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Chmiel et al.

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[54] **ADHESIVE FOR BONDING CURED EPDM RUBBER**

[75] **Inventors:** **Chester T. Chmiel, Granger, Ind.;**
Daniel J. Cotsakis, Carlisle, Pa.

[73] **Assignee:** **Uniroyal Plastics Company, Inc.,**
Mishawaka, Ind.

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[22] **Filed:** **Nov. 3, 1986**

Related U.S. Patent Documents

Reissue of:

[64] **Patent No.:** **4,501,842**
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[51] **Int. Cl.⁴** **C08L 9/00; C08L 15/02;**
C08L 53/00

[52] **U.S. Cl.** **524/432; 524/450;**
524/474; 524/505; 525/95; 525/125; 523/351

[58] **Field of Search** **524/432, 450, 474, 505;**
525/95, 125; 523/551

[56] **References Cited**

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Primary Examiner—Allan M. Lieberman
Attorney, Agent, or Firm—Pennie & Edmonds

[57] **ABSTRACT**

An adhesive for bonding cured EPDM membranes is provided comprising

- (A) a halogenated butyl rubber
- (B) a pre-cross linked butyl rubber
- (C) a styrene/ethylene butylene/styrene block thermoplastic rubber,
- (D) a thermoplastic petroleum based hydrocarbon feedstock derived aliphatic monomer resin and
- (E) an aliphatic isocyanate.

12 Claims, No Drawings

ADHESIVE FOR BONDING CURED EPDM-RUBBER

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This invention relates to an improved solvent based contact adhesive which is useful for providing a strong bond between sheets of cured ethylene-propylene-diene terpolymers (EPDM).

EPDM rubber is widely used in the tire industry. However, the bonding techniques used in tires requires special surface preparation and high pressure and heat conditioning. When EPDM membranes are used as material other than for tires, such as for a roofing material, it is sometimes necessary to prepare a lap seam bonding to EPDM membranes to itself.

In the prior art, such as Skeist, I., Handbook of Adhesives, pp. 880, New York, Reinhold Publishing Corp., 1977, it is suggested that a neoprene-based adhesive may be used for bonding EPDM rubber. Currently the com-

monly used adhesive is one based on neoprene dissolved in a mixture of solvents and incorporating resins, fillers, curatives and stabilizers to a total solids content of about 23%. This compound develops a T-peel adhesion of approximately 2 lbs./inch width.

Adhesives based on neoprene generally have excellent resistance to creep and cold flow, but have the drawback of providing only low levels of bond strength to cured EPDM.

Known contact adhesives based on butyl or polyisobutylene polymers while developing good ultimate bond strengths to cured EPDM, have unsatisfactory creep, cold flow and heat strength characteristics. In addition, it is known that mixtures of neoprenes and butyls and/or polyisobutylenes do not overcome the shortcomings of either component as set forth above.

EPDM itself is a poor adhesive polymer. When EPDM is used as an adhesive the resulting compounds have little or no tack and when uncured are very thermoplastic.

It is therefore an object of the invention to provide an adhesive that will develop a good ultimate bond strength to the joining of cured EPDM membranes as well as maintaining satisfactory creep, cold flow and heat strength characteristics, all without the addition of special surface preparations or the use of high pressure and/or heat.

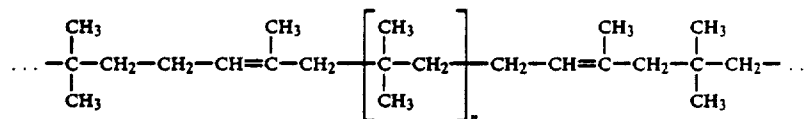
In accordance with the invention an adhesive formulation is provided comprising a blend of three rubbers, namely, (1) a halogenated butyl rubber, (2) a pre-crosslinked butyl rubber and (3) a three block copolymer with polystyrene end blocks and a rubbery poly(ethylene-butylene) mid block, together with a petroleum hydrocarbon based aliphatic thermoplastic resin having a high softening point and an aliphatic isocyanate.

The invention also provides an improved method for preparing said adhesive which method comprises the

separate milling or mixing in a Banbury (TM) mixer of said halogenated and pre-crosslinked butyl rubbers and sequential additions when solubilizing the ingredients with the butyl rubbers first and the isocyanate modifier last into a cool churn which has been purged of moisture.

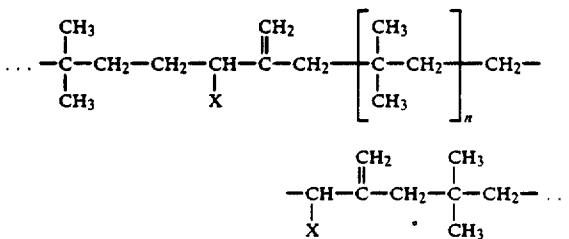
The halogenated butyl rubber ingredient is preferably Bromobutyl of 27-51 Mooney viscosity (ML 1+8 at 125° C.) and 2.0-2.5% bromine content. The halogenated butyl rubber may be added at a concentration of 20.0-45.0 parts per hundred parts of rubber. Chlorobutyl rubber may be used in place of bromobutyl rubber. The Mooney viscosity of said chlorobutyl rubber is in the range 27-51 (ML 1+8 at 125° C.) and possesses a 1.1-1.3% chlorine content. Adhesives incorporating chlorobutyl rubber impart bond strengths between cured EPDM sheets higher than those given with neoprene adhesives currently used but lower than those given by the preferred bromobutyl rubber adhesives of this invention.

The molecular structure of regular butyl rubber may be schematically shown as represented by Skeist, I., Handbook of Adhesives pp. 255, New York, Reinhold Publishing Corp., 1977, as follows:



Where n is about 50

Halogenation of the above polymer is derived through a proprietary process with up to 90% of the halogenation situated allylic to the double bond with retention of most of the unsaturation. This is schematically represented as follows:

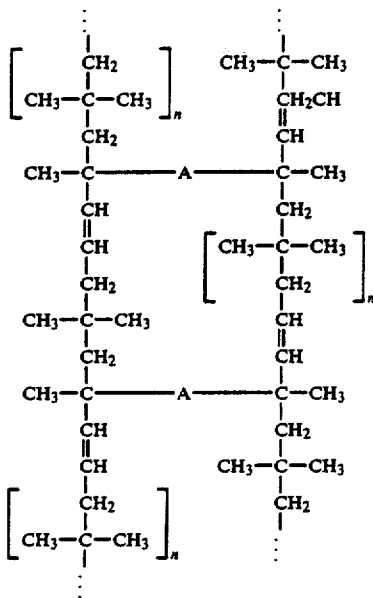
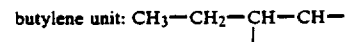


Where X is Cl or Br and n is about 50

These halogenated butyl rubbers may be of the bromobutyl or chlorobutyl type made by Polysar Ltd., Sarnia, Ontario, Canada or by Exxon Chemical Company, Houston, Tex.

The pre-crosslinked butyl rubber is also derived from regular butyl rubber through a proprietary process by incorporating a crosslinking agent during the polymerization of the rubber. The finished product may be schematically represented as follows:

-continued



Where n is about 50 and A is a crosslinking agent such as 1,4 divinyl benzene, methyl divinyl benzene 1,3 butadiene, isoprene, 2-ethyl 1,3-butadiene, 1,6 hexadiene, 1,6-hexanediol-diacrylate, 2 methyl-1,3-butadiene, butyleneglycol dimethylacrylate, 1,4 butanediol diacrylate, thiodiglycol dimethacrylate, diallyl maleate, decamethylene glycol diacrylate, 2-chloro 1,3 butadiene, polyethylene glycol dimethacrylate, 1 phenyl ethylene-1,2-dimethacrylate.

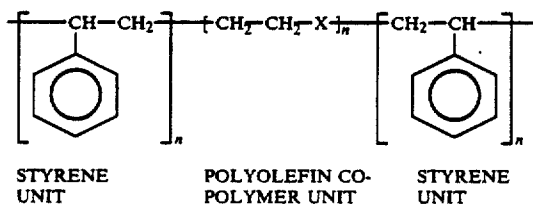
Not all of the unsaturation is reacted so that part of the butyl rubber is still soluble.

Such pre-crosslinked butyl rubber may be of the type made by Polysar Ltd., Sarnia, Ontario, Canada and may be of a weight percent solubility in cyclohexane of 15-50 percent and a concentration 40.0-65.0 parts per hundred parts of rubber.

The styrene(ethylene-butylene)styrene block thermoplastic rubber ingredient may be of the type produced by Shell Chemical Company, Houston, Tex. with a styrene content of 28-29% by weight, a midblock content of 71-72% by weight and tensile strength of 4500-5000 lbs./in² and said block copolymer used at a concentration of 15.0-20.0 parts per hundred of rubber.

A block copolymer also applicable in this invention is one where the butylene in the midblock is replaced by propylene to give a styrene-(ethylene propylene)-styrene block copolymer.

The general formula for these block copolymers is:



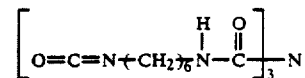
Where X = propylene unit: $-\text{CH}_2-\text{CH}_2-$ or $-\text{CH}_2-\text{CH}(\text{CH}_3)-$

and n is from 20 to 1200 and n' is from 70 to 700.

Refer to U.S. Pat. No. 3,917,607 assigned to Ronald K. Crossland and James T. Harlan.

The low molecular weight high softening point, thermoplastic, aliphatic type hydrocarbon based resin is made from petroleum monomers. The aliphatic resin is introduced to impart improved compatibility between the block copolymer and butyl rubbers, and to improve the high temperature heat strength of the butyl rubbers. The aliphatic resin is derived from hydrocarbon feedstock monomers possessing 5-9 carbon atoms polymerized to varying molecular weight ranges so as to give softening points of 162° C. to 181° C. The preferred resin is one possessing a higher softening point range from 175°-181° C. The higher softening resin when incorporated into the formulations of this invention impart higher strengths to butyl and block copolymers mixtures at the test temperatures of about 70° C. An example of high softening point resins applicable in the invention is the Piccovar (TM) series produced by Hercules, Inc. Wilmington, Del. with a softening point of 175°-181° C., an acid number of less than 1 and a bromine number of 16.0-20.0 at a concentration of 120.0-160.0 parts per 100 rubber.

The organic isocyanate ingredient of the invention functions to provide a cure of the halogenated butyl rubber when exposed to moisture. Useful organic isocyanates include 1,6 hexamethylene diisocyanate; 2,4 and 2,6-toluene diisocyanate; 4,4-diphenylmethane diisocyanate; polymethylene polyphenylisocyanate; 4,4-dicyclohexylmethane diisocyanate; xylylene diisocyanate; but, most of these tend to give either short gel times or reduced high temperature heat strength. A preferred type is Desmodur (TM) N-75 isocyanate available in a 75% solution from Mobay Chemical Corporation, Pittsburgh, Penn. This material has an NCO content of 15.0-17.0% and is an aliphatic compound which is an adduct based on 1,6 hexamethylene diisocyanate:



Said isocyanate is used at concentrations in the range of 20.0-35.0 parts per 100 rubber.

To scavenge moisture inadvertently incorporated into the adhesive during manufacture and packaging, an adsorbent of the alkali-metal alumino-silicate zeolite family of compounds is added. Typical Molecular Sieves are 5A or 13X supplied by the Linde division of Union Carbide, New York, N.Y. Said Molecular Sieves are used at a concentration of 5.0-15.0 parts per 100 parts of rubber.

Optionally, where high temperature performance is required, zinc oxide may be added at a concentration of 0.5-2.0 parts per 100 parts of rubber. A typical zinc oxide is Prottox 166 produced by New Jersey Zinc Co.

The zinc oxide is added to allow some modulus increase of the halogenated butyl rubber, but little enough so that the solution stability is not adversely affected.

The aforementioned ingredients are dispersed in an organic liquid having a solubility parameter of 8.5-8.9 and a hydrogen bonding index 3.0-3.5. Said solvent is used at a concentration of 500.0-640.0 parts per 100 parts rubber giving a total solids level of 31.0-37.0 percent. To improve ease of application and drying of the adhesive, the dispersing medium may be a blend of 2 or more solvents.

Carbon black may also be added for pigmenting purposes and/or to improve mill or Banbury (TM) processing of the butyl polymers. The carbon black may be of medium reinforcement character, having an ASTM number from N-285 thru N-330. Said carbon black is used at a concentration of 2.0-20.0 parts per 100 parts rubber.

In order to maximize solution stability, the ingredients are processed and mixed in a controlled sequence. The halogenated butyl and pre-crosslinked butyl are separately milled or mixed in Banbury (TM) mixer to homogenize them and work some of the nerve out. It has been found that carbon black improves the processing of the mill or the Banbury (TM) mixed batches. Solubilization of the adhesive is initiated by dispersing the mill/Banbury batches in 75% of the solvent. It is important that the heat build up be kept at a minimum throughout the solubilizing procedure. This is followed, after a period of 2-3 hours, by the addition of the thermoplastic resin, thermoplastic rubber and molecular sieves to begin scavenging moisture. At this point the mixing vessel should be sealed and purged with nitrogen. After another 2-3 hours, the zinc oxide should be added with the remaining solvent. The mixing vessel is then resealed and purged followed by mixing for 1 hour minimum or until smooth. This is followed by cooling of the churn to no more than 80° F. Any evaporated solvent is then replaced, along with blending in of the isocyanate.

The above procedure results in a compound with a storage stability of greater than six months. It has been found that a substantive deviation from the above procedure may result in a drop in stability to much less than six months.

The following examples, while not intending to be limiting of the invention, illustrate the invention in greater detail.

EXAMPLE 1

This example illustrates the adhesion level generated by the industry standard neoprene-based adhesive such as N-100 distributed by Carlisle Corp.

Test samples were prepared by vigorously washing the surface of a particular 0.065" thick cured EPDM membrane with a cloth soaked with heptane. 1" x 6" strips were then cut. A thin coat of the N-100 adhesive was then brushed onto the strips and allowed to dry 15 min. T-peel adhesion samples were prepared by bringing the whole adhesive coated side of one strip together with the adhesive coated side of another strip, followed by lamination with a hand roller. Lap shear adhesion samples were prepared by bringing strips together so a 1" x 1" contact area was formed, followed by lamination with a hand roller. Adhesion samples were then allowed to stand undisturbed for 7 days at 25° C. This was followed by adhesion testing on an Instron (TM) tensile tester with the jaw speed set for 2 in./min. and testing being performed at 25° C. and 70° C. The following results were obtained:

TABLE 1

Test @ 2 in./min.	25° C. Results	70° C. Results
T-Peel Adhesion (lbs./in. width)	2.2	1.5
Lap Shear Adhesion (lbs./in. ²)	14.8	12.0

All test samples showed adhesive failure at the adhesive/membrane interface.

EXAMPLE 2

This example illustrates the adhesion level generated by the adhesive and manufacturing procedure of the instant invention.

The following formulation was used to prepare the adhesive invention:

Ingredient	Parts by Weight
<u>Mill Batch A</u>	
Polysar Bromobutyl X-2	45.0
Cabot Regal 300 Carbon Black	2.0
	47.0
<u>Mill Batch B</u>	
Polysar Butyl XL-20	40.0
	40.0
<u>Churn Batch</u>	
Mill Batch A	47.0
Mill Batch B	40.0
Shell Kraton G1652	15.0
Hercules Piccovar AB180	150.0
Protax 166 ZnO	2.0
Molecular Sieves #5A	10.0
Toluene	400.0
Hexane	100.0
Desmodur N-75 (75% solids solution)	25.0
	789.0
Total Solids:	35.8%

The Bromobutyl with carbon black and pre-crosslinked butyl were mixed separately on a two roll mill for 20 minutes minimum. Above mill batches could also be processed in a Banbury (TM) for a minimum of 6 minutes. These mill batches were then cut-up and added to an adhesive churn loaded with 75% or 375 PPHR of the above solvents, hexane and toluene. This was allowed to mix 2 hours minimum. This was followed by the addition of the Piccovar AB180, the Kraton G1652, the Molecular Sieves #5A. At this point, the churn was sealed and purged with dry nitrogen. This was allowed to mix an additional 2 hours minimum, followed by the addition of the zinc oxide and the remaining 25% or 125 PPHR of solvent. The churn was again sealed, dry nitrogen purged and allowed to mix 1 hour minimum or until smooth. The churn was then cooled down to 80° F. maximum, followed by volume adjustment to compensate for evaporated solvent and Desmodur N-75 isocyanate. Adhesion test samples were then prepared, treated and tested in the same fashion described in Example 1. Test results were as follows:

TABLE 2

Test @ 2 in./min.	25° C. Results	70° C. Results
T-Peel Adhesion (lbs./in. width)	6.4	2.4
Lap Shear Adhesion (lbs./in. ²)	35.7	18.8

All 25° C. tested samples showed a mixture of adhesive and cohesive failure within the adhesive; 70° C. tested samples showed all cohesive failure.

EXAMPLE 3

This example illustrates the resulting loss of adhesion when the high softening point thermoplastic resin level falls below 120 PPHR. Resin concentration in this instance was 100 PPHR. T-peel adhesion samples only were prepared and aged in the same fashion discussed in Example 1. Test results were as follows:

TABLE 3

Test Temperature	T-Peel Adhesion @ 2 in./min. (lbs./in. width)
25° C.	4.5
70° C.	0.7

25° C. tested samples showed mixed adhesive and cohesive failure within the adhesive, 70° C. tested samples showed all cohesive failure.

EXAMPLE 4

This example illustrates the resulting loss in adhesion when the isocyanate is eliminated from the compound. T-peel adhesion samples only were prepared and aged in the same fashion discussed in Example 1. Test results were as follows:

TABLE 4

Test Temperature	T-Peel Adhesion @ 2 in./min. (lbs./in. width)
25° C.	4.0
70° C.	0.9

All test samples showed cohesive failure within the adhesive.

EXAMPLE 5

This example illustrates the resulting loss in adhesion when the zinc oxide is eliminated from the compound. T-peel adhesion samples only were prepared and aged in the same fashion discussed in Example 1. Test results were as follows:

TABLE 5

Test Temperature	T-Peel Adhesion @ 2 in./min. (lbs./in. width)
25° C.	6.3
70° C.	1.2

25° C. tested samples showed mixed adhesive and cohesive failure within the adhesive; 70° C. tested samples showed all cohesive failure.

EXAMPLE 6

This example illustrates the resulting loss in stability when manufacturing procedure is varied from that procedure stated herein. 2.0 PPRH of zinc oxide was added to the Bromobutyl Banbury stock instead of to the mixing churn. The resulting adhesive was extremely rough and snotty in appearance and gelled in only 2.5 weeks.

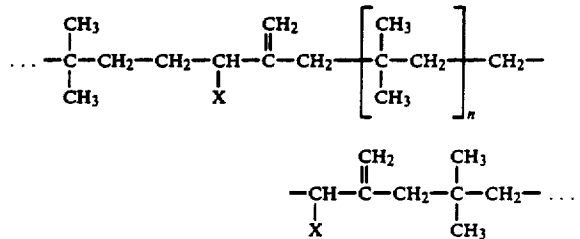
EXAMPLE 7

This example illustrates the resulting loss in stability when mixing vessel temperature at the point of isocyanate addition is significantly above 80° F. The mixing sequence followed was that described in example 2, except, the solution temperature at the point of isocya-

nate addition was not reduced to lower than 140° F. The resulting adhesive looked very good initially, but gelled in only 2 weeks.

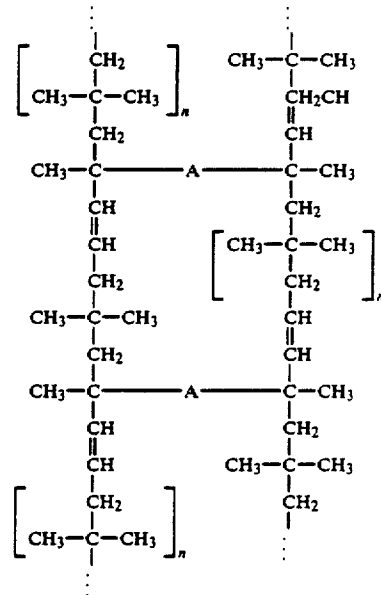
What is claimed is:

1. An adhesive for bonding cured EPDM comprising: (A) a halogenated butyl rubber of the formula:



where X is Cl or Br and n is about 50

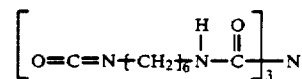
- (B) a pre-crosslinked butyl rubber of the formula:



where A is a crosslinking agent and n is about 50

- (C) a styrene/ethylene butylene/styrene block thermoplastic rubber,
 (D) a thermoplastic, petroleum hydrocarbon feedstock derived aliphatic monomer resin derived from C₅-C₉ streams polymerized to varying molecular weights to give a softening point range of 162°-181° C. and
 (E) an aliphatic isocyanate; wherein (A) is at a concentration of 20.0-45.0 PPHR, (B) is at a concentration of 40.0-65.0 PPHR, (C) is at a concentration of 15.0-20.0 PPHR, (D) is at a concentration of 120-160 PPHR and (E) is at a concentration of 20-35 PPHR.

2. An adhesive of claim 1 where (E) is an aliphatic isocyanate adduct based on 1,6 hexamethylene diisocyanate of the formula:



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3. An adhesive of claim 2 wherein said halogenated butyl rubber has a bromine content of 2.0-2.5% or a chlorine content of 1.1-1.3%.

4. An adhesive of claim 2 wherein said pre-cross-linked butyl rubber has a weight percent of solubility in cyclohexane of 15-50 percent.

5. An adhesive of claim 2, wherein said block thermoplastic rubber contains a styrene content of 28-29% by weight, a mid-block content of 71-72% by weight and a tensile strength of 4500-5000 lbs. per square inch.

6. An adhesive of claim 2, wherein said thermoplastic, aliphatic type hydrocarbon resin has a softening point of 175°-181° C., an acid number of less than 1 and a bromine number of 16.0-20.0.

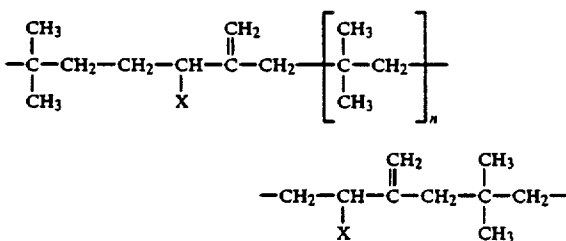
7. An adhesive of claim 2, wherein said aliphatic isocyanate is based on 1,6 hexamethylene diisocyanate adduct with an NCO content of 15.0-17.0 percent concentration.

8. An adhesive composition of claim 2, further comprising an adsorbent of the alkali-metal alumino-silicate zeolite family of compounds at a concentration of 5.0-15.0 PPHR; zinc oxide at a concentration of 0.5-2.0 PPHR; an organic liquid having a solubility parameter of 8.5-8.9, and a hydrogen bonding index of 3.0-3.5 at a total concentration of 500.0-640.0 PPHR resulting in a total solid level of 31.0-37.0 percent and carbon black concentration of 2.0-20.0 PPHR.

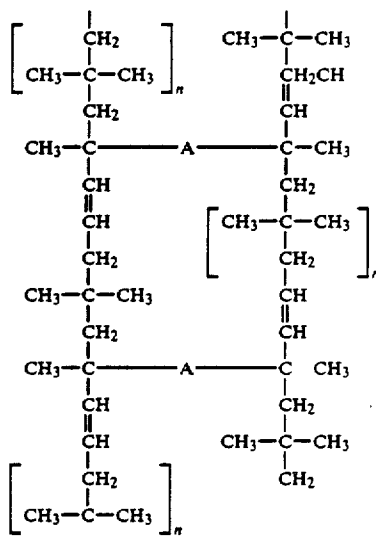
9. An adhesive composition of claim 1 wherein A is 1,4 divinyl benzene, methyl divinyl benzene, 1,3 butadiene, isoprene, 2-ethyl 1,3-butadiene, 1,6 hexadiene, 1,6 hexanediol-diacrylate, 2 methyl-1,3-butadiene, butylene glycol dimethacrylate, 1,4 butanediol diacrylate, thiodiglycol dimethacrylate, diallyl maleate, decamethylene glycol diacrylate, 2-chloro 1,3 butadiene, polyethylene glycol dimethacrylate, 1 phenyl ethylene-1,2 dimethacrylate.

10. A process for making an adhesive for the bonding of cured EPDM membrane comprising:

(A) Milling or mixing separately, with carbon black, about 20.0 to about 45.0 parts PHR of a halogenated butyl rubber of the formula:



where X is Cl or Br and n is about 50 and about 40 to about 65 parts PHR a pre-crosslinked butyl rubber of the formula:



where A = Crosslinking Agent and n is about 50.

(B) [Solubizing] Solubilizing the butyl rubbers of (A) with about 15 to about 20 parts PHR of a styrene/ethylene butylene/styrene block thermoplastic rubber, about 120 to about 160 parts PHR of a thermoplastic, petroleum hydrocarbon feedstock derived aliphatic monomer resin derived from C₅-C₉ streams polymerized to varying molecular weights to give a softening point range of 162°-181° C., about 20 to about 35 parts PHR of an aliphatic isocyanate based on an adduct of 1,6-hexamethylene diisocyanate, about 5 to about 15 parts PHR of an alkali-metal alumino-silicate zeolite adsorbent, and about 0.5 to about 2 PHR of zinc oxide [and carbon black] in an organic liquid having a solubility parameter of 8.5-8.9 and a hydrogen bonding index of 3.0-3.5.

11. The adhesive of claim 8 or claim 9 which is formulated by the process comprising:

(A) milling or mixing separately with carbon black, the halogenated butyl rubber component and the pre-crosslinked butyl rubber component; and

(B) solubilizing the butyl rubbers of (A) with the styrene/ethylene butylene/styrene block thermoplastic rubber component, the thermoplastic petroleum hydrocarbon feedstock, the aliphatic isocyanate, about 5 to about 15 parts PHR of an alkali metal alumino-silicate zeolite adsorbent, and about 0.5 to about 2 parts PHR of zinc oxide in an organic solvent having a solubility parameter of 8.5-8.9 and a hydrogen bonding index of 3.0-3.5, such that the resultant adhesive has a storage stability of greater than 6 months.

12. The adhesive made by the process of claim 10.

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