

PATENT SPECIFICATION

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(54) POLYURETHANE FOAM COMPOSITION AND METHOD OF MAKING SAME

(71) We, UNION CARBIDE CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flexible polyurethane foams which can be thermally bonded to substrates and more particularly to polyurethane foams formulated from polyisocyanates and polyether polyols.

It is known in the art that the urethane linkages of polyurethane foams are formed by the exothermic reaction of a polyfunctional isocyanate and a polyfunctional active hydrogen-containing compound in the presence of a catalyst and a blowing agent. In accordance with the "one-shot process" which is the most widely used industrial technique, direct reaction is effected between the polyisocyanate, and the active hydrogen-containing compound or compounds and is regulated by the catalyst system and surfactant.

It is also well known that suitable active hydrogen-containing compounds include polyether polyols and polyester polyols. However, it is equally well known that while flexible polyurethane foams formulated from polyester polyols have excellent flame lamination properties, those flexible polyurethane foams formulated from polyether polyols are unacceptable for flame lamination. Unfortunately the polyesters used in this application are much more expensive than the polyether polyols. This means that fabricators wishing to bond polyurethane foams derived from polyether polyols must resort to the use of an additional component, namely, an adhesive in order to bond flexible polyurethane foams derived from

polyether alcohols. The inconvenience and added expense of this procedure is obvious.

Two previous solutions to this problem have been provided but each introduces problems of its own which has left much room for improvement in this art. First of all United States Patent Specification No. 3,205,120 describes the preparation of polyether-based polyurethane foams suitable for fabrication of laminates by a heat sealing technique wherein the conventional commercial polyether polyol flexible polyurethane foam reaction mixture contained a minor amount of a polyol having a molecular weight of 200 to 1500. The preferred low molecular weight polyol was tris-(dipropylene glycol) phosphite. Other low molecular weight polyols disclosed in this reference include alkylene oxide adducts of polyhydroxy alkanes, and phosphorus-containing acids. It was later found that there are processing difficulties encountered in the production of these types of polyether polyurethane foams that stem from the high reactivity of the polyether polyol mixture. These difficulties at least cancel the cost advantage of the polyether polyol based foam over polyester polyol based foam with the result that there has been no great incentive for laminate manufacturers to switch from polyester to polyether.

The second improvement described in United States Patent Specification No. 3,497,416 comprises the use, in the production of heat-sealed polyurethane foam laminates, of polyurethane foam which is produced by reacting, in the presence of a foaming agent, a polyether polyol with the reaction product of an aromatic polyisocyanate and dipropylene glycol or dibutylene glycol. This reaction product, a quasi-prepolymer, is prepared by using an excess of an aromatic polyisocyanate over the amount of dipropylene glycol and/or dibutylene glycol used. While this disclosure consti-

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tutes a further advance in the art, it is still not completely satisfactory for commercial use by laminate manufacturers because in order to obtain an open foam one must incorporate a powerful cell opening agent, such as, dimethylformamide. The use of a cell opener is normally not used in polyurethane foam processing. In addition these polyurethane foams have very high compression sets which are unacceptable for most end use applications.

It has now been found possible to bond a flexible polyether polyurethane thermally to a substrate without the disadvantages of the prior art by using the method of the present invention.

According to the present invention there is provided a polyol composition useful for preparing a polyurethane foam, which composition comprises:—

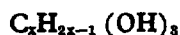
(a) a graft copolymer of a polyether polyol having a molecular weight of at least 2000 and containing an average of at least two hydroxyl groups per molecule, the graft copolymer being formed by polymerising one or more ethylenically unsaturated monomers dissolved or dispersed in the polyether polyol in the presence of a free radical catalyst, and (b) from 1 to 7%, based on the weight of the graft copolymer, of at least one polyol modifier consisting of:

(1) an alkylene glycol having from 2 to 8 carbon atoms;
(2) a glycol ether having the empirical formula:



wherein n is an integer from 2 to 4 and m is an integer from 2 to 4 when n is 2, is 2 or 3 when n is 3, and is 2 when n is 4;

(3) a triol having the empirical formula:



wherein x is an integer from 3 to 10;

(4) an alkanolamine having the empirical formula:



wherein y is an integer having values of from 2 to 10, z is 1 or 2 and p is an integer from 2 to 4, or

(5) a polyhydric mononuclear phenol.

There is also provided a foam-forming composition containing the polyol composition of the invention; and a method of thermally bonding flexible polyether polyurethane foam to a substrate which comprises:

(A) reacting and foaming a composition consisting essentially of:

(a) a polyisocyanate reactant containing at least two isocyanato groups per molecule;

(b) a graft polymer of a polyether polyol having a molecular weight of at least 2000

and containing an average of at least 2 hydroxyl groups per molecule;

(c) a blowing agent;

(d) a catalyst for the urethane-forming reaction;

(e) a surfactant; and

(f) one to seven percent, based on the weight of the graft copolymer, of at least one polyol modifier consisting of

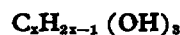
(1) an alkylene glycol having 2 to 8 carbon atoms,

(2) a glycol ether having the empirical formula:



wherein n is an integer having values of 2 to 4 and m is an integer having values 2 to 4 when n is 2, 2 to 3 when n is 3 and 2 when n is 4;

(3) a triol having the empirical formula



wherein x is an integer having values of 3 to 10;

(4) an alkanolamine having the empirical formula



wherein y is an integer having values of 2 to 10, and z is 1 or 2 and p is an integer from 2 to 4; or

(5) a polyhydric mononuclear phenol;

(B) Heating the surface of the foamed composition of (A) above its melting or fusion temperature;

(C) Contacting the melted or fused surface of the foamed composition of (A) with a substrate, whereby a flexible polyurethane foam/substrate laminate is formed; and

(D) Cooling the flexible polyurethane foam/substrate laminate below the melting or fusion point of the flexible polyurethane foam.

Although one to seven percent of polyol modifier can be used in this invention, it is preferred to use two to six percent based on the weight of the graft copolymer employed in the foaming composition.

Illustrative of the alkylene glycols having 2 to 8 atoms used in this invention are ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,2-butyleneglycol, 1,3-butyleneglycol, 1,4-butyleneglycol, 1,2-pentylene glycol, 1,5-pentylene glycol, 1,2-hexylene glycol, 1,4-hexylene glycol, 1,2-heptylene glycol, 1,7-heptylene glycol, 1,2-octylene glycol, and 1,8-octylene glycol.

Exemplary glycol ethers useful in this invention include diethylene glycol, di(1,2-propylene) glycol, di(1,3-propylene) glycol, triethylene glycol, tetraethylene glycol, tri(1,2-propylene) glycol, tri(1,3-propylene) glycol and dibutyleneglycol.

Representative examples of triols useful in this invention include glycerine, 2-methyl-2-hydroxymethyl-1,3-propane diol and 2-ethyl-2-hydroxymethyl-1,3-propane diol.

5 Alkanolamines which can be used include: tri-*n*-propanolamine, tri-isopropanolamine, tri-*n*-ethanolamine, and *N,N'*-dihydroxyethyl ethylene diamine.

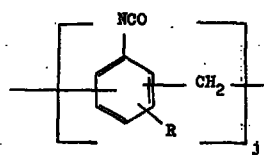
10 Representative polyhydric mononuclear phenols include catechol, resorcinol, hydroquinone, pyrogallol, hydroxyhydroquinone and phloroglucinol.

15 The polyisocyanate reactants used in making the flexible polyurethane foams of this invention are known in the art and any such reactants can be suitably employed in producing the flexible polyurethane foams. Among such suitable polyisocyanates are those represented by the general formula:



wherein *i* has an average value of at least 2 and is usually no more than 6, and *Q* represents an aliphatic, cycloaliphatic or aromatic radical which can be an unsubstituted hydrocarbyl group or a hydrocarbyl group substituted, for example, with a halogen atom or an alkoxy group. For example, *Q* can be an alkyl-ene, cycloalkylene, arylene, alkyl-substituted cycloalkylene, alkarylene, or aralkylene radical including corresponding halogen- and alkoxy-substituted radicals. Typical examples of polyisocyanates which can be used in preparing the polyurethanes of this invention are any of the following including mixtures thereof: 1,6-hexamethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1-methyl-2,4-diisocyanatocyclohexane, bis(4-isocyanato phenyl)methane, phenylene diisocyanates such as 4-methoxy-1,4-phenylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 4-bromo-1,3-phenylene diisocyanate, 5,6-dimethyl-1,3-phenylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, crude tolylene diisocyanate, 6-isopropyl-1,3-phenylene diisocyanate, durylene diisocyanate, triphenylmethane-4,4',4''-triisocyanate, and other organic polyisocyanates known to the polyurethane art. Of the aforesaid types of isocyanates, those containing aromatic nuclei are generally preferred.

50 Also useful as the polyisocyanate reactants are polymeric isocyanates having units of the formula:



55 wherein *R* is a hydrogen atom and/or a methyl group and *j* has an average value of at least 2.1. Preferably *j* has an average value of from

2.1 to 3.0. Particularly useful polyisocyanates of this type are the polyphenylmethylenepolyisocyanates produced by phosgenation of the polyamine obtained by acid catalyzed condensation of aniline with formaldehyde. Polyphenylmethylenepolyisocyanates of this type are available commercially under such trade names as PAPI, NIAX, Isocyanate AFPI, Mondur MR, Isonate 390P, NCO-120, Thanate P-200, NCO-10 and NCO-20. PAPI, NIAX, MONDUR and ISONATE are Registered Trade Marks. These products are low viscosity (50-500 centipoises at 25°C) liquids having average isocyanato functionalities in the range of 2.25 to 3.2 or higher, depending upon the specific aniline-to-formaldehyde ratio used in the polyamine preparation.

Other useful polyisocyanates are combinations of diisocyanates with polymeric isocyanates containing more than 2 isocyanate groups per molecule. Illustrative of such combinations are: a mixture of 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate and the aforesaid polyphenylmethylenepolyisocyanate and/or polymeric tolylene diisocyanates obtained as residues from the manufacture of the diisocyanates.

On a combined basis, the polyether polyol component and organic polyisocyanate usually constitute the major proportion by weight of the polyurethane-forming reaction mixture. In general, the polyisocyanate and polyether polyol reactants are employed in relative amounts such that the ratio of total-NCO equivalents to total active hydrogen equivalents (of the polyether polyol and any water, when used) is from 0.8 to 1.5, preferably from 1.0 to 1.15 equivalents of -NCO per equivalent of active hydrogen. This ratio is known as the Isocyanate Index and is often also expressed as percent of the stoichiometric amount of polyisocyanate required to react with total active hydrogen. When expressed as a percent, the Isocyanate Index may be from 80 to 150, and is preferably within the range from 100 to 115. In general it is not necessary to take the polyol modifier into account since the amount used is always relatively small.

In producing the flexible polyurethane foams of the present invention, a graft copolymer of a polyether polyol either alone or in combination with an ungrafted polyether polyol is employed for reaction with the polyisocyanate reactant to provide the urethane linkage. The polyol reactants used have an average of at least 2 and usually not more than 6 hydroxyl groups per molecule and include compounds which consist of carbon, hydrogen, and oxygen and compounds which also contain phosphorus, halogen and/or nitrogen. Such polyols also have an average molecular weight of at least 2000.

Among the suitable ungrafted polyether polyols that can be employed are the

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poly(oxyalkylene) polyols, that is alkylene oxide adducts of water or a polyhydric organic compound used as the initiator or starter. Suitable polyhydric organic initiators include the following individually or in combination: ethylene glycol; diethylene glycol; propylene glycol; 1,5-pentanediol; hexylene glycol; dipropylene glycol; trimethylene glycol; 1,2-cyclohexanediol; cyclohexane-1,1-dimethanol; glycerine; 1,2,6-hexane triol; 1,1,1-trimethylolethane; 1,1,1-trimethylpropane; 3-(2-hydroxyethoxy)- and 3-(2-hydroxypropoxy)-1,2-propane diols; 2,4-dimethyl-2-(2-hydroxyethoxy) methylpentanediol-1-5; 1,1-tris[(2-hydroxyethoxy) methyl] ethane; 1,1,1-tris[2-hydroxy propoxy] methyl propane; pentaerythritol; sorbitol; sucrose; and alpha-methyl glucoside.

The above-described ungrafted polyether polyols are prepared in accordance with well known techniques comprising the reaction of the polyhydric starter and an alkylene oxide in the presence of an oxyalkylation catalyst which is usually an alkaline metal hydroxide. The oxyalkylation of the polyhydric initiator is carried out at temperatures ranging from 90°C to 150°C and usually at an elevated pressure up to 200 psig, employing a sufficient amount of alkylene oxide and adequate reaction time to obtain a polyol of desired molecular weight which is conveniently followed during the course of the reaction, by standard hydroxyl number determinations. As is well known in the art the hydroxyl numbers are determined by and are defined as the number of milligrams of potassium hydroxide required for the complete neutralization of the hydrolysis product of the fully acetylated derivative prepared from one gram of polyol or mixture of polyols. The hydroxyl number is also defined by the following equation which indicates its relationship with the molecular weight and functionality of the polyol:

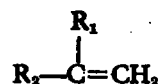
$$\text{OH} = \frac{56.1 \times 1,000 \times f}{\text{M.W.}}$$

wherein OH equals hydroxyl number of the polyol, f equals average functionality, that is, the average number of hydroxyl groups per molecule of polyol, and M.W. equals average molecular weight of polyol.

The alkylene oxide usually employed in the ungrafted polyether polyol reactants are the lower alkylene oxides, that is, compounds having from 2 to 4 carbon atoms including ethylene oxide, propylene oxide, butylene oxides (1,2' or 2,3') in combination thereof. When more than one type of oxyalkylene unit is desired in the polyol product, the alkylene oxide reactants may be fed to the reaction system sequentially to provide polyoxyalkylene chains containing respective blocks of different oxyalkylene units or they may be fed simul-

taneously to provide substantially random distribution of the units. Alternatively, the polyoxyalkylene chains may consist essentially of one type of oxyalkylene unit, such as, oxypropylene capped with oxyethylene units.

The graft polymer polyether polyols are produced by polymerizing one or more ethylenically unsaturated monomers dissolved or dispersed in a polyether polyol in the presence of a free radical catalyst. Suitable polyether polyols for producing such composition include, for example, any of the above described polyols. Illustrative of suitable ethylenically unsaturated monomers are those encompassed by the general formula:—



wherein R_1 is a hydrogen atom, a methyl group or any of the halogen atoms (i.e. fluorine, chlorine, bromine, or iodine); and R_2 is R_1 or a cyano, phenyl, methyl-substituted methyl, or alkenyl radical having from 2 to 6 carbon atoms such as vinyl, allyl and isopropenyl group. Typical examples of such polymerizable monomers are the following which may be employed individually or in combination: ethylene, propylene, acrylonitrile, methacrylonitrile, vinyl chloride, vinylidene chloride, alpha-methyl styrene, and butadiene. These and other polymer polyol compositions which are suitably employed either individually or in combination with polyether polyols described above are those described in British Patent Specification No. 1,063,222 and United States Patent Specification No. 3,383,351. Such compositions are prepared by polymerizing the monomers in the polyol at a temperature between 40°C. and 150°C. employing any free radical-generating initiator including peroxides, persulfates, percarbonates, perborates, or azo compounds, such as, hydrogen peroxide, dibenzoyl peroxide, benzoyl hydroperoxide, lauroyl peroxide, and azobis(isobutyronitrile).

When used in the practice of this invention, the grafted polymer polyol composition usually contains from 5 to 50, and more usually from 10 to 40 weight percent of the ethylenically unsaturated monomer polymerized in a polyether polyol. Especially suitable polymer/polyols are those containing:

(A) from 10 to 30 weight per cent of a copolymer of (1) acrylonitrile or methacrylonitrile, and (2) styrene or alpha-methyl styrene, the said copolymer containing from 50 to 75 and from 50 to 25 weight per cent of (1) and (2), respectively;

(B) from 90 to 70 weight per cent of the polyether polyol and particularly tri-functional polyols such as alkylene oxide adducts of glycerine.

Preferably the polyether polyol reactant com-

prises 80% by weight of the reaction product of glycerine with 1,2-propylene oxide having a molecular weight of 3000, and 20% by weight of a mixture of styrene and acrylonitrile graft polymerized thereon, either alone or in combination with the reaction product of glycerine with a mixture of 86% by weight of 1,2-propylene oxide and 14% by weight of ethylene oxide having a molecular weight of 3500.

The urethane-forming reaction is effected in the presence of a minor amount of a catalyst preferably comprising an amine catalyst and a metal catalyst useful in promoting gelation of the foaming mixture. The amine component of the polyurethane-forming reaction mixture is usually a tertiary amine. Suitable amine-catalysts include one or more of the following: N-methyl-morpholine; N-ethylmorpholine; N-octadecylmorpholine; N,N,N',N', tetramethylethylenediamine; N,N,N',N', tetramethyl-1,3-butanediamine; hexadecyldimethylamine; and N,N-dimethyl-benzylamine. The amine catalyst may be introduced to the polyurethane-producing reaction mixture as such or as a solution in a suitable solvent.

The amine catalyst is present in the final polyurethane-producing reaction mixture in an amount of from 0.05 to 3 parts by weight of active catalyst, that is, the amine (exclusive of other components in solutions thereof) per 100 parts by weight of the polyether polyol reactant.

Metal catalysts which are also used in conjunction with the amine catalyst in producing polyurethanes from polyether polyols include organic derivatives of tin, particularly the tin compounds of carboxylic acids such as stannous octoate, stannous oleate, stannous acetate, stannous laurate, dibutyl tin dilaurate, and other such tin salts. Additional metal catalysts are organic derivatives of other polyvalent metals such as zinc and nickel (e.g., nickel acetylacetonate). In general, the amount of such metal co-catalysts which can be present in the polyurethane-producing reaction mixture is within the range from 0.05 to 2 parts by weight per 100 parts by weight of the polyether polyol reactant.

Foaming is accomplished by the presence in the reaction mixture of varying amounts of a polyurethane blowing agent, such as, water, which upon reaction with isocyanate generates carbon dioxide *in situ*, or through the use of blowing agents which are vaporized by the exothermic reaction, or by a combination of the two methods. These various methods are known in the art. Thus in addition to or in place of water, blowing agents which can be employed in the process of this invention include methylene chloride, liquefied gases which have boiling points below 80°F (27°C) and above -60°F (-52°C), or other inert gases such as nitrogen, carbon dioxide added as such, methane, helium and argon. Suitable liquify-

ing gases include aliphatic and cyclofluorocarbons which vaporize at or below the temperature of the foaming mass. Such gases are at least partially fluorinated and may also be otherwise halogenated. Fluorocarbon blowing agents suitable for use in foaming the formulations of this invention include trichloromonofluoromethane, dichlorodifluoromethane, 1,1-dichloro-1-fluoroethane, 1,1,1-trifluoro-2-fluoro-3,3-difluoro-4,4,4-trifluorobutane, hexafluorocyclobutane and octafluorocyclobutane. Another useful class of blowing agents include thermally-unstable compounds which liberate gases upon heating, such as N,N'-dimethyl-N,N'-dinitrosoterephthalamide. The generally preferred method of foaming for producing flexible foams is the use of water or a combination of water plus a fluorocarbon blowing agent such as trichloromonofluoromethane.

The amount of blowing agent employed in the foaming reaction will vary with factors such as density that is desired in the foam product. Usually, however, from 1 to 30 parts by weight of the blowing agent per 100 parts by weight of the polyether polyol reactant is preferred.

The polyurethane foam of this invention may be formed in accordance with any of the processing techniques known to the art such as, in particular, the one-shot technique. In accordance with this method, foamed products are provided by carrying out the reaction of the polyisocyanate and polyether polyol simultaneously with the foaming operation. It is to be understood that the relative amounts of the various foaming components of the conventional foam formulations are not narrowly critical. The polyether polyol and polyisocyanate are present in the foam-producing formulation in a major amount. The relative amounts of these two components is the amount required to produce the urethane structure of the foam and such relative amounts are well known in the art. The source of the blowing agent such as water, auxiliary blowing agents, amine catalyst and metal catalyst used in the present invention are each present in a minor amount necessary to achieve the function of the individual component. Thus the blowing agent is present in an amount sufficient to foam the reaction mixture, the amine catalyst and metal catalyst are each present in a catalytic amount (i.e., an amount sufficient to catalyze the reaction to produce the urethane at a reasonable rate) and the surfactant is present in a foam-stabilizing amount. The preferred amounts of these various components are as given herein.

Suitable surfactants include a foaming stabilizer, as for example, a Pluronic (Registered Trade Mark) hydrolyzable polysiloxane-polyoxyalkylene block copolymer such as block copolymers described in United States Patent Specifications Nos. 3,834,748 and 2,917,480.

Another useful class of emulsifying agents or surfactants is the non-hydrolyzable polysiloxanes or polyoxyalkylene block copolymers such as those described in United States Patent Specification No. 3,505,377.

The preferred substrates are polyurethanes, paper, kraft paper, leather, hides, cotton, linen, silk, hemp, jute, wool, flax, nylons, polyesters, Orlon (Registered Trade Mark), Dacron (Registered Trade Mark), rayon, acetates, styrene polymers, and vinyl chloride polymers. The invention is not limited to any substrate and hence includes not only the above-enumerated substrates but also both ferrous and non-ferrous metals, vitreous materials including glass, ceramics, clays, china, and porcelain; cellulosic substrates including wood, ply-wood, cane, bamboo, and rattan; proteinaceous materials including gelatin; natural fibres; as well as, building materials, including brick, granite, sandstone, plaster, tile, wall board, and cement blocks; thermosetting polymers such as phenol and urea resins, epoxy resins, and coumarone indene polymers; and thermoplastic polymers such as acrylonitrile polymers, polycarbonates, polyacetals, polyamides, synthetic rubber, polyethylene, and polypropylene.

The laminated structures of the invention can be used for various purposes such as insulation or padding of clothing where the substrate would be cloth, the sound deadening and insulation of building materials, e.g. preformed panels. Blocks of polyurethane foam can be heat sealed to each other (butt-welded) to form larger sections from smaller sections. Single-ply or multi-ply laminates can be fabricated with the laminates produced by this invention.

Other uses for the laminates of this invention include the preparation of preformed cushioning for furniture, automobile seats, and crash pads.

The laminates of the invention are produced by heating part or all of the surface of the urethane foam described above to a temperature above the fusion temperature of the foam to form a tacky liquid or semi-liquid layer, and thereafter or concurrently with the heating operation, applying the substrate to the tacky surface of the foam and holding in contact therewith while cooling until the surface cools and resolidifies, thereby forming an adhesive bond between the foam and the substrate. The fusion temperature of the foam will vary depending upon the nature and proportion of the components therein, but in general is in the range of from 204°C. to 315°C. It is in general desirable not to heat the surface of the foam to a temperature higher than 38°C. above the fusion temperature of the particular foam.

Preferred methods include flame treatment of the surface or a heat sealing means with the polyurethane foam passing continuously

over the heating source and then passing directly into contact with the desired substrate. Dielectric heating, heating lamps, e.g. infrared lamps, hot plates, and hot air guns can also be used.

Although not necessary, it is preferred to employ a moderate amount of pressure in contacting the substrate with the polyurethane foam whose surface has been brought above its melting or fusion point. The pressure can be as low as that resulting from the weight of the foam or the substrate but is preferably in the range of 0.1 to 100 or more pounds per square inch.

The invention is further described in the Examples which follow. All parts and percentages are by weight unless otherwise specified.

Foaming Procedure I—Bench Scale.

The general procedure used for the preparation of the flexible polyurethane foams used in this invention is as follows.

Polyether polyol was dispensed into a container along with the polyol to be evaluated by stirring with a spatula until a homogeneous solution was obtained. Optional additives such as flame retardants can be added at this point if desired to prepare a flame retardant polyurethane foam. Surfactant, water, amine catalyst, and fluorocarbon blowing agent were then added to the mixture followed by mixing with a spatula.

The contents of the container were agitated for 15 seconds at 2000 revolutions per minute. Stannous octoate co-catalyst was then added by means of a hypodermic syringe. After agitating for an additional 8 seconds, the polyisocyanate reactant was added rapidly and agitation continued for another 7 seconds. The mixture following agitation was then poured into a parchment lined box (12" × 12" × 12") supported by a wooden mold. The foam was allowed to rest in the mold for at least 3 minutes and then cured for 5 minutes (unless otherwise noted in the examples) at 125°C. The foams were then allowed to cure for 24 hours at ambient temperature before evaluation. After cutting, the following properties were determined:

Height of rise
Breathability
Density
Foam-to-foam bond strength
Burning extent (flame retardant foams only)
During foam preparation, cream time, rise time and top collapse are measured.

Breathability denotes the porosity of a foam and is roughly proportional to the number of open cells in a foam. In accordance with the NOPCO test procedure described by R. E. Jones and G. Fesman, "Journal of Cellular Plastics", January, 1965 breathability was measured as follows: a 2" × 2" × 1" piece of foam was cut from near the center of the test specimen. Using a NOPCO foam breath-

- ability tester, type GP—2Model 40GD10, air was drawn through the one inch portion at a pressure differential of 0.5 inches of water less than atmospheric pressure. The air flow was parallel to the direction of original foam rise. The degree of openness of the foam (or foam breathability) is measured by air flow and is expressed as standard cubic feet per minute (SCFM).
- Foam density, expressed in pounds per cubic foot, (pcf) is the weight of the foam divided by its volume.
- Foam-to-foam bond strength is determined by bonding two foam samples cut to a size $\frac{1}{8}$ inches by 2 inches by six inches with a Ventrod Model 8HTV Heat Sealing Machine. Dwell time and temperature was set at a maximum and foam sample was sealed. This procedure was repeated several times as noted by "number of cycles" in the Examples, infra. A bond was formed which was 2 inches long by $\frac{1}{8}$ inches wide. The bonded foam sample was allowed to age at ambient conditions for at least twenty-four hours. Bond strengths were then determined using a Table Model TM Instron machine set at a cross-head speed of two inches per minute and two inches per minute chart speed. The foam samples were held using pneumatic tensile jaws. Bond strengths were reported in pounds per linear inch.
- Cream time is the time in seconds that the foaming mixture takes to become heterogeneous. This condition was ascertained by observing the time taken for the clear mixture to change to a milky white color.
- Rise time is the time in seconds taken to achieve maximum height of rise in the foam.
- Top collapse is the amount in inches a foam decreases in height after maximum rise.
- Examples 1 to 4.
- The enhancement of the thermal bonding properties of a conventional polyurethane foam was demonstrated in the following Examples by the addition of varying amounts of dipropylene glycol as the polyol modifier.
- Using the procedure described supra 72 parts of polyether polyol I (the reaction product of glycerine with a mixture of 86% 1,2-propylene oxide and 14% ethylene oxide having a molecular weight of 3500) was blended with 24 parts of polyether polyol II (the product obtained by the interaction of 80% of an adduct polymer obtained by reacting glycerine with 1,2-propylene oxide having a molecular weight of 3000 interpolymerized with 20% of a blend of styrene and acrylonitrile) and employed as the polyether polyol components of the urethane foaming composition together with 4 parts of dipropylene glycol as the polyol modifier. Four parts of water was added as blowing agent together with 2 parts of amine catalyst (1) [a blend of a major amount of dimethylaminopropionitrile and a minor amount of bis(2-dimethylaminoethyl) ether], 1 part of L-6202 (a commercial silicone-polyether copolymer foam stabilizer available from Union Carbide Corp.), 0.15 parts of stannous octoate, 2 parts of dichlorodifluoromethane, and 53.5 parts of tolylene diisocyanate (a mixture of 80% 2,4-tolylene diisocyanate and 20% 2,6-tolylene diisocyanate). The Isocyanate Index was 105. The Isocyanate Index is the per cent of the stoichiometric amount of polyisocyanate required to react with total active hydrogen. This index is preferably in the range of 100 to 115. The hydroxyl number of the total polyol blend including the dipropylene glycol additive was 79.3. Pertinent physical properties of the foam obtained including foam-to-foam bond strengths are presented in Table I together with 3 additional Examples and a Control A demonstrating the improvement in foam-to-foam bond strengths with increasing amounts of dipropylene glycol modifier and the extremely low bond strength in the Control A in which no dipropylene glycol modifier was used. The data in Table I also show that based on settling and breathability data foams are more difficult to make, that is, the stannous octoate operating latitude is diminished as the dipropylene glycol modifier concentration is increased. This demonstrates that the amount of low molecular polyol modifier used in this invention has a critical upper limit as defined supra. These data presenting bond-to-bond strengths values also establish that the lower limit is critical as well.

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TABLE I

Examples 1-4

Effect of Dipropylene Glycol on Foam-to-Foam Bond Strengths

Example No.	1	2	3	4	Control A
Polyether Polyol I (parts)	72	71.3	70.5	69.7	100
Polyether Polyol II (parts)	24	23.7	23.5	23.3	0
Dipropylene Glycol (parts)	4.0	5.0	6.0	7.0	0
Water (parts)	4.0	4.0	4.0	4.0	3.0
Amine Catalyst ⁽¹⁾ (parts)	2.0	2.0	2.0	2.0	0.1 Amine Catalyst ⁽²⁾
Surfactant L-6202 ⁽³⁾ (parts)	1.0	1.0	1.0	1.0	1.0 L-520
Stannous Octoate (parts)	0.15	0.15	0.10	0.10	0.25
Dichlorodifluoromethane	2.0	2.0	2.0	2.0	0
80/20 TDI (105 index)	53.5	54.6	56.1	57.4	49.0
Hydroxyl Number of polyol blend (includes dipropylene glycol)	79.3	87.1	95.0	102.9	49.0
Cream Time (sec.)	9.5	8.5	8.0	8.0	13.0
Rise Time (sec.)	74	73	78	78	115
Top Collapse (in.)	0.0	0.2	1.2	0.8	0.0
Height of Rise (in.)	7.6	7.9	6.9	6.8	5.2
Breathability (SCFM)	6.3	5.5	6.3	5.0	3.3
Density (pcf)	1.50	1.47	1.49	1.49	2.01
Foam-to-Foam Bond Strength (lbs./in.)					
3 cycles	2.9	2.9	4.8	4.7	0.4
4 cycles	3.7	4.3	4.2	5.2	0.6

⁽¹⁾ Blend of a major amount of dimethylaminopropionitrile and a minor amount of bis(2-dimethylaminoethyl) ether.

⁽²⁾ Polysiloxane-polyoxyalkylene block copolymer marketed by Union Carbide Corp.

⁽³⁾ 70% Solution of bis(2-dimethylaminoethyl) ether in dipropylene glycol.

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As the concentration of dipropylene glycol modifier is increased in these Examples, the hydroxyl number of the total polyol blend increase along with the bond-to-bond strengths. 5 Controls B—I show that mere adjustment of the hydroxyl number of the polyether polyol component will not give results equivalent to the compositions containing low molecular weight polyols as well. This is demonstrated in 10 Table II where urethane foaming Control compositions comparable to those in Examples 1 to 4 were prepared and foamed with the exception that no dipropylene glycol modifier was present. Polyether Polyol I was used as 15 the polyether polyol component together with the series Polyether Polyol III, IV, V and VI. These latter polyols are all reaction products of glycerine and propylene oxide having average molecular weight of 3000, 2240, 1500 and 700 20 respectively. A comparison of Tables I and II demonstrate clearly that whereas Example 1, having an adjusted hydroxyl number of 79.3, gave excellent foam to foam bond strengths the Controls D and G using Polyether Polyol IV with an adjusted hydroxyl number of 75.3 25 gave markedly inferior bond-to-bond strengths. Thus, a blend of conventional polyether polyols with a low molecular weight polyol modifier such as dipropylene glycol is surprisingly and unexpectedly unique in improving bond-to- 30 bond strengths of thermally bonded polyurethane foams. This unexpected finding is also corroborated in Table II where it can be seen that the Control H which used Polyether Polyol V, having an hydroxyl number of 112 35 and an average molecular weight of 2240 afforded a polyurethane bond with a very low bond-to-bond strength, further supporting the conclusion that molecular weight variations of a base polyol are not the controlling key to 40 obtaining polyurethane foams with high bond-to-bond strength.

TABLE II
Controls B-I

Control	B	C	D	E	F	G	H	I
(parts) Polyether Polyol I	100	-	-	100	-	-	-	-
(parts) " " III	-	100	-	-	100	-	-	-
(parts) " " III	-	-	100	-	-	100	-	-
(parts) " " IV	-	-	-	-	-	-	100	-
(parts) " " V	-	-	-	-	-	-	-	100
(parts) " " VI	-	-	-	-	-	-	-	-
Water (parts)	3.0	3.0	3.0	4.0	4.0	4.0	2.5	3.0
Amine Catalyst (a) (parts)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Stannous Octoate (parts)	0.25	0.25	0.20	0.25	0.25	0.20	0.20	0.10
Surfactant L-520 (parts) (b)	1.0	1.0	1.0	1.0	1.0	1.0	-	-
L-540/Y-4499 (c) parts	-	-	-	-	-	-	3.0	-
L-540 (parts) (b)	-	-	-	-	-	-	-	1.0
80/20 TDI (105 index)	38.4	40.0	42.3	48.6	50.1	52.8	45.3	69.5
Polyol Hydroxyl Number	49.0	58.5	75.3	49.0	58.5	75.3	112.0	240.0
Cream Time (sec.)	13	12	12	12	12	12	16	15
Rise Time (sec.)	115	123	127	88	104	100	130	90
Top Collapse (in.)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Height of Rise (in.)	5.2	5.0	5.5	7.1	7.1	7.3	-	-
Breathability (SCFM)	5.3	4.0	4.5	4.3	5.5	6.0	-	-
Density (pcf)	2.01	2.00	1.96	1.58	1.62	1.55	-	-
Foam-to-Foam Bond Strength (lbs./inch)	-	-	-	-	-	-	0.9	-
3 cycles	0.7	0.5	0.2	0.8	1.5	0.9	1.1	-
4 cycles	0.5	0.2	0.4	0.8	1.3	0.7	-	-
5 cycles	-	-	-	-	-	-	-	-

(a) 70% Solution of bis(2-dimethylaminoethyl) ether in dipropylene glycol.
 (b) Polysiloxane-polyoxyalkylene block copolymer marketed by Union Carbide Corp.
 (c) Blend of 92.3 wt. % L-540 and 7.7 wt. % Y-4499 (350 Centistoke dimethyl silicone oil).

Examples 5 to 10.

5 A comparison of ethylene glycol with diethylene glycol as the polyol modifier of this invention is shown in Table III. In these examples the base polyether polyol chosen was Polyether Polyol II demonstrating the use of a graft polymer polyol alone. All of the examples show satisfactory to excellent foam-to-foam bond strengths.

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Examples 11 to 14.

Examples 11 to 14 show the effectiveness of dipropylene glycol as the polyol modifier of

polyurethane foam composition in respect of the achievement of good foam-to-foam bond strengths. A comparison with controls J and K in which no dipropylene glycol was used demonstrates the effectiveness of this simple polyol modifier in improving foam-to-foam bond strength as demonstrated in Table IV. These data demonstrate that no bond strength is obtained when Polyether Polyol I is used and only 1 pound per linear inch foam-to-foam bond strength obtained when Polyether Polyol II is used in the absence of the polyol modifier, dipropylene glycol.

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TABLE III

Examples 5-10

Example No.	5	6	7	8	9	10
Polyether Polyol II (parts)	98	98	98	98	98	98
Diethylene Glycol (parts)	2	2	—	—	—	—
Ethylene Glycol (parts)	—	—	2	2	2	2
Water (parts)	4.3	4.3	4.3	4.3	4.3	4.3
*Amine Catalyst (parts)	0.2	0.2	0.2	0.2	0.2	0.2
Surfactant L-540 (1) (parts)	1.0	1.0	1.0	1.0	1.0	1.0
Stannous Octoate (parts)	0.10	0.15	0.025	0.05	0.10	0.15
Hydroxyl Number of Polyol Blend	64.3	64.3	79.2	79.2	79.2	79.2
Cream Time (sec.)	14	14	15	14	14	14
Rise Time (sec.)	106	88	170	137	108	98
Height of Rise (in.)	7.9	8.6	7.3	7.8	8.5	8.8
Breathability (SCFM)	3.5	1.1	2.8	3.8	1.5	0.4
Density (pcf)	1.45	1.44	1.50	1.45	1.39	1.38
Foam-to-Foam Bond Strength (lbs./inch) 3 cycles	2.5	4.2	6.0	4.4	3.4	3.9
4 cycles	2.5	4.0	6.0	4.2	3.3	4.6

* blend of a major amount of N,N-dimethylethanolamine and a minor amount of bis(2-dimethylaminoethyl)ether.

(1) Polysiloxane-polyoxyalkylene block copolymer marketed by Union Carbide Corp.

Example 15.

The superiority in foam-to-foam bond strength of a polyurethane foam formulated from a composition containing the polyol modifier, dipropylene glycol, over that of Control L containing an organic polyisocyanate reaction product of an excess of an aromatic polyisocyanate with a diol, designated a Prepolymer Isocyanate, was demonstrated. Control L was carried out with a Prepolymer Isocyanate pre-

pared by reacting 9.8 grams of dipropylene glycol with 100 parts of the isomeric mixture of 2,4 and 2,6 tolylene diisocyanate (an excess) as disclosed in United States Patent Specification No. 3,497,416. The formulations and the physical properties including foam-to-foam bond strengths of Example 15 and Control L are shown in Table V. At both three cycles and four cycles the foam-to-foam bond strength, of Example 15, is demonstrated to be superior to Control L.

TABLE IV

Example No.	Control J	Control K	11	12	13	14
Polyether Polyol II(parts)	100	-	95	70	45	20
Polyether Polyol I (parts)	-	100	-	25	50	75
Dipropylene Glycol (parts)	-	-	5	5	5	5
Water (parts)	3.0	3.0	3.0	3.0	3.0	3.0
Amine Catalyst (%) (parts)	0.2	0.2	0.2	0.2	0.2	0.2
L-520 (?) (parts)	1.0	1.0	1.0	1.0	1.0	1.0
Stannous Octoate (parts)	0.25	0.25	0.15	0.15	0.15	0.15
80/20 TDI (100 index)	35.9	36.6	42.1	42.1	42.1	42.1
Polyol Blend Hydroxyl Number	44.1	48.1	84.5	84.7	84.6	84.2
Cream Time (sec.)	11	10	10	10	10	9.5
Rise Time (sec.)	101	99	107	106	118	119
Breathability (SCFM)	2.15	2.02	1.91	1.95	2.15	2.04
Foam-to-Foam Bond Strength (lbs./inch) 3 cycles	1.0	0.0	3.7	2.4	3.4	4.0
4 cycles	1.3	0.0	3.6	3.1	3.4	4.0

(1) Blend of a major amount of N,N-dimethylethanolamine and a minor amount of bis(2-dimethylaminoethyl)ether.

TABLE V

Example 15

	15	Control L
Polyether Polyol II	95	100
Dipropylene glycol (parts)	5	—
Water (parts)	3.0	3.0
Amine Catalyst ⁽¹⁾ (parts)	0.15	0.30
Stannous Octoate (parts)	0.15	0.10
Silicone surfactant (parts)	1.0	0.5
TDI 80/20 (parts)	42.1	17.1
Prepolymer Isocyanate (parts)	—	30.25
Cream Time (sec.)	12	12
Rise Time (sec.)	113	187
Height of Rise (in.)	5.4	4.7
Breathability (SCFM)	1.5	1.10
Density (pcf)	1.95	2.26
Foam-to-Foam Bond Strength (lbs./inch) 3 cycles	3.40	2.4
4 cycles	3.25	2.0

⁽¹⁾ Blend of a major amount of N,N-dimethylethanolamine and a minor amount of bis(2-dimethylaminoethyl)ether.

Examples 16 to 22.

FOAMING PROCEDURE II—MACHINE SCALE.

5 A series of comparative machine scale flexible polyurethane foams was prepared at a through-put rate of about 70—80 pounds per minute. The foams were all prepared as follows:

10 Blends of conventional polyurethane foaming compositions were mixed with the polyol modifiers to be evaluated by weighing the proper amounts into a fifty gallon drum and tumbling several hours to effect mixing. The mixture was referred to as the polyol stream. A constant stream of polyol blend (21,000—22,000 grams per minute) along with an activator stream consisting of water, amine catalyst and silicone surfactant (800—1000 grams per minute), a separate stream consisting of additional silicone surfactant (150—300 grams per minute), a separate stream of auxiliary blowing agent (trichlorofluoromethane; 300—500 grams per minute) and a separate stream of tolylene diisocyanate (10,000—11,000 grams per minute) was intro-

duced to a hybrid foam machine under low foam pressure conditions. To prepare flame retardant foams, NIAK (Registered Trade Mark) Flame Retardant 3CF, tris(2-chloroethyl) phosphate, was added via a separate stream (1300—1500 grams per minute) or a blend of QYNV—1 vinyl resin (polyvinyl chloride dispersion resin sold by Union Carbide Corp.) and antimony oxide was added via the polyol stream.

The mixer speed was 5000 RPM, discharge nozzle 1 inch in diameter, conveyer angle 3.5 degrees and conveyer speed between 8 and 12 feet per minute. At ambient temperatures, the emerging foam mixture was poured onto a continuously moving conveyer belt. The foam was allowed to set and cure in the form of ten foot long 26 inch wide, 18 inch high slabs. After twenty-four hours of aging at ambient temperature, the foams were cut and physical properties determined. The results along with other physical properties are reported in part in Table VIII.

The results in Table IX show excellent foam physical properties are obtained using either

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diethylene glycol or dipropylene glycol as the modifier polyol. The control T foam exhibits poor humid age compression sets. Humid age compression sets of foams made according to the present invention have good compression sets before and after humid aging.

Bond strength values in all of the examples except Example 17 were superior to the control T. Based on the totality of all of the work in this area including both hand mixing and machine mixed foams the bond strength values of Example 17 are anomalous.

TABLE VIII

Examples 16-22

Formulation and Reactivity Data

Example No.	Control T	16	17	18	19	20	21	22
Polyether Polyol I (parts)	95	75	75	75	75	75	75	75
Polyether Polyol II (parts)	—	25	25	25	25	25	25	25
Dipropylene Glycol (parts)	—	2.0	—	4.0	2.0	—	4.0	4.0
Diethylene Glycol (parts)	—	—	3.16	—	—	3.16	—	—
KM-1 (1) (parts)	5	4.16	—	—	4.16	—	—	—
QYNV-1 (2) (parts)	—	10	—	—	—	—	10	—
Antimony Oxide (parts)	—	5	—	—	—	—	5	—
Water (parts)	4.0	3.0	4.0	3.0	3.0	3.0	4.0	4.0
Catalyst (A) (parts)	—	0.10	0.125	0.125	0.125	0.125	0.125	0.125
Catalyst (B) (parts)	0.15	—	—	—	—	—	—	—
Silicone Surfactant (a) (parts)	0.3	—	—	—	—	—	—	—
Silicone Surfactant (b) (parts)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Silicone Surfactant (a) (parts)	1.2	—	—	—	—	—	—	—
Silicone Surfactant (b) (parts)	—	0.3	0.5	0.3	0.5	0.3	0.3	0.5
Stannous Octoate* (parts)	0.2	0.125	0.10	0.15	0.125	0.10	0.15	0.125
80/20 TDI parts index	51.0 105	42.5 105	53.1 105	42.8 105	42.5 105	43.0 105	53.0 105	53.0 105
NIAX Flame Retardant 3CF (parts)	7.0	—	7.0	7.0	7.0	7.0	—	7.0
Trichlorofluoromethane	—	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Cream Time (sec.)	4	3	6.5	5	5	5	2.5	5
Rise Time (sec.)	76	62	100	115	112	126	53	104
Gel Time (sec.)**	99	71	119	140	136	153	65	127

Footnote for Table VIII on previous page.:

- * Added to the foam mixture as a 50/50 blend by weight with Polyether Polyol I.
- ** Gel Time is the time it takes for the foam to reach strength great enough to cause visual resistance to a pipe cleaner as it is pushed into the foam bun.
- (¹) Tris(dipropylene glycol phosphite)
- (²) Polyvinyl Chloride dispersion resin; inherent viscosity 1.17–1.35 (ASTM D 1243 Procedure A)
- (A) 70% solution of bis(2-dimethyl aminoethyl)ether in dipropylene glycol
- (B) Major amount of dimethyl ethanolamine and a minor amount of bis(2-dimethyl-aminoethyl)ether
- (a) Silicone polyether copolymer molecular weight ca. 20,000
- (b) Silicone polyether copolymer molecular weight ca. 10,000.

Foams prepared in Examples 16 to 22 were tested for flame lamination properties according to the following procedure. Foam samples were cut into $\frac{1}{4}$ inch thicknesses and passed into a laminator. The substrate used was a cloth-backed vinyl automotive upholstery material.

The width of the half-inch foam and vinyl/cloth substrate was 36 inches. The laminating flame consisted of propane gas and air in a ratio of 58:400.

The foam was passed over the flame at a given speed and pressed to the substrate with nip rollers set 0.4 inches apart. Foam thickness after lamination was measured and subtracted from the original thickness to determine the amount of foam burned off. Bond strengths were determined by tearing the laminates (cut 1" $\times$ 6") using an Instron machine as described previously. Bond strengths were determined at different times after lamination to determine the rate at which they build. Speed of lamination was varied to make the test more critical. During each test a polyester polyol polyurethane foam of 1.8 pcf density prepared on a commercial machine was used as a control. During Instron testing it was recorded whether or not the bond between the foam and the substrate was separating (referred to as bond tear) or whether the foam was tearing (referred to as foam tear). It is well known in the art, that once the strength of the foam/substrate bond exceeds a certain value, the foam will tear. At this point, it is impossible to determine the foam/substrate bond value. It is also well known in

the art that samples that give foam tear are of excellent quality.

The foam physical properties and heat sealing results are presented in Table IX. The flame lamination results are presented in Table X.

It may be concluded from these last data that:

1. Flame lamination properties of the compositions used in the present invention are excellent by commercial standards. This can be demonstrated by bond strength results as well as the number of Examples giving foam tear.

2. The Control U polyester polyol polyurethane foam bond strength values are higher than those in the Examples due to higher tensile/elongation values of the foam. This is well known in the art and does not detract from the excellent results of the polyether polyol polyurethane foams in the Examples.

3. Humid aging data demonstrates foams prepared according to this invention are superior to polyester foam (Control U) as can be seen from the fact that the latter totally degraded after three 5-hour humid aging cycles resulting in zero bond strength.

4. Control T laminates took longer to develop bond strength than foam laminates of the present invention. This was determined qualitatively immediately after lamination by pulling samples apart. This constitutes a serious commercial disadvantage for foams made according to the composition of Control T.

TABLE IX

Examples 16-22

Foam Physical Properties and Heat Sealing Results

Example No.	Control T	16	17	18	19	20	21	22
Breathability (SCFM)	2.4	1.5	2.9	1.9	3.2	1.5	2.5	4.1
Density (pcf)	1.56	1.91	1.47	1.79	1.82	1.79	1.57	1.49
Tensile Strength (psi)	21.4	19.2	18.3	19.1	17.5	17.1	19.1	17.4
Elongation (%)	288	232	207	231	229	202	210	210
Tear Strength (lbs./inch)	3.34	2.6	3.1	2.09	3.2	2.4	2.9	3.0
ILD	43	42	43	44	39	46	41	41
65%	78	82	82	82	74	85	80	77
25% Return	25	25	25	28	25	78	23	24
Compression Set (%)								
50%	13.0	11.7	11.9	7.7	8.1	7.4	14.7	10.4
75%	13.8	13.3	11.4	7.1	7.1	7.1	17.5	10.2
90%	13.1	16.2	12.8	7.8	7.6	7.6	24.7	10.9
Humid Age Compression Sets (%)								
80%	26.5	28.7	14.3	13.6	14.0	12.6	51.1	19.6
75%	33.6	67.2	23.3	13.7	15.0	14.0	68.3	21.9
Humid Age Load Loss	6.3	10.1	8.0	7.9	11.7	7.2	4.7	3.5
Foam-to-Foam Bond Strengths (lbs./inch)								
3 cycles	1.8	4.6	1.0	2.7	3.4	2.5	4.4	3.5
4 cycles	2.6	4.3	1.0	2.7	2.9	3.5	4.3	3.6

(1) Measured in accordance with ASTM 1564-68

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TABLE X
Examples 16-22
Flame Lamination Results

Example No.	Control T	16	17	18	19	20	21	22	Control U
Test 1									
Lamination Speed, 60 ft./min.									
Bond Strengths After 30 minutes	2.1	0.7	2.7	2.7	3.0	2.1	1.1	2.7	4.1
After 60 minutes	2.8	1.1	2.6	2.6	3.0	2.1	1.4	2.6	4.0
After 90 minutes	2.8	1.2	2.8	2.8	2.9	1.8	1.5	2.3	4.2
After 24 hours	2.9	2.0	2.4	2.2	2.7	2.2	2.8	2.6	4.2
Number of samples giving bond tear	10	12	4	1	0	0	12	0	4
Number of samples giving foam tear	2	0	8	11	12	12	0	12	8
Bond Strengths After 5 hours Humid Aging	2.0	0.4	3.5	2.1	2.4	2.3	0.7	1.7	2.4
Bond Strengths After Three 5-Hour Humid Aging cycles	0.7	0.1	0.8	1.25	0.4	0.8	0.2	1.3	0.0
Burn off (inches)	0.045	0.045	0.050	0.040	0.030	0.030	0.050	0.040	0.040
Test 2									
Lamination Speed, 80 ft./min.									
Bond Strengths									
After 15 minutes	↑	↑	2.1	2.1	2.1	2.0	↑	1.5	2.8
After 90 minutes	↑	↑	2.7	2.5	2.6	2.0	↑	2.3	3.6
After 24 hours	↑	↑	2.1	2.4	2.4	1.8	↑	2.3	3.2
Number of samples giving bond tear	Not Run	Not Run	6	5	6	2	Not Run	6	8
Number of samples giving foam tear	Not Run	Not Run	3	4	3	7	Not Run	3	1
Bond Strengths After 5 hours Humid Aging	↑	↑	2.1	2.0	2.0	1.7	↑	1.5	1.5
Bond Strengths After Three 5-Hour Humid Aging Cycles	Not Run	Not Run	0.7	0.8	0.6	0.8	Not Run	0.8	0.0
Burn off (inches)	Not Run	Not Run	0.028	0.020	0.028	0.023	Not Run	0.029	0.040

TABLE X (Continued)

Examples 16-22

Flame Lamination Results

Example No.	Control T	16	17	18	19	20	21	22	Control U
Test 3									
Lamination Speed, 120 ft./min.									
Bond Strengths									
After 30 minutes			0.6	0.9	0.6	0.7		0.7	1.5
After 90 minutes			0.6	1.3	0.8	0.8		0.6	1.1
After 24 hours			0.6	0.9	0.6	0.6		0.7	1.1
Burn off (inches)			0.015	0.015	0.016	0.018		0.018	0.013

Examples 23 to 28.

When Examples 16 to 22 are repeated with the exception that the cloth-back vinyl automotive upholstery material is replaced by paper, nylon, cotton, leather, rayon acetate, or polyvinyl chloride sheet, respectively, comparable bond strengths are obtained between these substrates and polyurethane foam.

10 WHAT WE CLAIM IS:—

1. A polyol composition useful for preparing a polyurethane foam, which composition comprises:—

(a) a graft copolymer of a polyether polyol having a molecular weight of at least 2000 and containing an average of at least two hydroxyl groups per molecule, the graft copolymer being formed by polymerizing one or more ethylenically unsaturated monomers dissolved or dispersed in the polyether polyol in the presence of a free radical catalyst, and (b) from 1 to 7%, based on the weight of the graft copolymer, of at least one polyol modifier consisting of:

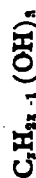
(1) an alkylene glycol having from 2 to 8 carbon atoms;

(2) a glycol ether having the empirical formula:



wherein n is an integer from 2 to 4 and m is an integer from 2 to 4 when n is 2, is 2 or 3 when n is 3, and is 2 when n is 4;

(3) a triol having the empirical formula:



wherein x is an integer from 3 to 10;

(4) an alkanolamine having the empirical formula:



wherein y is an integer having values of from 2 to 10, z is 1 or 2 and p is an integer from 2 to 4; or

(5) a polyhydric mononuclear alcohol.

TABLE X (Continued)

Examples 16-22

Flame Lamination Results

Example No.	Control T	16	17	18	19	20	21	22	Control U
Test 3									
Lamination Speed, 120 ft./min.									
Bond Strengths									
After 30 minutes			0.6	0.9	0.6	0.7		0.7	1.5
After 90 minutes			0.6	1.3	0.8	0.8		0.6	1.1
After 24 hours			0.6	0.9	0.6	0.6		0.7	1.1
Burn off (inches)			0.015	0.015	0.016	0.018		0.018	0.013

↑ Not Run

↑ Not Run

Examples 23 to 28.

When Examples 16 to 22 are repeated with the exception that the cloth-back vinyl automotive upholstery material is replaced by paper, nylon, cotton, leather, rayon acetate, or polyvinyl chloride sheet, respectively, comparable bond strengths are obtained between these substrates and polyurethane foam.

(1) an alkylene glycol having from 2 to 25

8 carbon atoms;

(2) a glycol ether having the empirical formula:



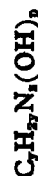
wherein n is an integer from 2 to 4 and m is an integer from 2 to 4 when n is 2, is 2 or 3 when n is 3, and is 2 when n is 4;

(3) a triol having the empirical formula:



wherein x is an integer from 3 to 10;

(4) an alkanolamine having the empirical formula:



wherein y is an integer having values of from 2 to 10, x is 1 or 2 and p is an integer from 2 to 4; or

(5) a polyhydric mononuclear uhenol.

10 WHAT WE CLAIM IS:—

1. A polyol composition useful for preparing a polyurethane foam, which composition comprises:—

(a) a graft copolymer of a polyether polyol having a molecular weight of at least 2000 and containing an average of at least two hydroxyl groups per molecule, the graft copolymer being formed by polymerizing one or more ethylenically unsaturated monomers dissolved or dispersed in the polyether polyol in the presence of a free radical catalyst, and (b) from 1 to 7%, based on the weight of the graft copolymer, of at least one polyol modifier consisting of:

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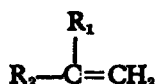
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2. A composition as claimed in claim 1 wherein the graft copolymer is a graft polymer polyether polyol having from 2 to 6 hydroxyl groups per molecule wherein the polymer is prepared by polymerizing a monomer of the formula:—



- wherein R_1 is a hydrogen or halogen atom and R_2 is R_1 or a cyano, phenyl, methyl-substituted methyl or alkenyl group having from 2 to 6 carbon atoms, dissolved or dispersed in the said polyether polyol in the presence of a free radical catalyst.

3. A composition as claimed in claim 1 or claim 2 wherein the polyether polyol comprises a polymer triol reaction product of glycerine with propylene oxide and ethylene oxide.

4. A composition as claimed in claim 3 wherein the polyether polyol comprises the reaction product of glycerine with a mixture of 86% by weight of 1,2-propylene oxide and 14% by weight of ethylene oxide and has a molecular weight of 3500.

5. A composition as claimed in any one of the preceding claims wherein the graft copolymer comprises from 10 to 30 weight per cent of a copolymer of from 25 to 50 weight per cent of acrylonitrile or methacrylonitrile and from 50 to 75 weight per cent of styrene or alpha-methyl styrene, and from 70 to 90 weight per cent of the said polyether polyol.

6. A composition as claimed in claim 5 wherein the graft copolymer comprises 80% by weight of the polyether polyol and 20% by weight of the copolymer.

7. A composition as claimed in any one of the preceding claims additionally containing the polyether polyol in its ungrafted form.

8. A polyol composition as claimed in claim 1 substantially as hereinbefore described.

9. A polyol composition as claimed in claim 1 substantially as hereinbefore described in any one of the Examples.

10. A composition for producing a flexible polyurethane foam comprising:

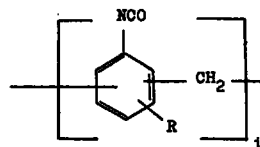
- a polyisocyanate reactant containing at least two isocyanato groups per molecule;
- a blowing agent;
- a catalyst for the urethane-forming reaction;
- a surfactant; and
- a polyol composition as claimed in any one of the preceding claims.

11. A composition as claimed in claim 10 wherein the polyisocyanate reactant is a compound having the general formula:—



wherein i has an average value of from 2 to

- 6 and Q is an aliphatic, cycloaliphatic or aromatic radical, or having the general formula:—



wherein R is a hydrogen atom and/or a methyl group and j has an average value of at least 2.1.

12. A composition as claimed in claim 10 or claim 11 wherein the polyol modifier is ethylene glycol.

13. A composition as claimed in claim 10 or claim 11 wherein the polyol modifier is 1,2-propylene glycol.

14. A composition as claimed in claim 10 or claim 11 wherein the polyol modifier is diethylene glycol.

15. A composition as claimed in claim 10 or claim 11 wherein the polyol modifier is di(1,2-propylene) glycol.

16. A composition as claimed in claim 10 or claim 11 wherein the polyol modifier is glycerine.

17. A composition as claimed in claim 10 or claim 11 wherein the polyol modifier is triethanolamine.

18. A composition as claimed in claim 10 or claim 11 wherein the polyol modifier is resorcinol.

19. A composition as claimed in any one of claims 10 to 18 wherein the catalyst comprises a tertiary amine in an amount of from 0.05 to 3 weight percent of the polyether polyol reactant and an organic derivative of a metal in an amount of from 0.05 to 2 weight percent of the polyether polyol reactant.

20. A composition as claimed in claim 10 substantially as hereinbefore described in any one of the Examples.

21. A method of thermally bonding flexible polyether polyurethane foam to a substrate which comprises:

- reacting and foaming a composition as claimed in any one of claims 10 to 20;
- heating the surface of the foamed composition of (A) above its melting or fusion point;
- contacting the melted or fused surface of the foamed composition of (A) with a substrate whereby a flexible polyurethane foam/substrate laminate is formed; and
- cooling the flexible polyurethane foam/substrate laminate below the melting or fusion point of the flexible polyurethane foam.

22. A method as claimed in claim 21 wherein the temperature of the melted or fused surface of the flexible polyurethane foam is from 204°C to 315°C.

23. A method as claimed in claim 21 or claim 22 wherein the flexible polyurethane



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foam surface is melted or fused by passing over a flame at a constant rate of speed.

24. A method as claimed in claim 21 or claim 22 wherein the flexible polyurethane foam surface is melted or fused by contact with a heat sealing means.

25. A method as claimed in any one of claims 21 to 24 wherein the substrate is maintained at ambient temperatures when contacted with the melted or fused surface of the flexible polyurethane foam.

26. A method of bonding a foam to a sub-

strate as claimed in claim 21 substantially as hereinbefore described in any one of the Examples.

27. A substrate/foam laminate when formed by a method as claimed in any one of claims 21 to 26.

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