

Polybutadiene Adhesive Compositions

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Synopsis

This paper deals with the development of adhesives that are useful for preparing flexible laminates. The adhesive compositions are based on the chemistry of 1,2-polybutadiene polymers and their reactions via chain extension and epoxidation. The resulting materials can be suitably formulated to produce resins that can be used to impregnate fibrous reinforcements which can be *B* staged; when laminated to copper, these materials give products with good peel strength, solder resistance, tear strength, and flame resistance. These adhesives can also be used to bond polyimide and polyester film to themselves and to copper. Typical properties of selected laminates include peel strength values of 8 lb/in. width, tear strength of 1–2 lb, oxygen index from 29 to 37, and excellent solder resistance.

INTRODUCTION

We have been engaged in the development of adhesive compositions for a variety of applications in the electrical industry. Some of these applications include flexible printed circuits, and various composite structures with polyimide and polyester film. We were interested in developing a *B* stageable thermosetting adhesive with good green strength (ability of the adhesive to hold the laminate together prior to final curing) for these applications. Our work is based on the chemistry of 1,2-polybutadiene polymers and their reactions of chain extension and epoxidation to produce the desired adhesive compositions. Some work on 1,2-polybutadiene based adhesives was reported previously, but little information was given on composition and process conditions.¹

EXPERIMENTAL

Material Identification

Hystl G-1000 is a hydroxy terminated 1,2-polybutadiene having a molecular weight of about 1350, a hydroxyl content of 1.18 milliequivalents per gram (meq/g), and a vinyl content of 85%; Dynachem Corp.

Hystl B-1000 is a straight 1,2-polybutadiene with no terminal functionality. Molecular weight of this liquid polymer is 1050 with a vinyl content of 85%; Dynachem Corp.

Isonate 125M is 4,4'-diisocyanato diphenylmethane (Upjohn Chemical Co.); styrene (Eastman Chemical Co.); *t*-butyl perbenzoate-peroxide catalyst (Pennwalt Corp., Lucidol Division).

Peracetic Acid is a 40% solution by weight from FMC Corp. All the chemicals were used as received without further purification.

Fire Retardant Chemicals used were Thermoguard S-711: antimony trioxide; 1.5 μ m particle size from M&T Chemicals; and FR-300BA—decabromodiphenyl oxide from Dow Chemical Co.

Copper: The material used for bonding was 1 oz. electrodeposited copper designated EDTA. It was obtained from the Circuit Foil Corp. This is a specially treated copper whose surface has been etched to enhance adhesion.

Fabrics

Nomex E54 is a permeable nylon paper (DuPont Co.).

Nomex is a nonwoven fabric designated WEBRIL SM-289.2 (Kendall Co.).

Fabric Y is a glass reinforced polyester fabric, obtained from Westinghouse Insulating Materials Division (IMD), Bedford, PA.

Dac-Glass is a polyester construction in which the polyester is interwoven among the glass fibers, obtained from Westinghouse IMD.

Four resins were prepared based on reaction with Hystl 1000:

Resin A is a chain extended polymer prepared by reacting Hystl G-1000 with Isonate 125 M in the presence of styrene.

Resin B is a chain extended polymer prepared by reacting Hystl G-1000 with Isonate 125M in the presence of toluene.

Resin C is an epoxidized polybutadiene prepared by the peracid oxidation of Hystl B-1000.

Resin D is an epoxidized chain extended polybutadiene prepared by the peracid oxidation of the reaction product between Hystl G-1000 and Isonate 125M.

Preparation of Adhesives

Resin A: To 80 g of a hydroxy terminated polybutadiene (Hystl G-1000) dissolved in 120 g of styrene and heated to 60°C was added the stoichiometric amount of 4,4'-diisocyanato diphenylmethane (11.75 g). A clear amber solution was obtained. The mixture was heated to 120°C over a period of about 1 hr at which point the mixture became hazy. It was further heated at 120°C for about 30 min while monitoring the increase in viscosity. Gradually the mixture viscosity increased to a point when the measured flow time was between 3 and 6 sec (flow tube: 62 mm long × 4 mm i.d.); 100 g of toluene was added and the reaction mixture cooled to room temperature. The milky viscous solution had a Gardner viscosity of R at 68% solids.

Resin B: To 200 g of a hydroxy terminated polybutadiene (Hystl G-1000) dissolved in 200 g of toluene and heated to 60°C was added the stoichiometric amount of 4,4'-diisocyanato diphenylmethane (29.5 g). A clear amber solution was obtained and the reaction mixture was heated at 60°C for 1½ hr and cooled to room temperature. A very viscous clear amber solution was obtained, Gardner viscosity Z1, solids = 53%.

Resin C: To a 500 cm³ three-neck flask equipped with a thermometer, stirrer and dropping funnel was added 60 g of Hystl B-1000, 1,2-polybutadiene. To this was added 60 g of toluene and the mixture stirred to form a clear, almost colorless solution. The solution was cooled to 20°C by means of an ice water bath, and 161 g of 40% peracetic acid containing 6.4 g of sodium acetate was added slowly over a period of 1 hr. This amount of peracid corresponds to 0.9 mole of peracid per double bond. The temperature was maintained between 20 and 25°C. A white solution formed upon addition of the peracid. After the final

addition, the reaction mixture was stirred for 4 hr while maintaining the temperature between 20 and 25°C. The reaction mixture was washed three times with 190 cm³ portions of a saturated aqueous solution of sodium chloride and then with 150 ml portions of a saturated solution of sodium chloride containing 5% KOH, and finally with distilled water until the aqueous layer was neutral. The white viscous mixture was filtered and excess solvent removed at reduced pressure (2–10 Torr) from room temperature to 90°C. A tan viscous liquid was obtained which was analyzed and found to contain 3.7% oxirane oxygen.² The epoxidation procedure was a modification of that reported by Greenspan.³ This percentage corresponds to an epoxide equivalent of 431.

Resin D: In a 1000 cm³ three-neck flask equipped with a stirrer, thermometer, and dropping funnel was added 128 g of Resin B plus 200 g of toluene. This solution was cooled to 20°C, and 40 g of a 40% peracetic acid solution containing 1.6 g of sodium acetate was added over a 1 hr period while maintaining the temperature between 20 and 25°C. This amount of peracid corresponds to 20% oxidation. At the end of the addition, an opaque pale yellow solution was obtained which was stirred for 4 hr at 20–25°C. The reaction mixture was washed two times with 100 cm³ portions of a saturated sodium chloride solution and two times with 100 cm³ portions of a saturated sodium chloride solution containing 5% KOH. The water layer was separated from the resin-solvent layer and the latter filtered. The filtered product was vacuum distilled to remove excess solvent and a straw colored, extremely viscous rubberylike product was obtained. This product was analyzed and found to contain 1.25% oxirane oxygen.² This percentage corresponds to an epoxide equivalent of 127.

Coating and Laminating Procedure

The fabrics were impregnated by immersing them in the adhesive compositions and pulling through a pair of grooved Mayer rods. They were then dried in a forced air oven to *B* stage the adhesive, usually 5 min at 125°C + 5 min at 150°C. The *B*-staged fabric was laminated to copper in a heated nip roll (150–180°C). The laminates were post cured in an oven for various times and temperatures. In general, Resins A and B were *B* staged 5 min at 125°C + 5 min at 150°C, laminated at 175°C, and post cured 40 min at 175°C. Resins C and D were *B* staged 5 min at 125°C, laminated at 150–160°C, and post cured 20 hr at 130°C.

Testing

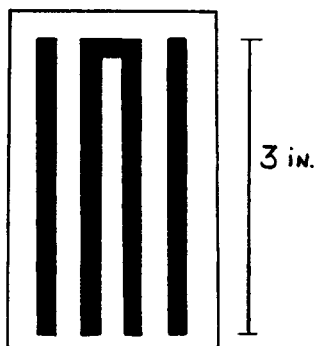
T-peel tests⁴ to measure bond strength were made on 1-in.-wide strips of the laminated materials at room temperature on a Dillon tester at a crosshead speed (CHS) of 0.9 in./min. In addition, laminates containing selected adhesive formulations were printed and etched (ammonium persulfate-H₂SO₄ etching solution) to obtain a conductor pattern with 1/6" wide strips. T-peel tests were also performed on these samples.

A 1 in.² piece of the etched laminate was placed on molten solder (260°C) for 15 sec and examined for blistering, shrinkage, and delamination.

Tear strength was measured on the etched sample (1 in. wide × 3 in. long) by slitting in half and pulling each end apart in the Dillon tester (CHS: 0.9 in./min).

Flammability of the coated fabrics was determined by measuring oxygen index (O.I.) values using a General Electric Oxygen Index Flammability Gauge. A $\frac{1}{4}$ × 4 in. strip of material was placed in a flame chamber and ignited. The minimum percentage of oxygen in nitrogen which will cause the sample to burn a 3 in. length is recorded.

Insulation resistance was measured using a General Radio Co. Megohm Bridge Type 1644A. A four adjacent conductor section was cut from each laminated sample and etched. See the following sketch:



The conductor width is 0.062 in. and the spacing between them is 0.040 in. A lead is connected to the center pair of conductors and a second lead is connected to the outer pair of conductors. The samples are conditioned for 96 hr at 35°C and 90%+ relative humidity. A continuous voltage of 45 V dc is applied between adjacent conductors. The potential is removed after the above conditioning time and the insulation resistance is measured at 100 V dc applied for at least 1 min with the polarity opposite to the previously applied potential.

RESULTS AND DISCUSSION

Base Resin Preparation

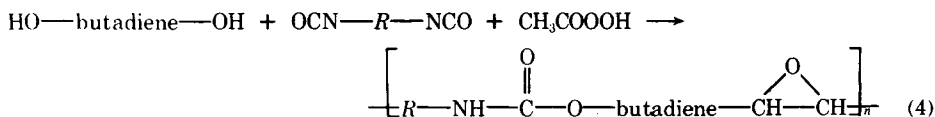
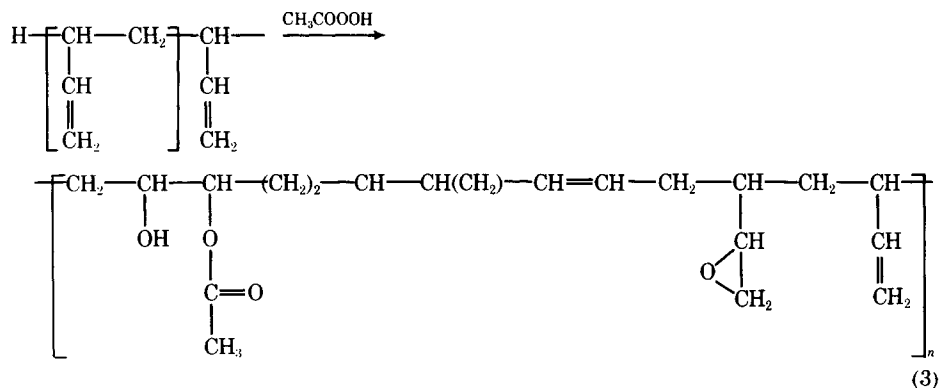
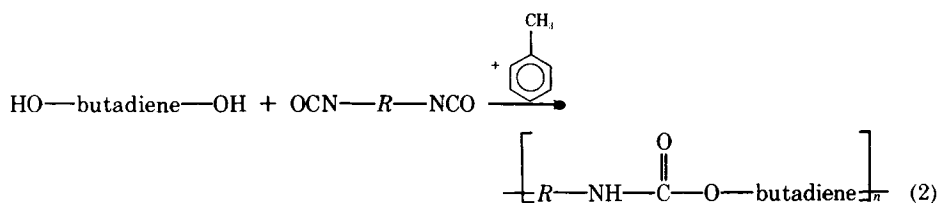
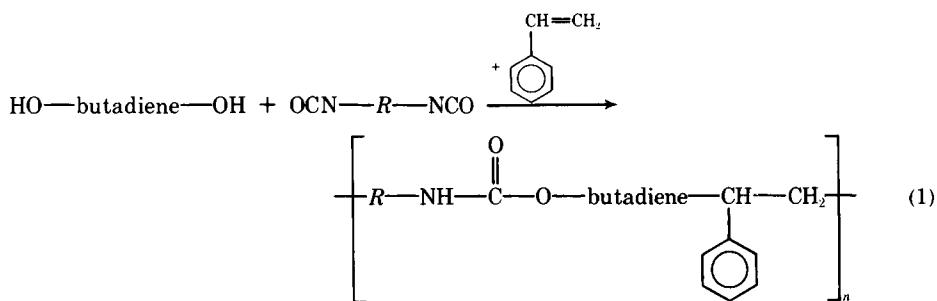
The liquid polybutadiene polymers containing reactive functional groups are ideally suited for chain extension with suitable monomers. The hydrocarbon nature of the polymer suggests that good dielectric properties could be obtained. A number of base resins have been prepared and were used as the starting points in all of our adhesive formulations. The variability in the properties of these base resins are shown in Tables I-IV.

In resin A, urethane groups are introduced into the polybutadiene matrix while at the same time, styrene is used as a reactive diluent to produce a copolymer. Careful control is needed with respect to stirring or mixing efficiency and in monitoring the viscosity increase, otherwise the reaction mixture will quickly gel in the flask. These parameters become critical when batch size is increased. Successful preparations have been made at 12 liter batch volumes. Resin stability is important with this system. Once the resin is prepared, it becomes gel-like "mucous" in texture within 24 hr, but this is reversible with stirring. Resin stabilization is achieved by blending Cellosolve into the mixture at about 26% by volume. The viscosity of this solution is *F* at 50% solids and the new composition is stable for at least 60 days at room temperature.

TABLE I
Properties of Urethane Extended Polybutadiene:
Styrene Copolymers (Resin A)

Batch No.	Flow time (sec)	Gardner viscosity	Solids, %	Comments
W12-51-66	5½	R	68	Milky viscous solution
W12-22-28	6	J	68	
W12-40-47	5½	R	68	
W12-66-88	5½	U	68	
W12-70-92	3	M	68	
W12-74-101	4	Q	68	

Resins A–D can be schematically represented by the following equations, respectively:



The amount of styrene was varied with respect to the Hystl G-1000 content and found to have a significant effect on the type of resin produced. The optimum ratio of Hystl/styrene was found to be 1:1.5 parts by weight.

In resin B, urethane groups are also introduced but toluene is used as the diluent and only a chain extended resin, rather than a copolymer as in resin A, is produced. Twenty-four hours after resin B is prepared, the Gardner viscosity rises to Z8-Z10; however, no signs of gelation were observed. There does not appear to be any stability problem with this resin since solutions have been standing at room temperature for over 3 months with no signs of gelation.

In resin C, the liquid polybutadiene is oxidized to produce epoxide groups along the butadiene chain. Epoxide contents can be controlled by adjusting the concentration of the peracid in the oxidation. The reactivity and resin-forming properties of the oxidized polybutadiene vary with its degree of oxidation. Batches of 200 g have been prepared in the laboratory. The only difficulty encountered was in the washing and separation of the oxidized polymer. During the washing operation, an exothermic reaction occurs and care is needed to minimize frothing and temperature rise. An ice water bath has been satisfactory in these experiments. Separation of the oxidized resin from the reaction mixture has presented a problem, but not a serious one. It was difficult to obtain complete phase separation.

TABLE II
Properties of Urethane Extended Polybutadiene
in Presence of Toluene (Resin B)

Batch No.	Gardner viscosity	Comments
W12-48-63	Z1	Clear light amber viscous solution
W12-43-52	Z2	
W12-55-72	Y	
W12-59-91	Z	

TABLE III
Properties of Epoxidized Polybutadiene
(Resin C)

Batch No.	% Oxirane oxygen	Epoxide equivalent	Comments
W12-44-53	3.7	431	Tan very viscous liquid
W12-52-68B	4.4	360	
W12-65-85	4.2	384	Amber very viscous liquid
W12-73-99	4.2	384	

TABLE IV
Properties of Epoxidized Chain Extended Polybutadiene
(Resin D)

Batch No.	% Oxirane oxygen	Epoxide equivalent	Comments
W12-56-73	1.25	127	Tan colored rubberylike material

In resin D, a chain extended polybutadiene was first prepared and then oxidized to introduce epoxide functionality into the polymer. In the preparation of this resin, the stoichiometry of the reactants is important. If the stoichiometric amount of peracid is used to oxidize the chain extended polybutadiene completely, an insoluble resin results. If, however, the amount of peracid is reduced to less than the stoichiometric, e.g., to ensure 20% oxidation, then a viscous rubbery resin is produced which can be useful as an adhesive.

Adhesive Formulations

An initial evaluation of the resins described above was made to determine their adhesive properties on three different fabrics (see Table V). Curing and laminating conditions are described in the experimental section. All of these resins are cured with a peroxide catalyst. The epoxidized resins are cured with standard epoxy curing agents such as acids, amines, anhydrides; peroxides are also used to effect crosslinking through the residual unsaturation remaining in the polymer. These resins do possess good properties. However, it was noted that resin C had poor "green strength" and the laminate containing this adhesive had to be held together under slight pressure to maintain good contact. Resin D, even though an epoxidized material, did have good "green strength." Chain extension to introduce urethane groups prior to epoxidation apparently imparted "green strength" properties to this resin. Resins A and B had particularly good "green strength." While all of the laminates were flexible, their flexibility varied in degree. In order of increasing rigidity, the laminates are ranked A/B/C/D in terms of the resin used.

Epoxidized Polybutadienes with Improved "Green Strength"

By blending the epoxidized polybutadienes (resin C) with resins A and/or B, compositions with excellent "green strength" can be obtained. Formulations were prepared containing (10–30%) of the epoxidized polymer plus Resins A and B and suitable curing agents. The blended compositions thus produced were applied to Dac-Glass and Fabric Y fabrics and laminated to copper. Excellent laminates were obtained with peel strengths up to 8 lb/in. width and good solder resistance. Details of these compositions are given in Appendix A.

Fire Retardant Compositions

Based on our initial studies of potential adhesive systems, several of these formulations were prepared with fire retardant additives, namely, antimony trioxide and decabromodiphenyl oxide. These compositions were used to prepare 8 × 10 in. copper-clad laminates using Dac-Glass and Fabric Y as fabrics. The laminates were printed and etched by the Westinghouse Flexible Products Plant, Bedford, PA and tested at R&D Center for the following properties: microscopic examination, peel strength, tear strength, LOI, solder resistance, and insulation resistance. A commercial laminate is included for comparison. The compositions and properties of these laminates are shown in Table VI. More detailed information on these compositions is given in Appendix B. The properties of these laminates are quite good. However, the insulation resistance of

TABLE V
Properties of Adhesive Compositions^a

Resin	Composition	Nomex 289.2	Peel strength (lb/in.)		Fabric Y	Tear strength (lb)	Solder resistance	LOI
			Dac-Glass					
A	Hystl G-1000 + Isonate 125M + styrene	4-5	7-10	7-12	All samples had values of 1-2 lb	All samples passed	All samples had a value of 22	
B	Hystl G-1000 + Isonate 125M + toluene	3-4	4-5	5-6				
C	Epoxidized polybutadiene	...	8-10	8-10				
D	Epoxidized chain extended polybutadiene	...	3-6	3-6				

^a Curing agent for A and B is *t*-butyl perbenzoate. Curing agents for C and D are *t*-butyl perbenzoate + methyl nadic anhydride (MNA) (0.25 g MNA/g of epoxidized polybutadiene).

TABLE VI
Properties of Copper-Clad Laminates^a

Item	Identification	Composition	Peel strength (lb./in.)	Tear strength (lb)	Solder resistance	LOI ^b	Insulation resistance ^b (MΩ)
A	W12-71-93A	Resin A + Sb ₂ O ₃ + FR-300BA + Catalyst	8	1	OK	37/36	200/4
B	W12-71-94B	Resin B + Sb ₂ O ₃ + FR-300BA + Catalyst	8	1	OK	26/29	1/2
C	W12-71-94C	Resin A + Epoxybutadiene + Sb ₂ O ₃ + FR-300BA + Catalyst	8	1	OK	36/35	100/0.2
D	W12-71-94D	Resin B + Epoxybutadiene + Sb ₂ O ₃ + FR-300BA + Catalyst	8	1	OK	30/29	0.3/1
E	WK-207351-40	Resin A + Epoxybutadiene + Sb ₂ O ₃ + FR-300BA + Catalyst	8	1	OK	36/35	300/10
F	Commercial laminate	Epoxy-glass	8	1/2	OK	31	25

^a Dac-Glass and Fabric Y Fabrics.

^b Fabric Y/Dac-Glass. Catalyst: 2% *t*-butyl perbenzoate.

all samples is far below the industrial requirement of $10^5 \text{ M}\Omega$. Microscopic examination of the etched laminates revealed voids within the impregnated fabric, thus exposing the bare fabric to the salt solution used during the aging and testing of these laminates. The insulation resistance readings of the dry samples were in the $10^{12} \text{ M}\Omega$ range except item F which was not tested dry. Furthermore, the IR readings of the wet samples fluctuated quite a bit and stable readings were not readily obtained. More work in this area is planned. At the present time, items A, C, and E offer the best combination of properties.

Other Systems and Applications

During the course of this investigation, several types of Nomex fabrics were evaluated as the resin carriers for preparing copper-clad laminates. These Nomex materials do offer some potential in this area with respect to flammability and perhaps insulation resistance. Some properties of adhesive systems using Nomex as carrier are presented in Table VII.

Resin A, described in the experimental section, has been used as an adhesive to prepare a number of other laminates. These involved bonding polyimide and polyester films to copper foil. A thin coating of the adhesive was spread on the films and *B* staged 5 min at 125°C + 10 min at 150°C and then laminated to the copper by passing the components through a heated nip roll at $150\text{--}170^\circ\text{C}$. Final curing of the laminated product was 40 min at 180°C in an air circulating oven. The properties of these laminates are shown in Table VIII.

Several other laminates were prepared using resin A to bond 5 mil polyimide film to itself using the procedure described above. These laminates are being

TABLE VII
Some Properties of Adhesive Systems
Using Nomex as a Carrier

Item	Composition	Peel strength (lb/in.)	Tear strength (lb)	LOI	Nomex type
A	Resin A + Sb_2O_3 (30%) + FR-300BA (40%) + Catalyst ^a	6-7	1-2	28	289.2
B	Resin A + Sb_2O_3 (30%) + FR-300BA (40%) + Catalyst ^a	7	1/2	25	287.2

^a t-butyl perbenzoate

TABLE VIII
Properties of Copper-Clad Laminates

Film	Copper	Adhesive thickness (mil)	Tear strength (lb)	Peel strength (lb)	Solder resistance
Polyimide (2 mil)	2 oz. EDTA	1.8	...	8	OK
Polyester (2 mil)	2 oz. EDTA	2.5	...	6	OK

considered for use as slot liners in stator cores of motors and generators that have operating excursion temperatures to about 280°C. Samples of this laminate (10 mils thick) were immersed in Exxon Turbo Oil 2380 and aged for 500 hr at 280°C under a nitrogen atmosphere. No sign of delamination or chemical attack was observed. When tested for peel strength, the polyimide film tore in the grips of the tensile machine. The laminate could be bent through an angle of 150 deg without cracking. Very slight shrinkage of the adhesive was noticed at the edges of the laminate, but did not appear to affect the strength of the laminate.

Resin D, described in the experimental section, has been used as a casting resin to prepare several small samples about 1/4 in. thick in aluminum dishes. The casting resin was a 100% solids formulation containing resin D, styrene and catalyst. The castings obtained were translucent amber colored. Some shrinkage was evident.

CONCLUSIONS

A number of adhesive resins based on 1,2-polybutadiene polymers have been developed for use in preparing flexible laminates. These resins have been formulated to produce fire retardant compositions. They have been used to impregnate fabrics such as "Dac-Glass" and "Fabric Y" and subsequently, nip roll laminated to give copper-clad laminates with excellent peel strength, solder resistance, flammability resistance, tear strength, etc. These adhesives have also been used successfully to bond 5-mils polyimide film to itself and to copper as well as polyester to copper.

The assistance of F. Homoki and E. Traynor of the Westinghouse Insulating Materials Division in the printing and etching of the laminates is greatly appreciated.

APPENDIX A

Composition of blend of epoxidized polybutadiene (10%) with a chain extended polybutadiene in presence of styrene.

W12-60-79

(1) Resin A	30 g at 68%
(2) Resin C	2.04 g
(3) toluene	10 g
(4) methyl nadic anhydride	0.51 g
(5) <i>t</i> -butyl perbenzoate	0.45 g

Total solids = 50%
Gardner viscosity = X

Composition of blend of epoxidized polybutadiene (30%) with a chain extended polybutadiene in presence of styrene.

W12-62-82

(1) Resin A	30 g at 68%
(2) Resin C	6.12 g
(3) toluene	16 g
(4) methyl nadic anhydride	1.51 g
(5) <i>t</i> -butyl perbenzoate	0.56 g

Total solids = 53%
Gardner viscosity = V

Composition of blend of epoxidized polybutadiene (10%) with a chain extended polybutadiene in presence of toluene.

(1) Resin B	30 g at 53.5%
(2) Resin C	1.6 g
(3) toluene	25 g
(4) methyl nadic anhydride	0.4 g
(5) <i>t</i> -butyl perbenzoate	0.36 g

Total solids = 31%
Gardner viscosity = X

Composition of blend of epoxidized polybutadiene (10%) with a chain extended polybutadiene in presence of toluene.

<u>2-63-83</u>	
(1) Resin B	30 g at 53.5%
(2) Resin C	4.8 g
(3) toluene	30 g
(4) methyl nadic anhydride	1.19 g
(5) <i>t</i> -butyl perbenzoate	0.43 g

Total solids = 34%
Gardner viscosity = V

The numbers in parentheses represent (1) chain extended polybutadiene in styrene or toluene; (2) epoxidized polybutadiene; (3) diluent; and (4) and (5) curing agents.

APPENDIX B: FIRE RETARDANT ADHESIVE COMPOSITIONS

Item A Table VI

(1) Hystl G-1000 + Isonate 125M + styrene	100 g at 68%
(2) Sb ₂ O ₃	20.4 g
(3) FR-300BA	27.2 g
(4) toluene	30 g
(5) <i>t</i> -butyl perbenzoate	1.36 g

Gardner viscosity = X

Item B Table VI

(1) Hystl G-1000 + Isonate 125M + toluene	100 g at 53.4%
(2) Sb ₂ O ₃	16 g
(4) FR-300BA	21.4 g
(4) toluene	80 g
(5) <i>t</i> -butyl perbenzoate	1.1 g

Gardner viscosity = Y

Item C Table VI

(1) Hystl G-1000 + Isonate 125M + styrene	40 g at 68%
(2) Epoxy polybutadiene	8.16 g
(3) toluene	20 g
(4) MNA	2.01 g
(5) Sb ₂ O ₃	11.2 g
(6) FR-300BA	14.95 g
(7) <i>t</i> -butyl perbenzoate	0.75 g

Gardner viscosity = W

Item D Table VI

(1) Hystl G-1000 + Isonate 125M + toluene	40 g at 53.5%
(2) Epoxy polybutadiene	6.4 g
(3) toluene	35 g
(4) MNA	1.58 g
(5) Sb ₂ O ₃	8.81 g
(6) FR-300BA	11.7 g
(7) <i>t</i> -butyl perbenzoate	0.58 g

Gardner viscosity = Y

Item E Table VI

Same as Item C except used 50% epoxy polybutadiene.

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