serious drawbacks to the use of conventional polyurethane compositions in applications requiring achievement of a fairly high fire-resistance. This has been especially true in applications involving fabrics or carpet materials where the necessity of improving fire retardant characteristics has never been more acute.

As used herein, the expression “fire retardant” is used to describe the property of resisting fire. There are several distinct stages in the burning process, namely, heating, degradation and decomposition, volatilization and oxidation. Accordingly, there are a variety of ways to extinguish a flame such as cooling the solid, altering the degradation and decomposition process to produce non-flammable volatiles, quenching the volatilization by adding too much air or eliminating air from the combustion zone, or interfering with the oxidation reaction in the gas phase. It will be seen that chemical fire retardants incorporated in the particular polyurethane compositions of the present invention operate both in the solid phase (altering thermal degradation processes or forming barriers at the surface) and in the vapor phase (interfering with oxidation).

SUMMARY OF THE INVENTION

An object of the present invention is to provide fire retardant polyurethane compositions without loss of other desirable properties, including tear and tensile strength.

Another object of the present invention is to provide a fire retardant solvent-free polymer composition which avoids evaporation of water and/or organic volatile materials into the atmosphere while curing.

A further object of the present invention is to provide improved fire retardant thixotropic polyurethane adhesive compositions which can be used as carpet backing adhesive.

Still a further object of the present invention is to provide low cost adhesive compositions which have excellent adhesion with respect to natural and synthetic materials, good resistance to aging and fire retardant characteristics.

Yet another object of the present invention is to provide fire retardant thixotropic polyurethane compositions which can be used as unitary backing, precoat adhesive or laminating adhesive for carpets. A still further object of the present invention is to provide carpet material having good tuft lock, bundle wrap and fire retardancy.

The fire retardant thixotropic adhesive compositions provided in accordance with the present invention comprise a mixture of a liquid hydroxyl-terminated diene homopolymer or copolymer, a low molecular weight polyol, an isocyanate, a filler, an oil extending hydrocarbon liquid, a fire retardant compound, and catalyst. These compositions have an initial Brookfield viscosity of between about 3,000 and about 100,000 centipoises at 5 rpm using a number 5 spindle. More especially, the adhesive compositions of the invention, without added fire retardant compound, comprise a mixture of a liquid hydroxyl-terminated diene homopolymer or copolymer, a polyol having an equivalent weight of between about 500 and about 2,200 present in an amount up to 5 times the equivalents of diene polymer; a polyol having an equivalent weight of between about 50 and about 300 present in an amount between about 1.5 and about 8 times the equivalents of diene polymer; an isocyanate material having a functionality of between 2 and 3 present in an amount to provide a NCO/OH equivalents ratio of between 0.95:1 and 1.5:1; a filler present in an amount between about 40 and about 800 parts per 100 parts by weight of diene polymer; an oil extending hydrocarbon liquid present in an amount up to 200 parts per 100 parts by weight of the diene polymer; water present in an amount up to 10 parts per 100 parts by weight of the diene polymer; and a catalyst capable of accelerating the cure time of the composition, present in an amount between about 0.02 and about 4 parts per hundred parts by weight of the diene polymer. The fire retardant compound added to this composition comprises between about 10 and about 250 parts per 100 parts by weight of diene polymer of a halogenated hydrocarbon (chlorine, fluorine, bromine or iodine), or between about 10 and about 250 parts per 100 parts by weight of diene polymer of a phosphate material, or between about 20 and about 800 parts per 100 parts by weight of diene polymer of hydrated alumina, or a combination of said components within the indicated proportions. The resulting fire retardant composition has an initial Brookfield viscosity at 5 rpm using a number 5 spindle of between about 3,000 and about 100,000 centipoises and the ratio of the viscosity at 1 rpm and 20 rpm for the thixotropic composition is between about 1.3:1 and 10:1. Conventional additives such as oxidation inhibitors, pot life stabilizers, pigments and the like can be incorporated in the fire retardant compositions for improved characteristics.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polymeric materials combined with isocyanate to produce the particular urethane adhesive compositions of the present invention are liquid, hydroxyl-terminated diene homopolymers and copolymers. The polymers possess predominantly primary, terminal hydroxyl groups of the allylic type and have a hydroxyl
content of between about 0.6 and about 0.9 milliequivalents per gram and a viscosity at 30°C of between about 30 and about 300 poises. The structure of the polymers accounts for their high reactivity, especially with aromatic diisocyanates. Oil extension, using low-cost process oils, provides formulation flexibility in controlling properties while the liquid systems are uncured, such as viscosity pot life, gel time and the like, as well as properties of the cured product, including flexibility, cut growth, elongation and the like.

Hydroxyl terminated homopolymers and copolymers contemplated for the present invention are disclosed in more detail in U.S. Pat. Nos. 3,637,558, 3,674,743 and 3,714,110, which patent disclosures are specifically incorporated by reference herein. These patents disclose polymers which have an average of at least 2.1 and preferably between about 2.1 and about 2.5 predominately primary, terminal allylic hydroxyls per molecule and being an addition polymer of 0 to 75 percent by weight of an alpha-monofunctionally unaturated monomer of 2 to 12 carbon atoms, the balance consisting essentially of a 1,3-diene hydrocarbon of about 4 to about 12 carbon atoms, said polymer having the majority of its unsaturation in the main hydrocarbon chain and a number average molecule weight of about 400 to about 25,000 as determined by cryoscopic, ebullioscopic and osmometric methods.

As disclosed in the aforementioned patents, the dienes which can be employed are unsubstituted, 2-substituted or 3,3-disubstituted 1,3-dienes of up to about 12 carbons atoms. The diene preferably has up to six carbon atoms and the substituents in the 2- and/or 3-position can be hydrogen, alkyl, generally lower alkyl, e.g., of one to four carbon atoms, aryl (substituted or unsubstituted), halogen, nitro, nitrile, etc. Typical dienes which can be employed are 1,3-butadiene, isoprene, chloroprene, 2-cyano-1,3-butadiene, isoprene, chloroprene, 2-cyano-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, etc.

Olefinically unsaturated monomers which can be incorporated into the diene polymer products used in this invention include alpha-mono olefinic materials of about two or three to 10 or 12 carbon atoms such as styrene, vinyl toluene, methyl methacrylate, methacrylate, acrylic esters, vinyl chloride, vinylidene chloride, etc. Acrylonitrile, acrylic acid, vinylidene cyanide, acrylamide, etc., provide low-molecular weight hydroxy-terminated diene intermediate copolymers which have sites suitable for cross-linking. As can be seen, the usable olefinic monomers can be ethylenes, substituted with halogen, aromatic hydrocarbon, or even cyano or carboxyl-containing radicals in some instances. The choice and amount of mono olefinic monomers employed will often be determined on the basis of properties desired. Generally the amount of monoolefinic monomer in the polymer will be about 0.75 percent by weight of the total addition polymer, preferably about 1 to 40 percent, or even about 10-40 percent.

Specific hydroxyl-terminated homopolymers contemplated for the present invention are those having the general formula:

\[ HO_1+(CH_2=CHCH_2)_m-(CH_2C=CHCH_2)_n+OH \]

where \( m = n = 44 \) to 65. Specific examples include resin R-45M having an equivalent weight of 1,330 and a hydroxyl content of 0.75 milliequivalents per gram; where \( n \) equals 57 to 65.

Specific hydroxyl-terminated copolymers contemplated for the present invention are those having the general formula:

\[ HO_1+(CH_2CH_2C=CHCH_2)_m-(C(X)=CHC=CHCH_2)_n+OH \]

where \( a = 0.75, b = 0.25, n = 57 \) to 65, and \( X \) is the styrene moiety. An example of such a styrene-butadiene copolymer is resin CS-15 which has an equivalent weight of 1,530 an iodine number of 335, and a hydroxyl content of 0.65 milliequivalents per gram.

The low molecular weight reinforcing polyols which can be employed in the present invention in order to obtain improved tensile strength, tear strength and adhesion are those polyols having an equivalent weight of between about 50 and about 300 and preferably those which have an average equivalent weight of between about 90 and about 250. The contemplated polyols, which can be di, tri or tetra functional, can have an average functionality of between 2.0 and 2.5. In general, these polyols are employed in an amount between about 1.5 and about 8 times the equivalents of liquid, hydroxyl-terminated diene polymer utilized in connection with the invention. Although bisisopropanol aniline is a preferred polyol for the invention, other polyols which can be used include bisisopropanol biphenol A, 2-ethyl-1,3-hexanediol, dipropylene glycol, diethylenglycol and bisisopropanol isophthalate.

Higher equivalent weight polyols, having an equivalent weight of between about 500 and about 2,200, can also be included in an amount up to about 5 times the equivalents of diene polymer, preferably between about 0.1 and about 5.0 times the equivalents of liquid, hydroxyl-terminated diene polymer. For example, polypropylene glycol can, if desired, be included in the fire retardant polyurethane compositions.

Isocyanates which can be employed to form the polyurethane upon reaction with the liquid, hydroxyl-terminated diene polymers include tolylene disocyanate (TDI), diphenyl methane 4, 4'-disocyanate (MDI) and polymeric disocyanates such as polyphenylene polyisocyanate (PAPI). Other isocyanate materials which can be used to produce urethane compositions of this invention include any one of a number of materials containing two or more isocyanate radicals, such as 1,5-naphthalene disocyanate, phényl isocyanates, trans-vinylene disocyanate, hexamethylene disocyanate, octamethylene disocyanate, 3,3'-dimethoxy-4,4'-biphenyl disocyanate, as well as related aromatic and aliphatic isocyanates, which can also be substituted with other organic or inorganic groups that do not adversely affect the course of the urethane forming reaction. The isocyanate material has a functionality of between 2 and 3 and is used in an amount to provide a NCO/OH equivalents ratio of between about 0.95:1 and about 1.5:1, and preferably between about 1.0:1 and about 1.2:1.

A prepolymer can be employed as the isocyanate. An isocyanate terminated prepolymer can be formed by adding an excess of disocyanate (e.g. tolylene disocyanate) to the hydroxyl-terminated diene homopolymer or copolymer.

Inorganic fillers are added in order to control viscosity and prevent overpenetration into the carpet fibers. Among the fillers which can incorporate into the ad-
hesive compositions of this invention include calcium carbonate, talc, clay, silica, zinc oxide, feldspar, asbestos, carbon black and mixtures of these fillers. In addition, fillers such as titanium dioxide and barium sulfate can be employed. Generally, the amount of filler utilized is between about 40 and about 800 parts per 100 parts by weight of the liquid, hydroxyl-terminated diene polymer and preferably the amount of filler is between about 100 and about 600 parts per hundred parts by weight of hydroxyl-terminated diene polymer. The fact that higher filler levels can be employed means that a significant economic advantage can be obtained using large amounts of inexpensive filler in the formulation.

In order to keep the viscosity from becoming too high with the filler loads utilized in connection with the invention up to about 200 and preferably up to about 100 parts of a hydrocarbon oil per 100 parts by weight of diene polymer are added. Preferably such hydrocarbon oil is a naphthenic or aromatic oil which has a viscosity at 100°F. of between about 50 and about 2,500 Saybolt universal seconds and preferably between about 150 and about 1,500 Saybolt seconds. Because of odor characteristics, naphthenic oils are the preferred materials. Paraffinic oils can be used, but occasionally a compatibility problem occurs with such oils. Since oil extension, which is desirable for lowering costs and improving processibility, sometimes tends to be harmful to certain physical properties, including adhesion and tuft lock, higher molecular weight extenders can be used to replace part or all of the oil employed. Examples of such extenders include asphalt, vulcanized vegetable oils, and lower molecular weight polystyrene. It has also been observed that when liquid fire retardant compounds partially or completely replace the hydrocarbon oil, improved tensile and tear strengths can be obtained, at the same time fire retardancy is being improved.

Catalysts employed in connection with compositions of the present invention in order to provide the necessary acceleration of cure time include triethylene diamine (DABCO), various tin, lead and zinc containing catalysts such as dibutyl tin dilaurate, nickel acetyl acetone, ferric acetyl acetonate, stannous octoate, cobalt naphthenate and the like as well as combinations of such catalysts. The amount of catalyst employed depends on the desired rate of cure at the curing temperature. Generally, catalyst is used in an amount varying between about 0.02 and about 4 parts per hundred parts by weight of the liquid, hydroxyl-terminated diene polymer and preferably is employed in an amount between about 0.1 and about 2.0 parts per hundred parts by weight of the diene polymer.

The fire retardant compound added to the polyurethane composition comprises between about 10 and about 250 parts and preferably between about 20 and about 150 parts per 100 parts by weight of diene polymer of a halogenated hydrocarbon (chlorine, fluorine, bromine or iodine), or between about 10 and 250 parts and preferably between about 20 and about 150 parts per 100 parts by weight of diene polymer of a phosphate material, or between about 20 and about 800 parts and preferably between about 100 and about 600 parts per 100 parts by weight of diene polymer of hydrated alumina, or a combination of said compounds. Among the halogenated hydrocarbons which can be employed are chlorinated organic substances containing between 50 and 80 percent chlorine, such as chlorinated aliphatic or cycloaliphatic compounds containing more than 8 carbon atoms, examples of which are paraffin, waxes, and hydrocarbon oils. In addition, the following materials can be employed: brominated castor oil, perchlorocyclopentadecane, tetra-bromobisphenol A, brominated epoxy resin, chlorinated diphenyl, and dibromonopentyl glycol.

Phosphate compounds which can be employed include cresyl diphenyl phosphate, tri (2,3-dibromo propyl) phosphate, diethyl-N, N-bis (2 hydroxyethyl) amino methyl phosphonate, tri (dichloropropyl) phosphate, tetraethyl pyrophosphate, tri (isodecyl) phosphate, diethyldihydrogen phosphonium chloride, and tetraethyl phosphonium chloride.

Preferred combinations include the combination of one of the aforementioned halogenated hydrocarbon compounds with alumina trihydrate and the combination of one of the aforementioned phosphate compounds with alumina trihydrate. For example, the combinations of alumina trihydrate and chlorinated paraffin, alumina trihydrate and cresyl diphenyl phosphate, and alumina trihydrate and isodecyl diphenyl phosphate are preferred.

Certain other inorganic compounds such as antimony oxide, bismuth oxide, antimony sulfide, sodium borate, zinc borate and the like can either be combined with the aforementioned compounds or substituted for a portion of said compounds, although the use of these other compounds is not necessarily as effective in achieving the desired fire retardancy.

Water can also be added to the compositions to create a polyurethane foam or sponge. Specifically, between 0 and about 10 parts of water per hundred parts by weight of the liquid, hydroxyl terminated diene polymer can be incorporated in the composition. Preferably, water is incorporated between about 1.0 and about 8 parts per hundred parts by weight of the diene polymer. Since the isocyanate moiety is sensitive to water, the isocyanate should be essentially isolated from water, air and the like before reaction. In addition, the diene polymer and other reactants, and particularly the fillers, which can contain variable amounts of water, should be dried or degassed in a vacuum to remove moisture before the reaction. The preferred procedure is to remove all the moisture from the ingredients and then incorporate the desired amount of water into the reaction mixture. By following this procedure it is possible to known precisely how much water is in the composition, and it is accordingly possible to obtain consistent results for each formulation.

Generally when larger amounts of high molecular weight polylol are used, amounts of the other ingredients used are at the upper end of the ranges listed above. Conversely, when low amounts of high molecular weight polylol are used, amounts of the other ingredients are at the lower end of the ranges listed above. These various amounts are adjusted to provide workable viscosities, desirable cure times, and required fire retardancy, etc., for each specific application.

Economically, it is often desirable to also incorporate various inhibitors and other conventional additives in the adhesive composition of the present invention. For example, oxidation inhibitors can be added to improve aging characteristics. Such inhibitors include alkylated phenol and aromatic amines.
Other substances, which can be added to the reaction mixture are pigments, plasticizers, surfactants, stabilizers and the like. Surfactants, for instance, can be added in order to increase the penetration of the adhesive composition in the backing cloth or primary fabric and around the pile so as to firmly bind the pile to the backing cloth. Surfactants, such as various silicone materials, serve to stabilize bubble formation. In some instances small amounts of diluting agents, which decrease the viscosity of the reaction mixture, can also be added to increase penetration. Emulsifiers can be incorporated to disperse limited soluble components. Dispersing aids can be incorporated to prevent filler settlement. In addition, dehydrating agents such as molecular sieves or zeolite materials, e.g., Linde 5A molecular sieve, can be incorporated in order to regulate water content. Preferably these materials are incorporated in the polyol blend, as hereinafter defined.

Generally, all ingredients except the isocyanate are preblended. This is commonly called the polyol blend. Conventional procedures can be employed for mixing or blending the ingredients for the polyol blend, including the use of double planetary and Cowie high speed mixers. The order of mixing can be varied to suit the characteristics of the mixing equipment being used. The power material can be blended with a little liquid to obtain a good dispersion and then the remainder of the liquid is added or liquid can be blended and then the powder material is incorporated. Mixing times will vary depending on the efficiency of the mixing equipment and the type of filler used. It will be understood that no particular criticality exists with respect to the incorporation of the fire retardant compounds.

As previously indicated the isocyanate moiety is sensitive to water and accordingly in the preferred practice moisture is initially removed from the reactants. Alternatively, the reactants can be mixed and then degassed, usually in a vacuum, to remove air bubbles and moisture from the mixture. Following this procedure a mixture can be degassed in a steam jacket kettle maintained under a vacuum of 10 to 50 millimeters of mercury for a time period which can be up to about 2 hours. Sometimes thin film evaporator type equipment is used to remove moisture.

The viscosity of the resulting adhesive composition after the isocyanate is added to the polyol blend is between about 3,000 and about 100,000 centipoises and preferably between about 8,000 and about 50,000 centipoises as measured using a Brookfield viscosity device, Model RVT, operated at 5 rpm (revolutions per minute) using a number 5 spindle. The viscosity measurement is made before catalyst is added to the composition so as to eliminate the effects of polymerization. The Brookfield viscometer and its operation are described in "Development of Research Technique for Evaluating the Low Temperature Fluidity of Automatic Transmission Fluids" published by Coordinating Research Council, Inc., February 1963, Appendix A. The thixotropic ratio for the adhesive composition should be high enough that filler does not settle out of the composition and also high enough to prevent overpenetration of the carpet while being low enough to enable the adhesive composition to be pumped, ready blended, and easily applied by doctoring procedures conventional in the art. The thixotropic ratio determined by viscosity measurements made at 1 and at 20 revolutions per minute is between about 1.3:1 and about 10:1 and preferably between about 2:1 and about 8:1. Among the thixotropic agents which can be incorporated to achieve the desired viscosity and the aforementioned ratio are clays, such as kaolin; asbestos; amines; and silica.

To apply the reactive ingredients to the carpet, the polyol blend and the isocyanate are preferably accurately metered and mixed in a multi-component mixer machine and continuously and immediately fed by hose onto the underside of carpet (underside being up). If desired, the catalyst, or water, or other components (including fire retardant compound) can be fed into a multi-component mix meter machine as separate accurately metered streams. To assure better mixing a portion of the extender oil can be incorporated with the isocyanate. Usually the ingredients are applied at a temperature between room temperature and about 150°F. Preferably the temperature of application is between about 80° and about 100°F.

After the adhesive composition has been applied to the underside of pile fiber or primary fabric substrate the adhesive composition is then conventionally spread with a doctor blade. As the mixture passes under the blade, the shearing action of the blade reduces the viscosity so that the mixture can be forced down into and around the tufts of yarn. After passing under the blade, the original high viscosity is regained preventing undesirable overpenetration. The amount of adhesive composition applied is normally just sufficient to obtain adequate adhesion of the pile fibers to the primary fabric substrate. Excess adhesive composition is not only wasteful, but also can cause penetration of the primary fabric, rendering yarn stiff and the final carpet unacceptable. Typically, coating weights for carpets vary from about 12 to about 37 ounces per square yard. Preferably, however, the amount of adhesive composition applied to the carpet ranges from about 20 to about 30 ounces per square yard. In effect the lower limit with respect to the amount applied is limited by the amount necessary to adequately achieve the desired goal, whether it be that of a laminating adhesive, precoat composition or unitary backing.

Curing time and temperature can be varied. Normally, curing is accomplished at a temperature in the range between about 225° and about 350° F. and preferably in the range of from about 275° to about 325° F. for a period of about 0.3 to about 3 minutes. An oven or heated drum can be used for curing.

Among the properties of a carpet which are directly affected by the nature of the adhesive applied are tuft lock, anti-fray properties, appearance, fire retardancy, and dimensional stability. Whereas closely woven carpets of high pile density may have adequate tuft lock retention without application of an adhesive, tufted carpets have virtually no tuft retention in the absence of an adhesive. Anti-fray properties are important with respect to the elimination of fraying of cut edges of tufted carpets. To achieve complete anti-fray characteristics, appreciable weight of adhesive coating is normally required. The appearance of a carpet is judged by hand and visual appearance after being laid. Certain adhesive compositions can provide a better hand to a carpet by introducing a certain degree of stiffness in the carpet. In addition, carpet stiffness also tends to prevent buckling, imparts a high degree of resilience and prevents slipping on a polished floor. Dimensional sta-
Ability of a carpet is obtained by locking the fibers together. In addition to other requirements, the adhesive employed for carpets must have long effectiveness and should have a high tensile strength. In addition, the adhesive should not be degraded by water or other common solvents which could be spilled on carpeting or with which the carpet is likely to come in contact. Moreover, the adhesive composition must be capable of application by simple conventional techniques. Thus, in addition to good adhesion characteristics, adhesive compositions must be judged by other criteria.

Some of the important characteristics of adhesive compositions utilized for carpet backing applications are T-peel, tuft lock and pill test. T-peel is a value obtained when the secondary fabric backing is pulled away from the primary fabric backing. This value is determined using a Scott tester. Adhesion of the scrim or secondary fabric backing to the primary fabric is referred to as the “peel strength.” This expression is used in its normal sense in the carpet manufacturing industry to mean the force required to peel apart a strip of two adhered components 2 inches wide which have been aged 24 hours. It is measured by gripping components in separate jaws of the Scott tensile tester and then moving the jaws apart at a rate of 2 inches per minute. A value of between 6 and 15 pounds is normally obtained. Generally, the lighter the coating weight, the lower the T-peel.

Tuft lock is a determination of the ability of the rug backing adhesive composition to hold fiber to both the primary and secondary fabric backing material. Tuft lock is determined by using a Scott tester to pull on one tuft of the pile to measure the force required to pull the tuft away from the primary and secondary fabric backing material.Normally, values for styrene-butadiene rubber latex will vary from 6 to 15 pounds of pull. At 20 to 30 pounds of pull, the yarns used in the carpet industry usually break.

One of the first tests established to determine carpet combustibility was the so-called “pill test” in which a pellet of methenimine (hexamethylenetetramine) was ignited by a match and allowed to burn out on the carpet. If the area of burned carpet is less than 3 inches from the point of ignition the carpet passes the test. The invention will be illustrated by the following examples, it being understood that there is no intention to be necessarily limited by any details thereof, since variations can be made within the scope of the invention. Unless otherwise indicated, parts by weight are based on 100 parts by weight of the diene polymer.

EXAMPLE I

A thixotropic adhesive composition was prepared by blending 100 parts by weight of a liquid, hydroxyl-terminated polybutadiene (resin R-45HT, manufactured by ARCO Chemical Company) having an equivalent weight of 1,180, a hydroxyl content of 0.85 milliequivalents per gram, and 0.05 weight percent moisture; 20 parts by weight of propyleneglycol (PPG–2000); 18.5 parts by weight of bisisopropanolamine (Isonol C-100, manufactured by Upjohn Company); 300 parts by weight of dry ground penta-acid treated calcium carbonate; five parts by weight of carbon black; one part by weight of 2,2'-methylenebis[4-methyl-6-tertbutyl-phenol]; 40 parts by weight diphenyl methane 4,4'-disocyanate; 0.1 part by weight of dibutyl tin dilaurate; 65 parts by weight of chlorinated paraffin having 50 percent chlorine (Chlorowax 50); and 50 parts by weight of cresyl diphenyl phosphate.

A nonfire retarded composition was also prepared by substituting 110 parts by weight of hydroncarbon oil for the aforementioned chlorinated paraffin and cresyl diphenyl phosphate. In all other respects the nonfire retarded and fire retarded compositions were identical. Comparison of the resulting compositions is shown in the following table.

<table>
<thead>
<tr>
<th>Tensile strength</th>
<th>Tear strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not fire retarded</td>
<td>230</td>
</tr>
<tr>
<td>Fire retarded</td>
<td>270</td>
</tr>
</tbody>
</table>

Carpet coated with the fire retarded composition had a tuft lock of 18. A 6 inches thick piece of inch fire retarded polymer composition did not burn at all (0.0 inch) when a bunsen burner flame was applied to it in the ASTM D1692 test procedure.

EXAMPLE II

A thixotropic adhesive composition was prepared by blending 100 parts by weight of a liquid, hydroxyl-terminated polybutadiene (resin R-45 HT, manufactured by ARCO Chemical Company) having an equivalent weight of 1,180, a hydroxyl content of 0.85 milliequivalents per gram; and 0.05 weight percent moisture; 20 parts by weight of polylurethane (PPG–2000); 18.5 parts by weight of bisisopropanolamine (Isonol C-100, manufactured by Upjohn Company); 300 parts by weight of dry ground fatty acid treated calcium carbonate; five parts by weight of carbon black; one part by weight of 2,2'-methylenebis(4-methyl-6-tertbutylphenol); 40 parts by weight of diphenyl methane 4,4'-disocyanate; 0.1 part by weight of dibutyl tin dilaurate; 65 parts by weight of chlorinated paraffin having 50 percent chlorine (Chlorowax 50); and 50 parts by weight of naphthenic process oil.

A nonfire retarded composition was also prepared by substituting 65 parts by weight of naphthenic process oil for the aforementioned chlorinated paraffin. In all other respects the compositions were identical. A comparison of the resulting compositions is shown in the following table.

<table>
<thead>
<tr>
<th>Tensile strength</th>
<th>Tear strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not fire retarded</td>
<td>239</td>
</tr>
<tr>
<td>Fire retarded</td>
<td>303</td>
</tr>
</tbody>
</table>

Carpet coated with this fire retarded composition had a tuft lock of 14.

EXAMPLE III

A thixotropic adhesive composition was prepared by blending 100 parts by weight of a liquid, hydroxyl-terminated polybutadiene (resin R-45 HT, manufactured by ARCO Chemical Company) having an equivalent weight of 1,180, a hydroxyl content of 0.85 milliequivalents per gram, and 0.05 weight percent moisture; 50 parts by weight of polylurethane (PPG–2000); 21 parts by weight of bisisopropanolamine (Isonol C-100, manufactured by Upjohn Com-
companied; 30 parts by weight of dibromoneopentyl glycol (FR 1138); 0.5 part by weight of mixed ester of thiodi- propionate (Plastinox 1212); 0.5 part by weight of 2,2'- 
methylenebis(4-methyl-6-tertbutylphenol); 200 parts by 
weight of alumina trihydrate; and 10 parts by weight of 
titanium dioxide.

The resulting mixture was blended with isocyanate to 
form the polyurethane. Specifically, 71.3 parts by 
weight of polyphenylmethane polysisocyanate was in-
corporated with the mixture, together with 0.2 part by 
weight of dibutyl tin dilaurate which served as a cata-
lyst.

The resulting composition when applied to carpeting 
was a thixotropic adhesive composition. The resulting 
polymer composition was subjected to an ASTM 
D-568 test modified in accordance with the procedure 
of Example III. The polymer burned for only 1/2 second 
before self-extinguishing.

EXAMPLE V
A thixotropic adhesive composition was prepared by 
blending 100 parts by weight of a liquid, hydroxyl-
terminated polybutadiene (resin R-45 HT, manufac-
tured by ARCO Chemical Company) having an equiva-
 lent weight of 1,180, a hydroxyl content of 0.85 millie-
quivalents per gram, and 0.05 weight percent moisture; 
50 parts by weight of polypropylene glycol (PPG-2000); 45 parts by weight of bisisopropanolani-
line (isonol C-100, manufactured by Upjohn Com-
pany); 25 parts by weight of 

\[
\text{R[P(OCH}_2\text{CH}_2\text{Cl}]}\text{O(\text{CH}_2\text{CH})_n\text{O}-} \quad (\text{OCH}_2\text{CH}_2\text{Cl})_2
\]

where R is CICH\text{CH}_2\text{OH}(\text{O})\text{P(CICH}_2\text{CH}_2\text{)}\text{OCH(\text{CH})}_m\text{O}.

The resulting mixture was blended with isocyanate to 
form the polyurethane. Specifically, 71.3 parts by 
weight of polyphenylmethane polysisocyanate was in-
corporated with the mixture, together with 0.2 part by 
weight of dibutyl tin dilaurate which served as a cata-
lyst.

The resulting composition when applied to carpeting 
was a thixotropic adhesive composition. The resulting 
polymer composition was subjected to an ASTM 
D-568 test modified in accordance with the procedure 
of Example III. The polymer burned for only 1/2 second 
before self-extinguishing.

EXAMPLE VII
A thixotropic adhesive composition was prepared by 
blending 100 parts by weight of a liquid, hydroxyl-
terminated polybutadiene (resin R-45 HT, manufac-
tured by ARCO Chemical Company) having an equiva-
 lent weight of 1,180, a hydroxyl content of 0.85 millie-
quivalents per gram, and 0.05 weight percent moisture; 
50 parts by weight of polypropylene glycol (PPG-2000); 45 parts by weight of bisisopropanolani-
line (isonol C-100, manufactured by Upjohn Com-
pany); 25 parts by weight of 

\[
\text{R[P(OCH}_2\text{CH}_2\text{Cl}]}\text{O(\text{CH}_2\text{CH})_n\text{O}-} \quad (\text{OCH}_2\text{CH}_2\text{Cl})_2
\]

where R is CICH\text{CH}_2\text{OH}(\text{O})\text{P(CICH}_2\text{CH}_2\text{)}\text{OCH(\text{CH})}_m\text{O}.

The resulting mixture was blended with isocyanate to 
form the polyurethane. Specifically, 71.3 parts by 
weight of polyphenylmethane polysisocyanate was in-
corporated with the mixture, together with 0.2 part by 
weight of dibutyl tin dilaurate which served as a cata-
lyst.

The resulting composition when applied to carpeting 
was a thixotropic adhesive composition. The resulting 
polymer composition was subjected to an ASTM 
D-568 test modified in accordance with the procedure 
of Example III. The polymer burned for only 1/2 second 
before self-extinguishing.
blending 100 parts by weight of a liquid, hydroxyl-terminated polybutadiene (resin R-45 HT, manufactured by ARCO Chemical Company) having an equivalent weight of 1,180, a hydroxyl content of 0.85 milliequivalents per gram, and 0.05 weight percent moisture; 50 parts by weight of polypropylene glycol (PPG 2000); 45 parts by weight of bisisopropanolamine (Isocure C-100, manufactured by Upjohn Company); 25 parts by weight of perchloroethylene; two parts by weight of antimony trioxide; 0.5 part by weight of mixed ester of thiopropionate (Plastinox 1212); 0.5 part by weight of 2,2'-methylenebis(4-methyl-6-tertbutylphenol); 25 parts by weight of kaolin; 200 parts by weight of alumina trihydrate; and 10 parts by weight of titanium dioxide.

The resulting mixture was blended with isocyanate to form the polyurethane. Specifically, 71.3 parts by weight of polyphenylmethane polysiocyanate was incorporated with the mixture, together with 0.2 part by weight of dibutyl tin dilaurate which served as a catalyst.

The resulting composition when applied to carpeting was a thixotropic adhesive composition. Using ASTM D-568 test modified per Example III the polymer composition burned for only 2 seconds before self-extinguishing.

EXAMPLE VIII
A prepolymer composition was prepared. The formulation consisted of 100 parts by weight of a liquid, hydroxyl-terminated polybutadiene prepolymer having 8.9 weight percent free NCO groups (R-45 HT resin identified in Example I reacted with tolylene diisocyanate); 20 parts by weight of polypropylene glycol (PPG 2000); 18.5 parts by weight of bisisopropanolamine; one part by weight of 2,2'-methylenebis(4-methyl-6-tertbutylphenol); 10 parts by weight of asbestos; 300 parts by weight of dry ground fatty acid treated calcium carbonate; five parts by weight of 5-A molecular sieve; five parts by weight of carbon black; 35 parts by weight of tricresyl phosphate; 65 parts by weight of chlorinated paraffin containing 50 percent chlorine (Chlorowax 50); 0.6 part by weight of dibutyl tin dilaurate.

The resulting prepolymer composition had a NCO/OH ratio of 1.07 and was cured for 30 minutes at approximately 200°F. This "dead lay" tile formulation had a tensile strength of between 135 and 142 pounds per square inch and a tear strength of about 48 pounds per linear inch.

Employing ASTM fire retardancy test D-1692 only between 0.9 and 1.1 inch of the material burned at a burning rate of about 0.5 inches per minute.

EXAMPLE IX
A prepolymer composition was prepared. The formulation consisted of 100 parts by weight of a liquid, hydroxyl-terminated polybutadiene prepolymer having 8.9 weight percent free NCO groups (R-45 HT resin identified in Example I reacted with tolylene diisocyanate); 20 parts by weight of polypropylene glycol (PPG 2000); 18.5 parts by weight of bisisopropanolamine; 1 part by weight of 2,2'-methylenebis(4-methyl-6-tertbutylphenol); 10 parts by weight of asbestos; 200 parts by weight of dry ground fatty acid treated calcium carbonate; five parts by weight of 5-A molecular sieve; five parts by weight of carbon black; 20 parts by weight of tricresyl phosphate; 40 parts by weight of chlorinated paraffin having 50% chlorine (Chlorowax 50); 0.6 part by weight of dibutyl tin dilaurate; 32 parts by weight of naphthenic process oil; 100 parts by weight of hydrated alumina; seven parts by weight of lecitin.

The resulting prepolymer composition had a NCO/OH ratio of 1.07 and was cured for 30 minutes at approximately 200°F. This "dead lay" tile formulation had a tensile strength of between 115 and 130 pounds per square inch and a tear strength of about 39 pounds per linear inch.

Employing ASTM fire retardancy test D-1692 the length which was burned in inches was between 0.8 and 1 inch at a burning rate of about 0.35 and 0.40 inches per minute.

EXAMPLE X
A thixotropic adhesive composition was prepared and applied as a backing to an automobile floor mat. The composition consisted of 100 parts by weight of a liquid, hydroxyl-terminated polybutadiene (resin R-45 HT, manufactured by ARCO Chemical Company) having an equivalent weight of 1,180, an hydroxyl content of 0.85 milliequivalents per gram, and 0.05 weight percent moisture; 16.8 parts by weight of bisisopropanolamine; 15 parts by weight of polypropylene glycol; 300 parts by weight of hydrated alumina; 10 parts by weight of titanium dioxide; five parts by weight of zinc oxide; 50 parts by weight of chlorinated paraffin having 50 percent chlorine (Chlorowax 50); one part by weight of a UV stabilizer (Tinuvin 327); one part by weight of the mixed ester of thiopropionate; one part by weight of 2,2'-methylenebis(4-methyl-6-tertbutylphenol); 0.005 part by weight of dibutyl tin dilaurate; and 40.5 parts by weight of diphenylmethane-4,4'-diisocyanate (Isionate 143-L, manufactured by Upjohn Company).

When the polymer composition was tested in accordance with ASTM test D-1692-68 the length burned in inches was 0.0 and the burning rate in inches per minute was 0.0. In addition, there was no melting or dripping observed. The time in seconds of burning after 60 second exposure to a bunsen burner flame was less than one second.

EXAMPLE XI
A thixotropic adhesive composition was prepared and applied as backing to an automobile floor mat. The composition consisted of 100 parts by weight of a liquid, hydroxyl-terminated polybutadiene (resin R-45 HT, manufactured by ARCO Chemical Company) having an equivalent weight of 1,180, an hydroxyl content of 0.85 milliequivalents per gram, and 0.05 weight percent moisture; 16.8 parts by weight of bisisopropanolamine; 15 parts by weight of polypropylene glycol; 10 parts by weight of diphenyl cresyl phosphate; 100 parts by weight of kaolin, 100 parts by weight of hydrated alumina; 10 parts by weight of titanium dioxide; five parts by weight of zinc oxide; 40 parts by weight of chlorinated paraffin having 50 percent chlorine (Chlorowax 50); 1 part by weight of a UV stabilizer (Tinuvin 327); one part by weight of the mixed ester of thiopropionate; one part by weight of 2,2'-methylenebis(4-methyl-6-tertbutylphenol); 0.005 part by weight of dibutyl tin dilaurate; and 40.5 parts by weight of diphenylmethane-4,4'-diisocyanate (Isionate 143-L, manufactured by Upjohn Company).
When the polymer composition was tested in accordance with ASTM test D-1692-68 the length burned in inches was 0.0 and the burning rate in inches per minute was 0.0. In addition, there was no melting or dripping observed although intumescence occurred. The time in seconds of burning after 60 second exposure to a bunsen burner flame was less than one second.

EXAMPLE XII

A thixotropic adhesive composition was prepared by blending 100 parts by weight of the liquid, hydroxysterminated polybutadiene employed in Example II; 20.2 parts by weight bissopropionolamine; 20 parts by weight of the polypolypropylene glycol of Example I; 110 parts by weight of cresyl diphenyl phosphate; 65 parts by weight of chlorininated paraffin having 50 percent chlorine (Chlorowax 50); 200 parts by weight of dry ground fatty acid treated calcium carbonate; 200 parts by weight of alumina trihydrate; five parts by weight of carbon black (Regal 99R made by Cabot Corp.); seven parts by weight of a barium cadmium stabilizer (Mark WS); one part by weight of 2,2'-methylene-bis(4-methyl-6-tertbutylphenol); one part by weight of mixed ester of thiopropionate (Plastinox 1,2,12); and 0.15 parts by weight of dibutyltin dilaurate.

The resulting mixture was blended with 36.4 parts by weight of polyphenylmethane polyisocyanate.

The resulting composition was applied to the back of a nylon carpet. A 25 foot length of this coated carpet was tested for fire retardancy by the Steiner 25 foot tunnel test (ASTM E-84). It had a flame spread rating of 31, a smoke rating of 150, and a fuel contribution rating of 20 compared to the read oak standard used in the test procedure. This is an excellent rating.

A ¾ inch strip of the polymer composition itself was subjected to a modified ASTM D-568 per Example III. The polymer burned for less than 2 seconds before self-extinguishing.

The compositions of the foregoing examples had a viscosity between about 3,000 and about 100,000 centipoises as measured using a Brookfield Viscosity Device, Model RVT, operated at 5 rpm using a number 5 spindle. The thixotropic ratio of said compositions, determined by viscosity measurements made at 1 and at 20 rpm, was between about 1.3:1 and about 10:1. In all cases the fire retardant compound was compatible with the polyurethane.

From the foregoing it will be seen that this invention is well adapted to obtain all of the ends and objects hereinafore set forth, together with other advantages which are obvious or inherent in the system. Characteristics of formulations prepared in accordance with the present invention include good fire retardancy; a 12 to 20 pound tuft lock; 75 to 100 percent bundle wrap; a backing destroying bond (i.e., the secondary fabric backing is torn upon attempted delamination); a good hand which is soft to firm without causing ‘boardiness’; a viscosity low enough to allow pumping, mixing and ease of application but high enough to prevent rapid uncontrolled penetration into the fibers (i.e., a thixotropic formulation); and rapid curing.

The thixotropic polyurethane adhesive compositions of the present invention have several advantages over the carboxylated styrene butadiene rubber latex adhesives which have been used for so many years. First the “cure” of carboxylated latex adhesive is primarily a drying cycle which cannot be catalyzed in order to shorten the time. In contrast, the thixotropic adhesive compositions of the present invention cure through a reaction with disocyanate which can be catalyzed to any desired degree. Moreover, the cure, if sufficiently catalyzed, will take place rapidly at lower temperatures (e.g., 200° F.). Rapid cure increases production and greatly decreases capital investment since smaller curing ovens are required. Fuel requirements are also greatly reduced. The thixotropic adhesive compositions of the present invention also have the advantage of having a higher early green strength which thereby reduces the chances of accidental delamination. Application of the thixotropic adhesive compositions of the present invention is also simpler than application of carboxylated latex adhesives. The composition of the invention can be discharged onto a carpet continuously by means of a hose or nozzle and the resulting adhesive adjusted using a conventional doctor blade to give the desired rate of application and degree of penetration. Another advantage is the fact that smaller and simpler equipment can be used with the thixotropic adhesive compositions of the present invention and this means a reduction in capital investment and required operators, thus reducing production costs.

The importance of fire retardancy characteristics is apparent in the applications which have been stressed. The need for high fire retardancy in carpets is particularly apparent for nursing homes and hospitals. The fire retardant polyurethane compositions, however, can also be used in other applications. For example, such compositions can be used to make fire retarded elastomeric automobile parts, conveyor belts, etc.

Obviously, many modifications and variations of the invention as hereinafter set forth can be made without departing from the spirit and scope thereof.

What is claimed is:

1. Carpet including a primary backing material, tufted yarn stitched through the primary fabric backing to provide a pile surface on one side of the primary backing and a loop of yarn on the underside of the primary backing and a layer of thixotropic fire retardant adhesive composition adhered to the underside of the primary backing and the loop of yarn, said thixotropic composition having a thixotropic ratio based on the viscosity at 1 rpm and at 20 rpm of between 1:3:1 and 10:1, said composition comprising liquid, hydroxyl-terminated diene polymer; high molecular weight polyol having an average equivalent weight between about 500 and 2,200 present in an amount up to 5 times the equivalent of the diene polymer, low molecular weight polyol having an equivalent weight of between about 30 and about 300 present in an amount between about 1.5 and about 8 times the equivalents of diene polymer; isocyanate having a functionality of between 2 and 3 present in in an amount to provide a NCO/OH equivalents ratio of between 0.95:1 and 1.5:1; filler present in an amount between about 40 and about 300 parts per 100 parts by weight of diene polymer; oil extending hydrocarbon liquid present in an amount of up to 200 parts per 100 parts by weight of diene polymer; fire retardant compound selected from the group consisting of halogenated hydrocarbon present in an amount between about 10 and about 250 parts per 100 parts by weight of diene polymer, a phosphate material present in an amount between about 10 and about 250 parts per 100 parts by weight of diene polymer, and a phosphate material present in an amount between about 10 and about 250 parts per 100 parts by weight of diene polymer.
polymer, hydrated alumina present in an amount between about 20 and about 800 parts per 100 parts by weight of diene polymer, and mixtures thereof; water present in an amount up to 10 parts per 100 parts by weight of diene polymer; and catalyst for said composition present in an amount between about 0.02 and about four parts per hundred parts by weight of the diene polymer.