Uı	nited S	tates Patent	[19]	[11]	E	Paten	t Number:	Re. 33,755
Do	wney et al	•		[45]	Reissued	Date	of Patent:*	Nov. 26, 1991
[54]		ASTICIZERS FOR THANE COMPOSITIO	NS		3,869,421 3,883,465	5/1975	Olstowski	260/33.6 AQ 260/31.2
[75]	Inventors:	William J. Downey, Lind Brauer, East Brunswick Chao, Bayonne, all of N	Jerry C.		3,886,102 3,886,111 3,933,725 3,963,656	5/1975 1/1976 6/1976	Yoshimura et al Dearlove et al. Meisert et al	
[73]	Assignee:	CasChem, Inc., Bayonne	, N.J.		3,980,606 4,001,165			260/31.8 R 260/33.6
[*]	Notice:	The portion of the term of subsequent to May 19, 2 disclaimed.			4,001,166 4,067,834 4,076,660 4,102,716	1/1978 2/1978	Olstowski Olstowski et al.	
[21]	Appl. No.:	428,700			4,122,058	10/1978	Olstowski	524/871
[22]	Filed:	Oct. 30, 1989				9/1979	Boetchler	
	Relat	ed U.S. Patent Documents	S					174/23 C
Reiss [64]	sue of: Patent No Issued: Appl. No. Filed:	May 19, 1987			4,231,986 4,264,486 4,281,210 4,329,442 4,349,640	11/1980 4/1981 7/1981 5/1982 9/1982	Brauer et al McLaughlin Brauer et al Pokorney Keeney et al	
U.S. [63]	Applications Continuatio 1985, aband	n-in-part of Ser. No. 713,377	, Ma r. 19,		4,355,130 4,373,057 4,375,521 4,396,053	2/1983	Hammond	
[51]	Int. Cl.5	C08K 5/10;	C08K 5/12	•	4,533,598 4,596,743 4,849,579	6/1986	Brauer et al	524/773 428/380 174/74 R
[52]	U.S. Cl 524/297		96; 524/284 73; 524/775 523/173	;	4,876,303	10/1989		524/296
[58] [56]	Field of Sea	524/296, 25 524/590, 773, 775, 297, 3 References Cited		•	1117682 130089	2/1982 1/1985	Canada . Canada . European Pat. C World Int. Prop	
• •	U.S. F	PATENT DOCUMENTS	5				•	
3	e. 30,321 7/1 3,047,520 7/1	980 Brauer et al	260/18 TN 260/18	1 8	•	nt, or Fir	Allan M. Lieberr m—Pennie & F ABSTRACT	
3	3,338,861 8/1 3,390,119 6/1 3,441,530 4/1 3,714,110 1/1 3,747,037 7/1	964 Kaestner et al	260/33.6 524/871 260/28.5 260/33.6 AQ	6 1 5 2	reaction proc polyol in the p	duct of presence ity paras	an isocyanate of a plasticizer of the meter of the two series of the meter of the two series of the meter of the two series of the meter of the mete	m comprising the compound and a compound having een about 8.3 and
		974 Olstowski				15 Cla	ims, No Drawin	gs

ESTER PLASTICIZERS FOR POLYURETHANE COMPOSITIONS

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Matter enclosed in heavy brackets [] appears in the 5 original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuous-in-part of application Ser. No. 713,377, filed Mar. 19, 1985, now abandoned.

TECHNICAL FIELD

The invention relates to polyurethane gels which contain novel plasticizers and which may be formulated as a grease-compatible, non-spewing material for use in reclaiming, encapsulating or sealing electrical cables or devices.

BACKGROUND ART

It is well-known in the art to extend polymers such as polyurethanes. This extended material will then be designated for use in a desired area of utility. Typical of ²⁵ such extending agents is mineral oil, such mineral oil extended polyurethanes being disclosed in U.S. Pat. Nos. 3,714,110 and 3,747,037.

It has also been determined that the mineral oil extended polyurethane is useful in the reclamation and 30 protection of insulated electrical devices. Such devices may, for example, be underground telephone cables which are exposed to fluid contaminants. These contaminants can seriously impair the electrical and mechanical properties of such a device. The protectant 35 material is pumped into the cable to remove water that has penetrated into interior free spaces. The material is pumped at low viscosity to achieve an appropriate distribution and it then cures in place to a high viscosity. The cured material acts as a hydrophobic barrier to 40 subsequent water penetration. In another application, this material may be utilized as an encapsulant for sealing sections of cable. In this manner, the material serves to prevent the penetration of fluid contaminants from the outset.

A mineral oil extended polyurethane which is useful for this purpose is disclosed in U.S. Pat. No. Re. 30,321. That patent defines a cured, cross-linked, mineral oil extended polyurethane prepared from specific polyurethanes and coupling agents, the latter being necessary to 50 der from the cured material. compatibilize the mineral oil with the cross-linking urethane elastomer.

Disadvantages of these mineral oil extended polyurethane systems were encountered, however, and these are described in U.S. Pat. No. 4,168,258. There it was 55 stated that, with the earlier mineral oil extended polyurethanes, the mineral oil would tend to migrate toward any grease present in the cable or device in order to be reclaimed or encapsulated. This grease is encountered This migration was shown to cause the formation of an oily film at the grease interface which tended to decrease the reclamation and encapsulant effectiveness of the polyurethane. In order to avoid these difficulties, the patent specifically defined a polyurethane-mineral 65 oil-coupling agent formulation relying on the presence of a polydiene moiety in the polyurethane structure. Mineral oil remained as the extending agent, with the

stated preference for including some aromatic carbon content therein.

It is also known that previous polyurethane compositions have been difficult to re-enter after they have fully cured primarily due to their high cast strength or aging hardness, as well as due to their opaque or cloudy color. The high cast strength and hardness of these prior art polyurethanes contribute to the difficulty of cutting through or removing cured material from a repaired 10 area. In some applications, the opaque color makes it difficult for the operator to establish the exact location to reenter a repair, and thus, clear soft polyurethane gels are preferred.

With either the clear or opaque products, the ability 15 of these polyurethanes to be easily reentered is important in the repair or encapsulation of insulated electrical or telephone cables when a second splice or connection must be made in the same area as the previous repair or encapsulation. There are also situations where the initial repair or encapsulation is improperly made and has to be re-done. For these reasons, the primary concern regarding the physical properties of these gels is to provide a polyurethane having a relatively low tear strength and hardness. Furthermore, it is highly desirable for these materials to maintain these properties over time.

A vegetable oil extended polyurethane which satisfies some of these requirements and provides an initially reenterable gel is disclosed in U.S. Pat. No. 4,375,521. There, vegetable oil extended polyurethanes of a three component system comprising a specific polyurethane, vegetable oil, and specific extending agent is disclosed for use in reclamation and encapsulation applications. However, these vegetables oil extended formulations usually provide opaque gels, and, more importantly, tend to cause cracking or stressing of the polycarbonate connectors which are usually present in the cable unit being reclaimed, encapsulated, or repaired. Furthermore, some of these gel formulations age harden over time to make reenterability difficult.

In U.S. Pat. No. 4,355,130, a polyalphaolefin extended polyurethane is disclosed which resolves the stress cracking problem. Such polyalphaolefin extended 45 polyurethanes comprise specific polyurethanes, a specific polyalphaolefin extender, and, for reclamation and encapsulation purposes, specific ester coupling agents. The coupling agent is required to compatibilize the formulation so that there will be no "spewing" of exten-

DISCLOSURE OF THE INVENTION

It is, therefore, an object of the present invention to provide an extended polyurethane gel system having improved compatibility with cable greases. These compositions also have utility as cable reclamation compounds and fiber-optic splice encapsulations for the telecommunications industry.

It is a further object to provide polyurethane gel more frequently in newer insulated electrical devices. 60 formulations which are defined in accordance with specific end use applications.

It has now been found that by utilizing the plasticizers of the present invention as the extending agents for polyurethanes gels, the resulting systems are well suited for a number of end use applications including electric or telecommunication cable reclamation and encapsulation or as general polyurethane elastomers. Such plasticized polyurethane gels generally comprise a specified

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polyurethane component and a plasticizer compound having a total solubility parameter of [between about 8.3 and 8.9 or between about 9.1 to 9.7.

The polyurethane gels of the present invention are characterized as having excellent compatibility of the 5 components, a broad viscosity range, good electrical properties, and the absence of cracking or stressing tendencies on polycarbonate connectors. It is particularly in the area of compatibility of the components and the electrical properties of the compositions that these 10 polyurethanes exhibit significant improvements over prior art mineral oil extended systems.

When used in the area of reclamation and encapsulation, these plasticized polyurethane gels provide excellent performance characteristics. They possess the low 15 viscosities necessary for initial introduction into the cable and the ability to retain these low viscosities for a period of time sufficient to enable them to fill the length of the free spaces in the cable or form a completely encapsulating cover. They also possess the ability to 20 displace and/or repel fluid contaminants and cure in place to form a gel-like urethane structure which neither spews forth nor exudes the plasticizer. This gel structure has sufficient rigidity to provide an excellent protective barrier, yet can be readily cut and removed if 25 re-entry is desired. The polyurethane gels are non-corrosive to copper wire and compatible with the conventionally used polycarbonate connectors and other polymeric materials utilized in cable manufacture. The sys-

The polyurethane which is used in these formulations is generally prepared by reacting approximately stoichiometric amounts of an isocyanate compound with a polyol. The plasticizer can be added to either component before they are reacted.

In a preferred embodiment, the isocyanate component is a polyisocyanate prepolymer which is in turn prepared by reacting an excess of an isocyanate compound with a polyol in a manner well known in the art. A portion of the plasticizer is added to the polyisocya- 40 nate prepolymer, and the mixture is then reacted with a polyol containing the remaining portion of the plasticizer to form the gels.

The isocyanate compounds of the invention which can be used for the preparation of the polyisocyanate 45 prepolymer or direct reaction with the polyol to form the polyurethane contemplate any organic polyisocyanate having 2 or more NCO groups per molecule and no other substituents capable of reacting with the hydroxyl groups of the polyol. This would include aliphatic poly- 50 isocyanates, cycloaliphatic polyisocyanates, or aromatic polyisocyanates. Typical of such polyisocyanate compounds are 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI), toluene diisocyanate methylene polyphenylisocyanate, 1,5 naphthalene diisocyanate, phenylene, diisocyanates, 4,4'-methylene bis(cyclohexylisocyanate), hexamethylene diisocyanate, biuret of hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate and combinations thereof, 60 as well as related aromatic, aliphatic, and cycloaliphatic polyisocyanates which may be substituted with other organic or inorganic that do not adversely affect the course of the reaction.

The term "aliphatic", as used herein, includes those 65 carbon chains which are substantially non-aromatic in nature. They may be saturated or unsaturated, unbranched, branched, or cyclic in configuration and may

gration. Such aliphatic isocyanates generally have an equivalent weight of from 60 to 160 and a viscosity of 1 to 1500 centipoises at 25° C. Exemplary of the liquid long chain aliphatic polyisocyanates are dodecyl diisocyanate, tridecyl diisocyanate, and the like. Polymethylene polyphenyl isocyanate is commercially available from Mobay Chemicals under the trademark Mondur MRS. Two preferred compounds, Mondur MRS and MRS-10, are dark-brown liquids having a slight aromatic odor. Specifically Mondur MRS has an NCO

contain substituents which do not adversely affect mi-

content of 31.5%, an amine equivalent of 133, a viscosity of 200 mPa-S at 25° C., and a density of 1.24 g/cc, while Mondur MRS-10 has an NCO content of 31.9%, an amine equivalent of 132, a viscosity of 80 mPa-s at 25° C. and a density of approximately 1.24 g/cc. Diphenylene methane diisocyanates are commercially available in a stabilized liquid form from Upjohn under the trademark Isonate 143L or from Mobay under the trademark Mondur CD. Specifically, Isonate 143-L is a light yellow, modified diphenyl-methane diisocyanate having an NCO content of 29.2 weight percent, an isocyanate equivalency of 144, an acidity value of less than 0.030 and a viscosity of 35 cps at 25° C., while Mondur CD is a light-yellow modified 4,4' diphenylmethane diisocyanate having an NCO content of 29.3

mercially available from Upjohn under the trademark tem is also convenient to handle and apply in the field. 30 PAPI, of which PAPI 94 is typical. PAPI 94 is a polymeric methylene diisocyanate containing approximately 98% of 4,4' isomer with the remaining 2% being the 2,4' isomer. PAPI 94 has an NCO content of approximately

weight percent and a viscosity of less than 100 mPa-s at

25° C. Various polyarylene polyisocyanates are com-

Suitable polyols for reaction with the organic polyisocyanates include caster oil, polyether polyols, polyester polyols, hydroxyl bearing homopolymers of dienes, hydroxyl bearing copolymers of dienes, amine based polyols, polymeric polyols, and combinations thereof. Such polyols generally have an equivalent weight of from 30 to 6000 and a viscosity of from 1 to 20,000 centipoises at 25° to 60° C. The higher equivalent weight materials, i.e., those having equivalent weights

One polyol which may be used in the preparation of these plasticized polyurethane gels is caster oil, a compound primarily composed of ricinolein, which is a glyceride of ricinoleic acid. A typical castor oil comprises a mixture of about 70% pure glyceryl triricinoleate and about 30% glyceryl diricinoleate-monoleate or monolinoleate and is available from CasChem, Inc. as DB Oil.

above about 250, are generally preferred.

Suitable polyether polyols include aliphatic alkylene glycol polymers having an alkylene unit composed of at (TDI), 4,4' diphenylmethanediisocyanate (MDI), poly- 55 least two carbon atoms. These aliphatic alkylene glycol polymers are exemplified by polyoxypropylene glycol and polytetramethylene ether glycol. Also, trifunctional compounds exemplified by the reaction product of trimethyol propane and propylene oxide may be employed. A typical polyether polyol is available from Union Carbide under the designation Niax PPG-425. Specifically, Niax PPG-425, a copolymer of a conventional polyol and a vinyl monomer, has an average hydroxyl number of 263, an acid number of 0.05, and a viscosity of 80 centistokes at 25° C.

The general term polyether polyols also includes polymers which are often referred to as amine based polyols or polymeric polyols. Typical amine based

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polyols include sucrose-amine polyols such as Niax BDE-400 or FAF-529 or amine polyols such as Niax LA-475 or LA-700, all of which are available from Union Carbide. As one skilled in the art would know, there are no free amino hydrogens in any of these com- 5 pounds.

The hydroxyl bearing homopolymers of dienes or hydroxyl bearing copolymers of dienes are prepared from dienes which include unsubstituted 2-substituted or 2,3-disubstituted 1,3-dienes of up to about 12 carbon 10 atoms. Preferably, the diene has up to about 6 carbon atoms and the substituents in the 2- and/or 3-position may be hydrogen, alkyl groups having about 1 to about 4 carbon atoms, substituted aryl, unsubstituted aryl, halogen, and the like. Typical of such dienes are 1,3-15 butadiene, isoprene, chloroprene, 2-cyano-1,3-butadiene, 2,3-dimethyl-1,2-butadiene, and the like. The preferred dienes are 1,3-butadiene and isoprene. A hydroxyl terminated polybutadiene is available from ARCO Chemicals under the designation Poly-BD R- 20 45HT. Specifically, Poly-BD R-45HT has a molecular weight of about 2800, a degree of polymerization of 50, a hydroxyl functionality of about 2.4 to 2.6, a hydroxyl number of 46.6, a hydroxyl value of 0.83, and an iodine number of 398.

A wide variety of aromatic and aliphatic diamines may form part of the amine-based polyols, such as N,Nbis(2-hydroxypropyl)aniline and N,N,N',N'-tetrakis(2hydroxypropyl)ethylenediamine. A typical aminebased polyol is available from Upjohn under the desig- 30 nation Isonol 100, an amber colored liquid polyol having a molecular weight of 209, a hydroxyl number of 534, an equivalent weight of 104.5, an average functionality of 2.0 and a viscosity of 1450 at 50° C. A typical aliphatic amine-based polyol is available from BASF 35 lated from equation 28 as follows: under the designation Quadrol, a viscous liquid polyol with four hydroxyl groups, two tertiary nitrogen atoms, a hydroxyl number of 770 and a viscosity of 53,000 cps at 25° C.

Polymeric polyols can be described as conventional 40 polyols with a stable dispersion of vinyl polymers. For example, U.S. Pat. No. 4,104,236 discloses such polyols with acrylonitrile-styrene polymers; a further typical polyol is available from Union Carbide under the designation Niax 24-32. Specifically, Nias 24-32, a copolymer 45 of a conventional polyol and a vinyl monomer, has an average hydroxyl number of 32 and a viscosity of 1300 centipoise at 25° C.

The plasticizer compounds which can be used in this invention include any compound or mixture of com- 50 pounds having a total solubility parameter of [between about 8.3 and 8.9 or between about 9.1 and 9.7. Compounds having solubility parameters higher than [9.7] 10.1 are too volatile for use in gel formulations [, while compatible with the polyurethane reaction product.

Suitable plasticizer components are esters such as the phthalates or adipates having between about 4 and 13 carbon atoms, since these compounds possess solubility parameters falling within the above-described critical 60 ranges. Certain synthetic ricinoleate compounds, such as glyceryl tri (acetyl ricinoleate) and similar compounds which have solubility parameters within the above-disclosed ranges, are also useful and, in most cases, preferred due to their greater compatibility with 65 a wide range of cable fillers or greases which are typically encountered in the reclamation or encapsulation of telecommunication or electrical cable.

Specific preferred compounds which can be used as plasticizers in accordance with the invention are listed below in Table I.

TABLE I

PLASTICIZER C	PLASTICIZER COMPOUNDS	
Compound	Solubility Parameter	
[soybean oil]	[8.3]	
[ditridecyl adipate]	[8.9]	
diundecyl phthalate	9.12	9.4
diisodecyl phthalate	[9.15]	9.5
glyceryl tri(acetylrieinoleate)	9.3	
dibutyl phthalate	[9.7]	10.1

The specific solubility parameter ranges have been determined by weight gain and conductor pull out tests as shown by the examples. Specifically, compounds having a total solubility parameter which results in a weight loss or in which a conductor cable can be easily pulled out are not satisfactory for use in this invention.

Also, one or more of the above-identified plasticizers can be used in combination without departing from the teachings of the invention provided that the overall solubility remains in the critical range.

The solubility parameters of the plasticizer compounds are determined as described in the article entitled "A method for Estimating Both the Solubility Patameters and Molar Volumes of Liquids," by R. F. Fedors, POLYMER ENGINEERING SCIENCE, Vol. 14, No. 2, February, 1974, pp. 147-154. This article is expressly incorporated by reference in this application.

As noted in the above-mentioned article, the total solubility parameter for a liquid at 25° C. can be calcu-

$$\gamma = \sqrt{\frac{\sum_{i} \Delta e_{i} / \sum_{i} \Delta v_{i}}{\sum_{i} \Delta v_{i}}}$$

wherein e_i and v_i are the additive atomic and group contribution for the energy of vaporization and molar volume, respectively. Based upon a vast amount of data on simple liquids, these contributions applicable at a temperature of 25° C. have been compiled in Table 5 of the article. Thus, in order to calculate the total solubility parameter for any liquid compound, all one needs to know is the chemical structure of the compound. Therefore, the term "total solubility parameter" as used in this application is intended to mean the solubility parameter of the compound at 25° C., which is calculated from the experimental energy of vaporization and molar volume values given in Table 5 of the Fedors article. The values which appear in Table 1 of this applithose having solubility parameters less than 8.3 are not 55 cation are the total solubility parameter for those compounds calculated in the manner previously described.

With respect to the weight change testing, there are different types of greases which may be encountered in telecommunications cable. The most common is FLEX-GEL cable filler and FLEXGEL is a registered trademark of the Western Electric Co. Inc. for their cable filling compounds for waterproofing electrical cable. Other cables may contain petroleum jelly (PJ) or polyethylene modified petroleum jelly (PEPJ). PEPJ is a higher melting point material than (PJ). It should be noted that the ricinoleates have a wider range of compatibility with all types of cable fillers than the other plasticizer compounds.

With respect to the use of these plasticizer compounds in the formulations of the present invention, it should be noted that those compounds having a solubility parameter between about 9.1 to 9.7 provide clear and transparent gels which are preferred for applica- 5 tions where reenterability is of primary importance. [Those compounds having solubility parameters between about 8.3 and 8.9 do impart a degree of opaqueness to the resulting gel with the lower values generally provide a higher degree of cloudiness or opaqueness in 10 the gel. However, all All the polyurethane gels according to this invention are soft with a low tear strength, and these properties are maintained over time to provide desirable reenterable compounds.

It should further be noted that all the suitable plasti- 15 cizer components according to the invention are low viscosity liquids at room temperature.

The polyurethane gels of the present invention are generally comprised of about 10 to 90 parts by weight of polyurethane, and correspondingly, about 90 to 10 20 parts by weight of plasticize. If amounts less than 10 parts of polyurethane are used, the resulting gel will have essentially no tear strength at all, while if less than 10 parts of plasticizer is used, the resulting formulation will not provide the improved properties. The preferred concentration with particular reference to the reclaiming or encapsulating utility comprises about 30 to 40 parts by weight of polyurethane reaction product, about 70 to 60 parts by weight of plasticizer.

If higher solids content grease compatible formulations are desired, the relative proportions would be about 90 to 50 parts by weight of polyurethane and about 10 to 50 parts by weight of plasticizer.

the present invention, finely divided solid fillers which are commonly employed in the art as either reinforcing or inert fillers may be utilized. The use of such solid fillers applies mainly to non-reenterable polyurethanes. Conventional fillers include carbon black, asphaltenes, 40 silica, silica-alumina, hydrated silica, zinc oxide, magnesium carbonates, clays, talc, and pulverized reclaimed rubber as well as various mineral fillers which are known in the art. Solid fillers may be employed in the amount of up to about 50 weight percent of the polyure- 45

The present formulations are preferably prepared at the application site by admixing the resin system with the hardener system. Depending on the desired utility, the resin and hardener are utilized in amounts meeting 50 the stoichiometric requirements. The resin component comprises the polyisocyanate or polyurethane prepolymer, and, all or a portion of the plasticizer. The hardener component comprises the polyol, and where applicable, the remaining portion of the plasticizer. The 55 catalyst and optional additives such as fungicides, pigments, anti-oxidants, moisture scavengers, and the like, are generally added to the hardener component. Catalysts are known to those skilled in the art and may comprise, for example, heavy metals utilized in amounts of 60 about 0.1 weight percent of the hardener component.

As noted, the polyurethane gels of the present invention possess the desired properties for a range of utilities, with primary emphasis on utilities such as reenterable encapsulants and reclamants for insulated electrical 65 devices. Initially, these materials are sufficiently fluid to be introduced into the core of a cable or mold surrounding a portion of the cable and to retain their fluidity for

a period of time sufficient to fill all the interior free

The term "reclamation" is used to include the situation wherein the polyurethane gel compositions of the invention are injected into damaged telecommunication or electrical cable to displace any fluid contaminants and restore the cable to its initial condition. As the gel cures, it expands and displaces the contaminants in the damaged cable.

The term "encapsulation" refers to the use of the polyurethane gels of the invention to seal a splice or connection to a cable. In this arrangement, the electrical connections are made to an existing cable, closure of polyethylene or similar material is made around the connection, and the gel composition is injected into the space between the closure and cable, where it expands and cures to form a moisture resistant seal.

In its reclaiming function, the polyurethane will thus displace the liquid penetrants from the free spaces within the cable. In the encapsulation utility, a sheath of polyethylene or other suitable material is placed around a repaired area of the cable. The polyurethane is then placed within the sheath, which acts as a mold for the final outer dimensions of the gel. Thereafter, for either application, a stable gel forms within a resonable period of time to provide a seal against penetration of water and other fluid materials or contaminants.

Where reentrability is desired, the selected polyure-30 thane provides a gel which is sufficiently soft so as to be readily removed. The insulating properties of these reenterable encapsulant and reclamant compositions are highly improved, particularly with regard to the dissipation factor and volume resistivity of the material. In accordance with the plasticized polyurethanes of 35 Furthermore, there is no exudation of components used and there is excellent compatibility with materials employed in the cable construction and with polycarbonate connectors. In addition, the instant plasticized polyurethanes can be utilized as hard volume (permanent) encapsulants and for general polyurethane elastomeric

EXAMPLES

The scope of the invention is further described in connection with the following examples which are set forth for the sole purpose of illustrating the preferred embodiments of the invention and which are not to be construed as limiting the scope of the invention in any manner. In these examples, all parts given are by weight unless otherwise specified.

EXAMPLE 1

The following formulations illustrate typical plasticizer/polyurethane gel systems of the invention which are intended for use as reenterable reclamants or encapsulants.

Resin system	A	В	С	D
polymethylene polyphenyl isocyanate ¹	23.8	23.8	23.8	3.0
castor oil ²	2.3	_	2.3	1.8
diundecyl phthalate	12.9	76.2	_	45.2
ditridecyl adipate	_	-	12.9	_
Hardener system	E	F	G	Н
hydroxyl terminated polybutadiene ³	32.0	32.0	32.0	13.4
castor oil	2.9	5.8	2.9	1.8

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	-continue	ed		
diundecyl phthalate	65.1	62.2	65.1	34.8

PAPI 901 from Upjohn ²DB Oil from CasChem. Inc.

³Poly-BD R45-HT from Arco Chemicals

The following polyurethane gels were then prepared by mixing Resin Systems A,B,C, and W with Hardener Systems E,F,G, and H, respectively. After curing, each of these formulations were found to be soft, clear gels 10 which are eminently suitable for use in applications such as the reclamation or encapsulation of telecommunication cable, when a reenterable formulation is desirable.

EXAMPLE 2

The following formulations were then prepared by mixing the following components together and allowing the mixture to cure.

	ī	J	K
polymethylene polyphenyl	5.0	5.5	4.3
socyanate astor oil ²	_	5.3	_
nydroxyl terminated solybutadiene ³	45.0	29.2	_
ditridecyl adipate	50.0	_	_
diisodecyl phthalate	-	60.0	65.0
polyoxypropylene diol ⁴	_		30.7

PAPI 901 from Upjohn ²DB Oil from CasChem. Inc.

³Poly-BD R45-HT from Arco Chemicals ⁴PPG-2025 from Union Carbide

These formulations were also found to be soft, clear, gels, which also would be suitable for reenterable repair 35 applications.

EXAMPLE 3 The following polymer system was prepared:

Component	Parts
polymethylene polynhenyl isocyanate ¹	13.6
polymethylene polyphenyl isocyanate ¹ castor oil ²	13.3
hydroxyl terminated polybutadiene ³	73.1

PAPI 901 from Upjohn

²DB Oil from CasChem. Inc ³Poly-BD R45-HT from Arco Chemicals

Then, 65 parts of this polymer system was mixed with 35 parts of the following plasticizers to prepare the 50 designated polyurethane formulations.

	Plasticizer	Formulation
	ditridecyl adipate	L
	dioctyl adipate	M
	diundecyl phthalate	N
6:7	mixture of dioctyl	0
3	adipate: mineral oil	
2:1	mixture of diisodecyl	P
	phthalate: mineral oil	

Dioctyl adipate has a total solubility parameter of [9.05] 8.91, which is outside the scope of the invention. Thus it was used in formulation M as a comparative example. The mineral oil extenders of formulations 65 [S and T] O and P were also used to illustrate comparative examples of plasticizer materials which are outside of the scope of the invention.

To determine the suitability of the above formulations for grease compatibility, the formulations were cured on FLEXGEL cable filler and, after curing, the weight change of the formulation was measured. Compatible formulations show a weight gain, which indicates that the grease is taken into the formulation.

Alternately, incompatible formulations show a weight loss which indicates an exudation or separation of the extruder or plasticizer from the gel. Test results are shown below in Table 2.

As a further measure of grease compatibility, an electrical conductor was coated with FLEXGEL cable filler and encapsulated with the above formulations. After the formulations cured, the conductor was pulled out of the polyurethane. The force necessary to separate the conductor from the polyurethane was measured and is also listed below in Table 2.

TABLE 2

Test Results				
Formulation	% Weight Change	Pullout Force (Lbs)		
L	+0.4	4.5		
M	— i .1	4.1		
N	+0.6	6.3		
Ö	-5.0	1.8		
P	-4.5	2.0		
	L M N O	## Formulation Weight Change L		

It is evident from the preceding table that plasticizers 30 having a total solubility parameter between about 9.1 and 9.7 [or between about 8.3 and 8.9] are grease compatible, whereas compounds having other solubility parameters are not.

EXAMPLE 4

The following formulation was prepared:

Component	Parts
polymethylene polyphenylisocyanate ¹ castor oil ²	4.8 4.6
hydroxyl terminated polybutadiene ³	25.6
glyceryl tri(acetyl ricinoleate)	65

PAPI 901 from Upjohn

²DB Oil from CasChem. Inc. 45 3Poly-BD R45-HT from Arco Chemicals

> This formulation was then tested for weight change and conductor pullout as described above. The results were:

% Weight change on	% Weight change on various cable fillers:		
FLEXGEL	+5.5		
PEPJ	+1.6		
ΡJ	+0.5		
Coated Conductor	pull out: 7.0 lbs		

This shows that the recinoleate plasticizer imparts the highest degree of compatibility with a variety of com-60 monly encountered cable fillers or greases to the formulation. Other ricinoleates having total solubility parameters within the above disclosed ranges should also perform similarly.

While it is apparent that the invention herein disclosed is well calculated to fulfill the objects above stated, it will be appreciated that numerous modifications and embodiments may be devised by those skilled in the art, and it is intended that the appended claims cover all such modifications and embodiments as fall within the true spirit and scope of the present invention.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

- 1. A polyurethane gel composition comprising about 5 10 to 90 parts by weight of the liquid reaction product of an organic polyisocyanate and a polyol having an equivalent weight above 250 in the presence of about 90 to 10 parts by weight of an ester plasticizer compound having a total solubility parameter of [between about 10 8.3 and 8.9] or between about 9.1 and 9.7.
- 2. The composition of claim 1 wherein the liquid reaction product comprises about 30 to 40 parts by weight, and the plasticizer compound comprises about 70 to 60 parts by weight.
- 3. The composition of claim 1 wherein said isocvanate compound is selected from the group consisting of aliphatic, cycloaliphatic, and aromatic polyisocyanates.
- 4. The composition of claim 3 wherein said isocyanate compound is polymethylene polyphenylisocyanate 20 or methylene diisocyanate.
- 5. The composition of claim 1 wherein said organic polyisocyanate is a polyisocyanate prepolymer prepared by reacting an excess of a polyisocyanate compound with a polyol.
- 6. The composition of claim 1 wherein said polyol is selected from the group consisting of castor oil, polyether polyols, hydroxyl-bearing homopolymers of dienes, hydroxyl-bearing copolymers of dienes, amine
- 7. The composition of claim 6 wherein said polyol is a hydroxyl terminated polybutadiene.
- 8. The composition [of] according to claim 1 wherein said [ester] plasticizer [compound] is [diphthalate[, or dibutyl phthalate].
- 9. A polyurethane gel composition comprising about 30 to 40 parts by weight of the liquid reaction product of an organic polyisocyanate compound and a polyol having an equivalent weight above 250 in the presence 40 about 9.1 and 9.7. of about 70 to 60 parts by weight of an ester plasticizer

compound having a total solubility parameter of [between about 8.3 to 8.9 or between about 9.1 and 9.7.

- 10. A polyurethane gel composition comprising the liquid reaction product of about 10 to 50 parts by weight of a polyisocyanate prepolymer and a polyol having an equivalent weight above 250 in the presence of about 90 to 50 parts by weight of an ester plasticizer compound having a total solubility parameter of [between about 8.3 and 8.9 or between 9.1 to 9.7.
- 11. The gel composition of claim 10 wherein the liquid reaction product is present in the range of from about 30 to 40 parts by weight and the ester plasticizer compound is selected from the group [ditridecyl adipate, diundecyl [,] phthalate, diisodecyl phthalate, or dibutyl phthalate and is present in a range of about 70 to 60 parts by weight.
- 12. A polyurethane composition comprising about 50 to 90 parts of the liquid reaction product of an organic polyisocyanate and a polyol having an equivalent weight about 250 in the presence of about 50 to 10 parts of an ester plasticizer compound having a total solubility parameter of [between about 8.3 and 8.9 or] between about 9.1 and 9.7.
- 13. The composition [of] according to claim 12 wherein said plasticizer is [ditridecyl adipate,] diundecyl phthalate, or diisodecyl phthalate , or dibutyl phthalate].
- 14. A polyurethane gel composition comprising about 10 based polyols, polymeric polyols, and mixtures thereof. 30 to 90 parts by weight of the liquid reaction product of an organic polyisocyanate and a polyol having an equivalent weight above 250 in the presence of about 90 to 10 parts by weight of ditridecyl adipate on dibutyl phthalate.
- 15. A polyurethane gel composition comprising about 10 tridecyl adipate, diundecyl phthalate, or diisodecyl 35 to 90 parts by weight of the liquid reaction product of an organic polyisocyanate and a polyol having an equivalent weight above 250 in the presence of about 90 to 10 parts by weight of a mixture of ester plasticizer compounds, said mixture having a total solubility parameter of between

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