PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{7} :
C09K 3/10, C08G 18/10

A1

(11) International Publication Number: **WO 00/46320**

(43) International Publication Date: 10 August 2000 (10.08.00)

(21) International Application Number: PCT/US00/03055

(22) International Filing Date: 4 February 2000 (04.02.00)

(30) Priority Data:
60/118,849 5 February 1999 (05.02.99) US

(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US).

(72) Inventor: WU, Ziyan; 30811 Sudbury Court, Farmington Hills, MI 48331 (US).

(74) Agent: SIMS, Norman, L.; Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: POLYURETHANE SEALANT COMPOSITIONS

(57) Abstract

In one aspect, this invention was a polyurethane sealant composition comprising (1) a urethane prepolymer having an isocyanate fuNctionality of at least 2.0 and a weight average molecular weight of at least 2,000; (2) a catalytic amount of a tin compound which catalyzes the reaction of isocyanate moieties with water or an active hydrogen containing compound; and (3) a stabilizing amount of an organophosphite which has an alkaryl ligand or both an aliphatic ligand and an aromatic ligand. The prepolymer may further comprise silane functionality or the composition may further comprise a compound or polymer which contains silane moieties and was compatible with the polyurethane prepolymer. The invention was also a method for bonding glass to a substrate which comprises contacting a sealant according to the invention with glass and another substrate with the sealant disposed between the glass and substrate and thereafter allowing the sealant to cure so as to bond the glass to the substrate.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

POLYURETHANE SEALANT COMPOSITIONS

This invention relates to polyurethane sealant compositions which were capable of being used without the need for a primer.

Polyurethane sealant compositions typically comprise at least one urethane prepolymer. Sealants useful for bonding to non-porous substrates, such as glass were described, for example, in U.S. Patent 4,374,237 and U.S. Patent 4,687,533, both. U.S. Patent 4,374,237 describes a polyurethane sealant containing urethane prepolymers which have been further reacted with secondary amine compounds containing two silane groups. U.S. Patent 4,687,533 describes a polyurethane sealant containing urethane prepolymers which contain silane groups which have been prepared by reacting a polyisocyanate having at least three isocyanate groups with less than an equivalent amount of an alkoxysilane having a terminal group containing active hydrogen atoms reactive with isocyanate groups to form an isocyanatosilane having at least two unreacted isocyanate groups. In a second step, the isocyanatosilane was mixed with additional polyisocyanate and the mixture was reacted with a polyol to form a polyurethane prepolymer having terminal isocyanato groups and pendant alkoxysilane groups.

However, when such sealants were used to bond glass substrates to painted substrates, such as for window installation in vehicle manufacturing, the lap shear strength of the bonded substrate may be less than desirable for safety or structural purposes. Consequently, a separate paint primer comprising a solution of one or more silanes was typically applied to a painted substrate prior to the application of the sealant in most vehicle assembly operations for bonding the windshield and the rear window. The use of a primer in assembly operations was undesirable in that it introduces an extra step, additional cost, the risk of marring the paint surface if dripped on an undesired location and exposes the assembly line operators to additional chemicals. It would be desirable to provide a polyurethane sealant which, when bonded to a painted substrate and cured, provides a bonded substrate with a higher lap shear strength, particularly when used in the absence of a paint primer.

In one aspect, this invention was a polyurethane sealant composition comprising

(1) a urethane prepolymer having an isocyanate functionality of at least 2.0 and a weight average molecular weight of at least 2,000;

(2) a catalytic amount of a tin compound which catalyzes the reaction of isocyanate moieties and water or an active hydrogen containing compound; and

(3) a stabilizing amount of an organophosphite which has an alkaryl ligand or both an aliphatic ligand and an aromatic ligand.

In a preferred embodiment the prepolymer further comprises silane functionality or the composition further comprises a compound or polymer which contains silane moieties and was compatible with the polyurethane prepolymer.

In another embodiment the invention was a method for bonding glass to a substrate which comprises contacting a sealant according to the invention with glass and another substrate with the sealant disposed between the glass and substrate and thereafter allowing the sealant to cure so as to bond the glass to the substrate.

The sealant composition of the invention was useful in bonding glass substrates to plastic, metal, fiberglass and composite substrates which may or may not be painted. The sealant composition gives unexpectedly high lap shear strength when no primer compositions have previously been applied to a painted plastic, metal, fiberglass or composite substrate. The adhesive compositions of the invention bond to acid resistant coating systems without the need for primers, achieve faster link-up in low temperature conditions and maintain adhesion when exposed to weathering conditions.

The prepolymers used in the invention can be conventional prepolymers used in polyurethane adhesive compositions. In a preferred embodiment the prepolymers were blended with a compound or polymer having silane functionality. In another preferred embodiment the prepolymer contains silane functionality as well as isocyanate functionality. A urethane prepolymer having silane functionality may be the entire prepolymer used in the adhesive or it may be blended with a prepolymer which does not have silane functionality.

Preferable urethane prepolymers for use in preparing the composition of the invention include any compound having an average isocyanate functionality of at least 2.0 and a molecular weight of at least 2,000. Preferably, the average isocyanate functionality of the prepolymer was at least 2.2, and was more preferably at least 2.4. Preferably the isocyanate functionality was no greater than 4.0, more preferably, no greater than 3.5 and most preferably, no greater than 3.0. Preferably, the weight average molecular weight of the prepolymer was at least 2,500, and was more preferably at least 3,000; and was preferably no greater than 40,000, even more preferably no greater than 20,000, more preferably, no greater than 15,000 and was most preferably no greater than 10,000. The prepolymer may be prepared by any suitable method, such as by reacting an isocyanate-reactive compound containing at least two isocyanate-reactive groups with an excess over stoichiometry of a polyisocyanate under reaction conditions sufficient to form the corresponding prepolymer.

Suitable polyisocyanates for use in preparing the prepolymer include any aliphatic, cycloaliphatic, araliphatic, heterocyclic or aromatic polyisocyanate, or mixture thereof. Preferably the polyisocyanates used have an average isocyanate functionality of at least 2.0 and an equivalent weight of at least 80. Preferably, the isocyanate functionality of the polyisocyanate was at least 2.0, more preferably at least 2.2, and was most preferably at least 2.4; and was preferably no greater than 4.0, more preferably no greater than 3.5, and was most preferably no greater than 3.0. Higher functionality may also be used, but may cause excessive cross-linking, and result in an adhesive which was too viscous to handle and apply easily, and can cause the cured adhesive to be too brittle. Preferably, the equivalent weight of the polyisocyanate was at least 100, more preferably at least 110, and was most preferably at least 120; and was preferably no greater than 300, more preferably no greater than 250, and was most preferably no greater than 200.

Examples of useful polyisocyanates include ethylene diisocyanate, isophorone diisocyanate, bis(4-isocyanate cyclohexyl) methane, trimethyl hexamethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane1,3- and 1,4-diisocyanate and mixtures of these isomers; 1-isocyanato3,3,5-trimethyl5-isocyanato methyl cyclohexane (see for example, German Auslegeschrift No. 1,202,785); 2,4- and 2,6-hexahydrotolylene diisocyanate and mixtures of these isomers, hexahydro1,3- and/or 1,4-phenylene diisocyanate, perhydro2,5'- and/or 4,4'-diphenyl methane diisocyanate, 1,3- and 1,4-phenylene diisocyanate, 2,4'- and 2,6-tolylene diisocyanate and mixtures of these isomers, diphenylmethane2,4'- and/or 4,4'-diisocyanate, naphthylene1,5-diisocyanate, triphenylmethane4,4',4"-triisocyanate, tetramethylxylene diisocyanates, polymeric derivatives of the previously described isocyanates, polyphenyl polymethylene polyisocyanates of the type obtained by condensing aniline with formaldehyde, followed by phosgenation and such as described, for example, in British Patents 874,430 and 848,671, perchlorinated aryl polyisocyanates of the type described in German Auslegeschrift 1,157,601, polyisocyanates containing carbodiimide groups of the type described in German

Patent 1,092,007, diisocyanates of the type described in U.S. Patent 3,492,330, polyisocyanates containing allophanate groups of the type described, for example, in British Patent 994,890, in Belgian Patent 761,626 and in published Dutch Patent Application No. 7,102,524, polyisocyanates containing isocyanurate groups of the type described in German Patents 1,022,789, 1,222,067 and 1,027,394 and in German Offenlegungsschrift 1,929,034 and 2,004,048, polyisocyanates containing urethane groups of the type described, for example, in Belgian Patent 752,261 or in U.S. Patent 3,394,164, polyisocyanates containing acrylated urea groups as described in German Patent 1,230,778, polyisocyanates containing biuret groups of the type described, for example, in German Patent 1,101,392, in British Patent 889,050 and in French Patent 7,017,514, polyisocyanates obtained by telomerization reactions of the type described, for example, in Belgian Patent 723,640, polyisocyanates containing ester groups of the type described, for example, in British Patents 965,474 and 1,072,956, in U.S. Patent 3,567,763 and in German Patent 1,231,688 and reaction products of the aforementioned isocyanates with acetals as described in German Patent 1,072,385. Preferred isocyanates were aromatic isocyanates. More preferred polyisocyanates include diphenylmethane-4,4'-diisocyanate and polymeric derivatives thereof, isophorone diisocyanate, tetramethylxylene diisocyanate,1,6-hexamethylene diisocyante and polymeric derivatives thereof, bis(4-isocyanatocylohexyl)methane, and trimethyl hexamethylene diisocyanate. The most preferred isocyanate is diphenyl methane diisocyanate.

The term “isocyanate-reactive compound” as used herein includes any organic compound having at least two isocyanate-reactive moieties, such as a compound containing an active hydrogen moiety, or an iminofunctional compound. For the purposes of this invention, an active hydrogen containing moiety refers to a moiety containing a hydrogen atom which, because of its position in the molecule, displays significant activity according to the Zerewitnoff test described by Wohler in the Journal of the American Chemical Society, Vol. 49, p. 3181 (1927). Illustrative of such active hydrogen moieties were -COOH, -OH, -NH_2, -NH-, -$CONH_2$, -SH, and -CONH-. Preferable active hydrogen containing compounds include polyols, polyamines, polymercaptans and polyacids. Suitable imino-functional compounds were those which have at least one terminal imino group per molecule, such as were described, for example, in U.S. Patent 4,910,279, which was hereby incorporated by reference in its entirety. Preferably, the isocyanate-reactive compound was a polyol, and was more preferably a polyether polyol.

Suitable polyols useful in the preparation of the prepolymers include, for example, polyether polyols, polyester polyols, poly(alkylene carbonate)polyols, hydroxyl--containing polythioethers, polymer polyols, and mixtures thereof. Polyether polyols were well-known in the art and include, for example, polyoxyethylene, polyoxypropylene, polyoxybutylene, and polytetramethylene ether diols and triols which were prepared by reacting an unsubstituted or halogen- or aromatic-substituted ethylene oxide or propylene oxide with an initiator compound containing two or more active hydrogen groups such as water, ammonia, a polyalcohol, or an amine. Such methods were described, for example, in U.S. Patents 4,269,945; 4,218,543; and 4,374,210; which were hereby incorporated by reference in their entirety. In general, polyether polyols may be prepared by polymerizing alkylene oxides in the presence of an active hydrogen-containing initiator compound. Most preferred, however, were ethylene oxide-capped polyols prepared by reacting glycerin with propylene oxide, followed by reacting with ethylene oxide.

Suitable alkylene oxides include ethylene oxide, propylene oxide, butylene oxides, styrene oxide, epichlorohydrin, epibromohydrin, and mixtures thereof. Suitable initiator compounds include water, ethylene glycol, propylene glycol, butanediol, hexanediol, glycerin, trimethylol propane, pentaerythritol, hexanetriol, sorbitol, sucrose, hydroquinone, resorcinol, catechol, bisphenyls, novolac resins, phosphoric acid, amines, and mixtures thereof.

Polyester polyols were also well-known in the art and may be prepared by reacting a polycarboxylic acid or anhydride thereof with a polyhydric alcohol. Examples of suitable polycarboxylic acids include succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, maleic acid, trimellitic acid, phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, tetrachlorophthalic acid anhydride, endomethylene tetrahydrophthalic acid anhydride, maleic acid anhydride, glutaric acid anhydride, fumaric acid, an mixtures thereof. Examples of suitable polyhydric alcohols include ethylene glycols, propane diols, butane diols, 1,6-hexanediol, 1,8-octanediol, neopentylglycol, glycerol, trimethylol propane, pentaerythritol, quinitol, mannitol, sorbitol, methyl glycoside, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols, polypropylene glycols, and mixtures thereof.

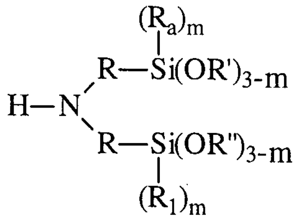
Suitable polymer polyols include dispersions of polymers of vinyl monomers in a continuous polyol phase, particularly dispersions of styrene/acrylonitrile copolymers. Also useful were the so-called polyisocyanate polyaddition (PIPA) polyols (dispersions of polyurea-polyurethane particles in a polyol) and the polyurea dispersions in polyols (PHD polyols). Copolymer polyols of the vinyl type were described, for example, in U.S. Patent Nos. 4,390,645, 4,463,107, 4,148,840 and 4,574,137, all incorporated by reference.

Preferably, the isocyanate-reactive compound has a functionality of at least 1.5, more preferably at least 1.8, and was most preferably at least 2.0; and was preferably no greater than 4.0, more preferably no greater than 3.5, and was most preferably no greater than 3.0. Preferably, the equivalent weight of the isocyanate-reactive compound was at least 200, more preferably at least 500, and was more preferably at least 1,000; and was preferably no greater than 5,000, more preferably no greater than 3,000, and was most preferably no greater than 2,500.

The prepolymer may be prepared by any suitable method, such as bulk polymerization and solution polymerization. The reaction to prepare the prepolymer was carried out under anhydrous conditions, preferably under an inert atmosphere such as a nitrogen blanket, to prevent cross-linking of the isocyanate groups by atmospheric moisture. The reaction was preferably carried out at a temperature between 0°C and 150°C, more preferably between 25°C and 80°C, until the residual isocyanate content determined by titration of a sample was very close to the desired theoretical value. The isocyanate content in the prepolymers was preferably in the range of 0.1 percent to 10 percent, more preferably in the range of 1.5 percent to 5.0 percent and most preferably in the range of 1.8 percent to 3.0 percent.

The prepolymer was present in the sealant composition in sufficient amount such that the sealant was capable of bonding glass to metal, plastic, fiberglass or composite substrates, preferably the substrates were painted and more preferably the substrates were painted with acid resistant paints. Preferably the polyurethane prepolymer was present in an amount of 30 percent by weight or greater based on the weight of the sealant, more preferably 50 percent by weight or greater and most preferably 65 percent by weight or greater. Preferably the polyurethane prepolymer was present in an amount of 99.8 percent by weight or less based on the weight of the sealant, more preferably 98 percent by weight or less and most preferably 85 percent by weight or less.

In those embodiments where the sealant was used to bond glass to substrates coated with acid resistant paints it was desirable to have a silane present in some form. The silane may be blended with the prepolymer. In another embodiment the silane was a silane which has an active hydrogen atom which was reactive with an isocyanate. Preferably such silane was a mercapto-silane or an amino-silane and more preferably was a mercapto-trialkoxy-silane or an amino-trialkoxy silane. In one embodiment, the silane having, an active hydrogen atom reactive with isocyanate moieties, can be reacted with the terminal isocyanate moieties of the prepolymer. Such reaction products were disclosed in U.S. Patent 4,374,237 and 4,345,053 relevant parts. In yet another embodiment, the silane having a reactive hydrogen moiety reactive with an isocyanate moiety can be reacted into the backbone of the prepolymer by reacting such silane with the starting materials during the preparation of the prepolymer . The process for the preparation of prepolymers containing silane in the backbone was disclosed in U.S. Patent 4,625,012, relevant portions. Such silane, having active hydrogen moieties, can be reacted with a polyisocyanate to form an adduct which was blended with the prepolymer reacted with a polyurethane prepolymer or reacted with a polyisocyanate and a compound having on average more than one moiety reactive with an isocyanate moiety. Preferably the adduct was a reaction product of a secondary amino- or mercapto-alkoxy silane and a polyisocyanate, the adduct having an average of at least one silane group and at least one isocyanate group per molecule (hereinafter "adduct"). Preferably the adduct has at least 1.5 isocyanate groups and at least one silane group per molecule, and most preferably has at least two isocyanate groups and at least one silane group per molecule. The adduct level in the sealant compositions was preferably in the range of 0.5 percent to 20 percent, more preferably in the range of 1.0 percent to 10 percent and most preferably in the range of 2.0 percent to 7 percent. The adduct may be prepared by any suitable method, such as, for example, by reacting an secondary amino- or mercapto-alkoxy silane with a polyisocyanate compound. Suitable polyisocyanates for use in preparing the adduct include those described above as suitable for use in preparing the prepolymer, particularly including isopherone diisocyanate, polymethylene polyphenylisocyanates, and aliphatic polyisocyanates such as hexamethylene diisocyanate. Preferably, the polyisocyanate was an aliphatic polyisocyanate and was most preferably an aliphatic polyisocyanate based on hexamethylene diisocyante with an equivalent weight of 195. The polyisocyanate used to prepare the isocyanate silane adduct preferably has a molecular weight of less than 2,000, more preferably less than 1,000. Suitable organofunctional silanes include amino- or mercapto-alkoxysilanes of the formula:



$$HS—R—Si(R_1)_m(OR')_{(3-m)}$$

wherein R is a divalent organic group, preferably C_{1-4} alkylene, R', R", R_1 and Ra were hydrogen or alkyl, preferably C_{1-4} alkyl, m is an integer from 0 to 2. Examples of such compounds include: N,N-bis[(3-triethoxysilyl)propyl]amine; N,N-bis[(3-tripropoxysilyl)propyl]amine; N-(3-trimethoxysilyl)propyl-3-[N-(3-trimethoxysilyl)-propylamino]propionamide; N-(3-triethoxysilyl)propyl-3-[N-3-triethoxysilyl)-propylamino]propionamide; N-(3-trimethoxysilyl)propyl-3-[N-3-triethoxysilyl)-propylamino]propionamide; 3-trimethoxysilylpropyl 3-[N-(3-trimethoxysilyl)-propylamino]-2--methyl propionate; 3-triethoxysilylpropyl 3-[N-(3-triethoxysilyl)-propylamino]-2-methyl propionate; 3-trimethoxysilylpropyl 3-[N-(3-triethoxysilyl)propylamino]-2-methyl propionate. Preferably the organofunctional silane was gamma-mercaptopropyl-trimethoxysilane (available as A189 from Union Carbide) or N,N'-bwas((3-trimethoxysilyl)propyl)amine.

In preparing the adduct, the silane and the polyisocyanate reactants were preferably combined so that the ratio of isocyanate groups to secondary amine or mercapto groups in the reaction mixture to prepare the adduct was at least 1.5, more preferably at least 2.0, and most preferably at least 2.5; and was preferably no greater than 6.0, more preferably no greater than 5.5, and most preferably no greater than 5.0. The adduct may be prepared by any suitable method, such as bulk or solution polymerization. The reaction between the polyisocyanate and the organofunctional silane was preferably carried out under anhydrous conditions, preferably under an inert atmosphere such as a nitrogen blanket, to prevent premature hydrolysis of the alkoxysilane groups and/or cross-linking of the isocyanate groups by atmospheric moisture. The polyisocyanate and alkoxysilane were preferably reacted under anhydrous conditions at a temperature between room temperature (20°C) and 80°C. Depending on the reagents, an exotherm may develop so that no external heating was required. Indeed, cooling may be necessary. The reaction was generally complete within two hours and may be catalyzed with a tin catalyst, suitably a tin salt such as a tin carboxylate, if desired. The reaction was suitably carried out in heat or in an inert liquid diluent or carrier. While any of the conventional inert organic solvents such as the benzene, toluene, xylene and other hydrocarbons or halohydrocarbons can be employed, it was preferable to use a compound having plasticizing properties, since the use of a plasticizer avoids the need for isolating the active reaction products from the reaction mixtures.

The reactions to prepare the prepolymer and the adduct may be carried out in the presence of urethane catalysts. Examples of such include the stannous salts of carboxylic acids, such as stannous octoate, stannous oleate, stannous acetate, and stannous laurate. Also, dialkyltin dicarboxylates such as dibutyltin dilaurate and dibutyltin diacetate were known in the art as urethane catalysts, as were tertiary amines and tin mercaptides. Preferably, the reaction to prepare the prepolymer was catalyzed by stannous octoate. The amount of catalyst employed was generally between 0.005 and 5 percent by weight of the mixture catalyzed, depending on the nature of the isocyanate.

The amount of silane present was that amount which enhances the adhesion of the adhesive to the painted surface without the need for a primer. The amount of silane present was preferably, 0.1 percent by weight or greater based on the weight of the sealant and most preferably 1.0 percent by weight or greater. The amount of silane used was preferably 10 percent by weight or greater or less and most preferably 2.0 percent by weight or less.

The composition of the invention also contains an organotin catalyst which catalyzes the reaction of isocyanate moieties with water or an active hydrogen containing compound. Such compounds were well known in the art. Included in the useful organotin compounds were alkyl tin oxides, stannous alkanoates, dialkyl tin carboxylates and tin mercaptides. Stannous alkanoates include stannous octoate. Alkyl tin oxides include dialkyl tin oxides, such as dibutyl tin oxide and its derivatives. The organotin catalyst was preferably a dialkyltin dicarboxylate or a dialkyltin dimercaptide. The dialkyltin dicarboxylate preferably corresponds to the formula $(R^2OC(O))_2\text{-Sn-}(R^3)_2$ wherein R^2 and R^3 were independently in each occurrence a C_{1-10} alkyl, preferably a C_{1-3} alkyl and most preferably a methyl. Dialkyl tin dicarboxylates with lower total carbon atoms were preferred as they were more active catalysts in the compositions of the invention. The preferred dialkyl dicarboxylates include 1,1-dimethyltin dilaurate, 1,1-dibutyltin diacetate and 1,1-dimethyl dimaleate. The organo tin catalyst was present in an amount of 60 parts per million or greater based on the weight of the sealant, more preferably 120 parts by million or greater. The organo tin catalyst was present in an amount of 1.0 percent or less based on the weight of the sealant, more preferably 0.5 percent by weight or less and most preferably 0.1 percent by weight or less

The sealant composition of the invention may also further contain a second catalyst which has good stability in the absence of atmospheric moisture, but which has a rapid cure rate in the presence of atmospheric moisture, such as a dimorpholinodialkyl ether, a di((dialkylmorpholino)alkyl) ether or a metal alkanoate, such as bismuth octoate. A preferred dimorpholinodialkyl ether was dimorpholinodiethyl ether. A preferred di((dialkylmorpholino)alkyl) ether was (di-(2-(3,5dimethylmorpholino)ethyl)ether). The dimorpholinodialkyl ether or di((dialkylmorpholino)alkyl) ether when employed, were preferably employed in an amount, based on the weight of the sealant, of 0.01 percent by weight or greater based on the sealant, more preferably 0.05 percent by weight or greater, even more preferably 0.1 percent by weight or greater and most preferably 0.2 percent by weight or greater and 2.0 percent by weight or less, more preferably 1.75 percent by weight or less, even more preferably 1.0 percent by weight or less and most preferably 0.4 percent by weight or less.

The composition further comprises a stabilizing amount of an organophosphite. The organophosphite should be present in a sufficient amount to enhance the durability of bond of the adhesive composition to the paint surface and the glass surface durability of an automobile. Preferably at least one of the phosphorous atoms was bonded to an oxygen atom which was bonded to an aromatic moiety, such as a phenyl. Preferably at least one of the phosphorous atoms was bonded to an oxygen atom bonded to an alkyl moiety. Preferably at least one of the phosphorous atoms was bonded to both an aromatic moiety and an alkyl moiety through oxygen moieties. The organophosphites preferred for use in this invention were phosphites wherein the ligands on the phosphite comprise one ligand with at least one aliphatic moiety and one ligand with at least one aromatic moiety or comprises at least one ligand having both aromatic and aliphatic structure; that is alkaryl. Ligand as used herein refers to the groups bound to the oxygens bound to the phosphorous atoms of the phosphite. In a preferred embodiment the phosphite corresponds to one of the following formulas

$$P\text{-}(OR^1)_3 \text{ or}$$

$$(R^1O)_2 \text{-}P\text{-}OR^2O\text{-}P\text{-} (OR^1)_2 .$$

Preferably R^1 is independently in each occurrence C_{6-18} alkyl, C_{7-30} alkaryl or C_{6-20} aryl; more preferably C_{6-12} alkyl and most preferably C_{9-12} alkyl. Preferably R^2 is independently in each occurrence C_{6-18} alkylene, C_{7-30} alkarylene; or C_{6-20} arylene; more preferably C_{7-30} alkarylene or C_{6-20} arylene; even more preferably C_{7-30} alkarylene and most preferably a divalent bisphenol structure for instance 1,3 propylene diphenyl or methylene diphenyl. Preferably the divalent bisphenol was based on bisphenol A or bisphenol F. As used herein alkyl means saturated straight or branched carbon chain. Alkylene means a divalent straight or branched saturated carbon chain. Aryl as used herein refers to a monovalent group comprising one or more aromatic rings such as phenyl, biphenyl or naphthyl. Arylene as used herein refers to a bivalent group which comprises aromatic rings such as phenylene, naphthalene or biphenylene. Alkaryl as used herein means an hydrocarbon group which contains both aliphatic and aromatic structural components; for example 1,3 propylene diphenyl or nonylphenyl. Alkarylene means a divalent group which has both aliphatic and aromatic structural components; that is such as 1,3 propylene diphenylene or methylene diphenylene.

Among preferred organophosphites were poly(dipropyleneglycol) phenyl phosphite (available form Dover Chemical Corporation under the trademark and designation DOVERPHOS 12), tetrakis isodecyl 4,4'isopropylidene diphosphite (available form Dover Chemical Corporation under the trademark and designation DOVERPHOS 675), and phenyl diisodecyl phosphite (available form Dover Chemical Corporation under the trademark and designation DOVERPHOS 7). Preferably the organophosphite was present in an amount of 0.1 percent by weight or greater and more preferably 0.2 percent by weight or greater. Preferably the organophosphite was present in an amount of 1.0 percent by weight or less and more preferably 0.5 percent by weight or less. It has been discovered that by selection of this class of organophosphites the adhesion to certain paint surfaces was significantly enhanced.

For formulating sealant compositions, the one or more prepolymer and the silane containing compound, if present, were combined, preferably with fillers and additives known in the prior art for use in elastomeric compositions. By the addition of such materials, physical properties such as viscosity, flow rate, sag, can be modified. However, to prevent premature hydrolysis of the moisture sensitive groups of the polymer, the filler should be thoroughly dried before admixture therewith. Exemplary filler materials and additives include materials such as carbon black, titanium dioxide, clays, calcium carbonate, surface treated silicas, ultraviolet stabilizers, antioxidants, and the like. This list, however, was not comprehensive and was given merely as illustrative. The fillers were preferably present in an amount of 15 percent by weight or greater based on the amount of the sealant. The fillers were preferably present in an amount of 70 percent by weight or less based on the sealant, more preferably 50 percent by weight or less and even more preferably 30 percent by weight or less.

The sealant composition also preferably contains one or more plasticizers or solvents to modify rheological properties to a desired consistency. Such materials should be free of water, inert to isocyanate groups, and compatible with the polymer. Such material may be added to the reaction mixtures for preparing the prepolymer or the adduct, or to the mixture for preparing the final sealant composition, but was preferably added to the reaction mixtures for preparing the prepolymer and the adduct, so that such mixtures may be more easily mixed and handled. Suitable plasticizers and solvents were well-known in the art and include dioctyl phthalate, dibutyl phthalate, a partially hydrogenated terpene commercially available as "HB-40", trioctyl phosphate, epoxy plasticizers, toluene-sulfamide, chloroparaffins, adipic acid esters, castor oil, xylene, 1-methyl-2-pyrolidinone and toluene. The amount of plasticizer used was that amount sufficient to give the desired rheological properties and disperse the components in the sealant composition. Preferably the plasticizer was present in an amount of 0 percent by weight or greater, more preferably 5 percent by weight or greater and most preferably 10 percent by weight or greater. The plasticizer was preferably present in an amount of 45 percent by weight or less and 40 percent by weight or less and most preferably 20 parts by weight or less.

The sealant composition of this invention may be formulated by blending the components together using means well-known in the art. Generally the components were blended in a suitable mixer. Such blending was preferably conducted in an inert atmosphere and atmospheric moisture to prevent premature reaction. It may be advantageous to add any plasticizers to the reaction mixture for preparing the isocyanate containing prepolymer so that such mixture may be easily mixed and handled. Alternatively, the plasticizers can be added during blending of all the components. Once the sealant composition was formulated, it was packaged in a suitable container such that it was protected from atmospheric moisture. Contact with atmospheric moisture could result in premature cross-linking of the polyurethane prepolymer-containing isocyanate groups.

The sealant composition of the invention was used to bond porous and nonporous substrates together. The sealant composition was applied to a substrate and the adhesive on the first substrate was thereafter contacted with a second substrate. Thereafter the adhesive was exposed to curing conditions. In a preferred embodiment one substrate was glass and the other substrate is a plastic, metal, fiberglass or composite substrate which may optionally be painted. This method was especially effective for substrates painted with an acid resistant paint. In preferred embodiments, the surfaces to which the adhesive was applied were cleaned prior to application, see for example U.S. Patents 4,525,511, 3,707,521 and 3,779,794. Generally the sealants of the invention were applied at ambient temperature in the presence of atmospheric moisture. Exposure to atmospheric moisture was sufficient to result in curing of the sealant. Curing may be further accelerated by applying heat to the curing sealant by means of convection heat, or microwave heating.

This sealant can be formulated to be applied to a painted surface, such as an automobile window flange, without the need to put a primer on the surface of the substrate prior to application of the sealant. Preferably in this embodiment the sealant contains silane either in the form of a prepolymer or as an additive as described hereinbefore. In another embodiment the sealant can be formulated without the presence of silane. In this embodiment a primer was generally applied to the surface of the substrate, such as an automobile window flange, prior to contacting the sealant to the second substrate. Primers which may be used were well known to those skilled in the art. In the embodiment where one of the substrates was glass, the glass was preferably contacted with a primer prior to the application of the sealant. Examples of useful primers for painted surfaces such as automobile window flanges were BetaSeal 43530 primer available from Essex Specialty Products, Inc.. Examples of useful primers for glass surfaces include BetaSeal 43518 primer and BetaSeal 43520A primer available from Essex Specialty Products, Inc.

The sealants of this invention were especially effective in bonding to acid resistant points, such as, DuPonts Gen IVA coating which was an oxylic melamine silane modified coating, melamine carbam coating, two part polyurethane coating and acid epoxy coating.

Working time was the time period after application to a substrate wherein the adhesive was sufficiently tacky to be applied to the surface of a second substrate bond with the second substrate. Preferably the sealant of the invention was formulated to provide a working time of 6 minutes or greater more preferably 10 minutes or greater. Preferably the working time was 15 minutes or less and more preferably 12 minutes or less. Molecular weights as described herein were determined according to the following procedure: determined using the Waters Model 590 Gel Permeation Chromatograph. This unit was connected to a multiwavelength detector and a differential refractometer to measure the elution volume. A column of styrogel was used for the size exclusion and it can determine molecular weights from 250 to 50,000. The molecular weight of the prepolymer was then determined by measuring the elution volume through this column using tetrahydrofuran as the eluting solvent. The molecular weight was then calculated from a calibration curve of molecular weight vs. elution volume obtained from a polystyrene polyethylene glycol column. The quoted molecular weights were weight average molecular weights unless otherwise specified.

In reference to polyurethane prepolymers, average isocyanate functionality was determined according to the following formula,

$$\frac{\text{(moles diol-NCO adduct x diol-NCO functionality) + (moles triol-NCO adduct x triol-NCO functionality) + (moles excess polyisocyanate monomer x its functionality)}}{\text{moles diol-NCO adduct + moles triol-NCO adduct + moles excess polyisocyanate monomer}}$$

wherein moles excess polyisocyanate monomer were calculated according to the following formula,

moles of isocyanate - (2x moles of diol + 3x moles of triol)

and the moles of isocyanate, diol and triol were based on the amount of each in the starting formulation.

The theoretical average molecular weight of the prepolymer was calculated as equal to the average isocyanate functionality times the isocyanate equivalent weight of the prepolymer.

Functionality of the raw material was generally disclosed by the raw material supplier. It can be determined empirically by means of titrating the polyol or isocyanate to determine the average number functional group per molecule. One skilled in the art knows how to determine the functionality based on data developed by titration.

Example 1

A polyether polyurethane prepolymer was prepared by thoroughly mixing 386 grams of a polyoxypropylene diol having an average molecular weight of 2000 and 559 grams of polyoxypropylene triol having an average molecular weight of 4500, in a 2-liter resin kettle equipped with a mechanical agitator, a nitrogen inlet adapter and a thermometer.

Under nitrogen purge, the mixture was heated to 50 °C. 170 grams of molten diphenylene methane 4, 4' diisocyanate were added to the mixture and the mixture thoroughly mixed. Then 0.1 gram of stannous octoate was introduced and the mixture was mixed for two hours. Finally, 484 grams of alkyl phthalate plasticizer and 16 grams of diethyl malonate were added to the mixture. The resulting prepolymer had an isocyanate content of 1.47 percent by weight.

Example 2

A moisture curable sealant composition was prepared under anhydrous conditions by first degassing under agitation the mixture of 1089 grams of the prepolymer of Example 1, and 15 grams of N,N' bis((3-trimethoxysilyl)propyl) amine in a planetary mixer for 30 minutes. At this point, all the aminosilane was fully reacted with some isocyanate groups on the prepolymer. Then, to the above mixture, 65 grams of Desmodur N-3300 (an aliphatic polyisocyanate resin based on hexamethylene diisocyanate, supplied by Bayer USA Inc.) was charged and mixed for 10 minutes. Subsequently, 450 grams of dried carbon black was added, and mixed for 25 minutes under the reduced pressure of 30 inches of mercury. Finally, 14 grams of modified catalyst and 6g of organophosphite, was added and mixed for 10 minutes under the reduced pressure. The compounded sealant was filled into sealant tubes.

Examples 3-5

Several sealant compositions were prepared as described in Example 2 which were tested for adhesion as described below. The compositions and results of the testing were contained in the tables below

TABLE 1

	Example 3*	Example 4	Example 5
Silanated NCO prepolymer	69.899%	69.899%	69.899%
Carbon black	29.328%	29.328%	29.328%
	0.298%	0.298%	0.298%
NMP	0.453%	0.453%	0.300%
Fomrez SUL-11A	0.0224%	0.0224%	0.00%
FomrezUL-28	0.00%	0.00%	0.0214%
Doverphos 7	0.00%	0.338%	0.00%
Doverphos 675	0.00%	0.00%	0.400%

*Comparative
DMDEE is dimorpholino diethyl ether
NMP is n-methyl pyrollidone
Fomrez SUL-11A is dibutyl tin oxide.
Fomrez UL-28 is dimethyl tin carboxylate

The Quick Knife Adhesion test was used to test the speed of the above sealant adhered to an acid resistant automotive coating system, Du Pont's Gen IVA coating. Gen IVA basecoat (~ 1.0 mil.) and clearcoat (~ 1.0 mil.) were sprayed on E-coated panels and baked at 255°F oven for 27 min. Rectangle beads with size of 9x9x9 cm were layered on the panels three to four hours after their baking. The sealant beads were allowed to stay at ambient environment (21°C/30%RH) for three hours before being removed to low temperature environment (5°C/50%RH) for extended period. Adhesion was checked using quick knife method immediately after the indicated time. The cured bead was then cut with a razor blade through to the painted surface at 45 angle while pulling back the end of the bead at 180 angle. Notches were cut every 3 mm on the painted surface. The degree of adhesion was evaluated as adhesive failure (AF) and/or cohesive failure (CF). In case of adhesive failure, the cured bead can be separated from the painted surface, while in cohesive failure, separation occurs within the sealant bead as a result of cutting and pulling.

	Days in Condition	Adhesion to panel	Days in Condition	Adhesion to panel
Example 3	3	NA	5	100%
Example 4	3	NA	5	100%
Example 5	3	70%	4	100%

Adhesion durability was tested by preparing peel samples, aging them at 110°C for the indicated time, and performing the peel adhesion test by quick knife method. The peel samples were prepared by applying two-step glass primer to glass coupons followed by the application of a sealant bead and pressing to obtain desired thickness (2-3 mm). The samples were allowed to cure at 23°C/50%RH condition for 1 week before put into 110°C oven. Samples were removed at 7, 15, 20, 24, 31 days and adhesion was tested.

	Example 5
0 days	100% CF
7 days	90% CF
15 days	90% CF
20 days	85% CF
24 days	85% CF
31 days	90% CF

Lap Shear Test:

A sealant approximately 6.3 mm wide by 8 mm high was applied along the width of the glass and approximately 6 mm to 12 mm from the primed end. The paint substrate was immediately placed on the sealant and the sample was allowed to cure at the condition of the 23°C and 50 percent relative humidity for 7 days. The sample was then pulled at a rate of 1 inch/minute (2.5 cm/min)with an Instron Tester. The load at break of the sample was recorded.

Weather Testing

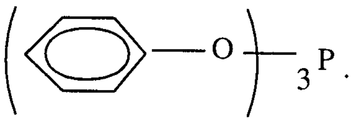
Weathering of the above sealant formulas were tested using Weather-O-Meter (WOM)conditions for 2000 hours and the lap shear test was performed. The WOM was operated according to SAE J1895 conditions. The samples were exposed continuously to the following cycles; 89ºC at 5 percent RH for 3.8 hours and 95 percent RH for 1 hour.

Example 3	2000 hr	414 psi	70% CF
Example 4	2000 hr	500 psi	100% CF
Example 5	2000 hr	507 psi	100% CF

<u>Examples 6-10</u>

Sealants as described in Example 2 with various organo phosphites were applied to a primed coupon of glass having a fit the sealant was then bonded to coupons of steel coated with Du Pont Gen IV coating as described in Examples 3-5. The coupons were then exposed to the WOM conditions for extended periods of time as listed below. After the designated times, the coupons were subjected to lap shear testing as described below.

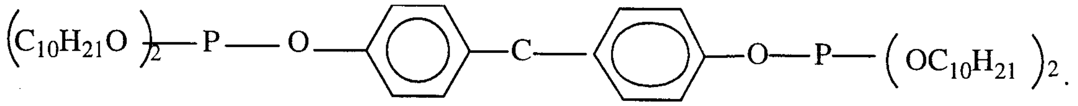
The phosphites used were described hereinafter. Phosphite 1 was available from Dover Chemical Corporation under the trademark and designation DOVERPHOS 6 and has the structure $(C_{10}H_{2}1O)_3$ P. Phosphite 2 was available from Dover Chemical Corporation under the trademark and designation DOVERPHOS 10 and has the structure



Phosphite 3 was available from Dover Chemical Corporation under the trademark and designation DOVERPHOS 49 and has the structure

$(C_{13}H_{27}O_3)$—P

Phosphite 4 was available from Dover Chemical Company under the trademark and designation DOVERPHOS 675 and corresponds to the structure



Phosphite 5 was available from Dover Chemical Company under the trademark and designation DOVERPHOS H-P4 and has a structure of

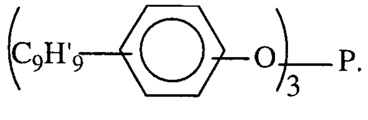


TABLE 2

Example 6/Phosphite 1

1500 Hrs.	**Load lbs (Kg)**	**Area in^2 (cm$^{2)}$**	**psi (Kpa)**	**Mode of Failure**
Trial 1	147.2 (66.8)	0.2 (1.)	736.0 (5070)	30%CF/30%G/40%AFP
Trial 2	139.1 (63.1)	0.27 (1.7)	515.2 (3552)	95%CF/5%G
Trial 3`	“	“	“	“
2000 Hrs				
Trail 1	89.99 (40.82)	0.29 (1.9)	310.3 (2139)	100AF
Trail 2	92.19 (41.19)	0.3 (2.)	307.3 (2119)	95%AF/5%CF
Trail 3	68.24 (30.95)	0.32 (2.1)	213.3 (1471)	50%CF/50%AF

Example 7/Phosphite 2

1500 Hrs.	**Load**	**Area**	**psi**	**Mode of Failure**
Trial 1	95.95 (43.52)	0.32 (2.1)	299.8 (2067)	5%CF/95AFP
Trial 2	141.6 (64.2)	0.26 (1.7)	544.6 (3755)	75%CF/25%T
Trial 3`	134.7 (61.1)	0.30 (1.9)	449.0 (3096)	95%AFP/5%CF
2000 Hrs				
Trail 1	117.7 (53.4)	0.31 (2.0)	379.7 (2618)	5%CF/95%AFP
Trail 2	137.6 (62.4)	0.33 (2.1)	417.0 (2875)	5%CF/95%AFP
Trail 3	111.9 (50.7)	0.34 (2.2)	329.1 (2269)	100%AFP

Example 8/Phosphite 3

1500 Hrs	**Load**	**Area**	**psi**	**Mode of Failure**
Trial 1	144,1 (65.4)	0.24 (1.5)	600.4 (4140)	85%CF/15%G
Trial 2	162.6 (73.7)	0.33 (2.1)	492.7 (3397)	80%CF/20%G
Trial 3`	174.2 (79.0)	0.32 (2.1)	544.4 (3753)	95%CF/5%G
2000 Hrs				
Trail 1	147.9 (67.1)	0.35 (2.2)	422.6 (2914)	5%CF/95%AFP
Trail 2	156.4 (70.9)	0.33 (2.1)	473.9 (2267)	5%CF/95%AFP
Trail 3	131.2 (59.5)	0.32 (2.1)	410.0 (2827)	5%CF/95%AFP

Example 9/Phosphite 4

1500 Hrs.	**Load**	**Area**	**psi**	**Mode of Failure**
Trial 1	175.8 (79.7)	0.37 (2.4)	475.1 (3276)	50%CF/50%AFP
Trial 2	139.5 (63.3)	0.36 (2.3)	387.5 (2672)	100%CF
Trial 3`	167.5 (76.0)	0.34 (2.2)	492.6 (3396)	100%CF
2000 Hrs				
Trail 1	169.6 (76.9)	0.34 (2.2)	498.8 (3439)	100%CF
Trail 2	182.8 (82.9)	0.39 (2.5)	468.7 (3231)	100%CF
Trail 3	151.6 (688)	0.38 (2.4)	398.9 (2750)	100%CF

Example 10/Phosphite 5

1500 Hrs	**Load**	**Area**	**psi**	**Mode of Failure**
Trial 1	112.8 (51.2)	0.35 (2.2)	322.3 (2222)	95%CF/5%G
Trial 2	118.7 (53.8)	0.35 (2.2)	339.1 (2338)	100%AFP
Trial 3`	135.7 (61.5)	0.31 (2.0)	437.7 (3018)	50%CF/50%AFP
2000 Hrs				
Trail 1	96.91 (43.91)	0.33 (2.1)	293.7 (2025)	25%T/75%CF
Trail 2	101.8 (46.2)	0.33 (2.1)	308.5 (2127)	25%/75%CF
Trail 3	84.9 (38.5)	0.33 (2.1)	257.3 (1774)	25%T/75%CF

As used in the table the following terms were defined
CF = Cohesive failure
G = Gassing
AFP = Adhesive failure to Glass Primer
T = Tunneling

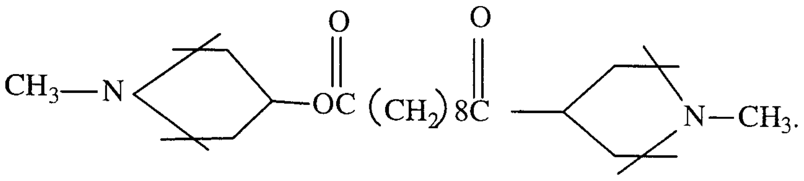
Gassing means air pockets were found in the adhesive bead after cutting. Tunneling means a long air pocket was found in the bead.

Example 11 to 16

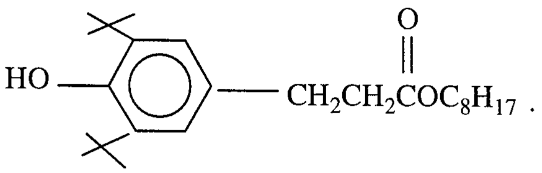
Samples prepared as described in Example 2 using phosphites and different stabilizers as described below were wrapped in cheesecloth and placed in foil bags, with 100nl of deionized water. The foil bags were sealed and placed in an oven at 70ºC for 7 and 14 days respectively. After the designated time, each sample was placed in a freezer bag for 16 hours at -20ºC. Thereafter the samples were subjected to ambient conditions for 2 hours then the peel test as described in Examples 3-5 was performed on each sample. Samples were thereafter subjected to ambient humidity for 5 and 9 days at 110ºC and the adhesion test was performed. The results were compiled in Table 3.

Examples

The adhesive compositions were also subjected to 110ºC at ambient humidities for varying times and the peel test was performed. Several different stabilizer compositions were used. Stabilizer 1 was available from Ciba Specialty Chemicals under the trademark and designation Tinuvin 765 and corresponds to the structure

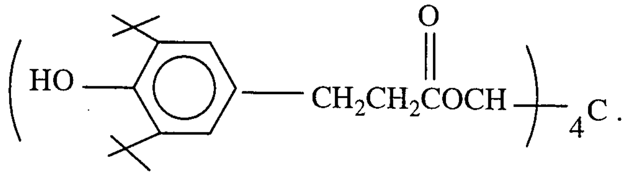


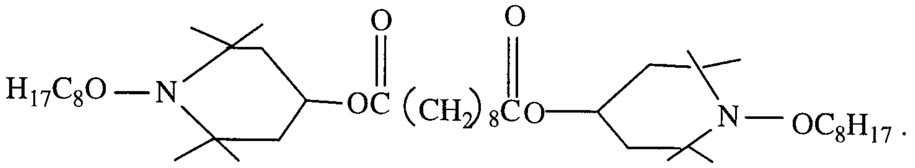
Stabilizer 2 was available from Ciba Specialty Chemicals under the trademark and designation Irganox 1135 and corresponds to the structure



Stabilizer 3 was available from Dover Chemical Company under the trademark and designation Dovernox DD 9821 and was a 1:1 blend of dinonyl phenol and a compound which corresponds to the formula

Stabilizer 4 was available for Ciba Specialty Chemicals under the trademark and designation Tinuvin 123 and corresponds to the formula





The results were compiled in Table 4.

TABLE 3

Ex-amples	Phosphite or Stabilizer		Mode of Failure	5D@110C	9D@110C
11	none	7 days	100%CF/100%CF		
		14 days	100%CF	90%CF/10%AF	60%CF/40%AF
12	Stabilizer 1	7 days	100%CF/100%CF		
		14 days	100%CF	100%CF	40%CF/60%AF
13	Stabilizer 3	7 days	100%CF/100%CF		
		14 days	100%CF	100%CF	100%AF
14	Phosphite 4	7 days	100%CF/100%CF		
		14 days	100%CF	100%CF	100%CF
15	Stabilizer 2	7 days	100%CF/100%CF		
		14 days	100%CF	100%CF	20%CF/80%AF
16	Stabilizer 4	7 days	100%CF/100%CF		
		14 days	100%CF	100%CF	10%CF/90%AF

TABLE 4

Exam-ple	Stabilizer	0 Day 05/18/99	4 Day 11/12/99	8 Day 11/6/99	10 Day 11/18/99	11 Day 11/19/99	14 Day 11/22/99	15 Day 11/23/99
11	No Stabilizer	100CF	100CF	60CF/40AF	50CF/50AF	30CF/70AF 40CF/60AF	100AF 100AF	100AF
14	Phosphite 4	100CF	100CF	100CF	100CF	100CF	25CF/75AF 20CF/80AF	20CF/80AF
12	Stabiizer 1	100CF	100CF	90CF/10AF	90CF/10AF	50CF/50AF 40CF/60AF	20CF/80AF 20CF/80AF	20CF/80AF
15	Stabilizer 2	100CF	100CF	50CF/50AF	NA	20CF/80AF	10CF/90AF	100AF
13	Stabilizer 3	100CF	80CF/ 20AF	90CF/10AF	35CF/65AF	20CF/80AF 20CF/80AF	100AF 100AF	100AF
16	Stabilizer 4	100CF	100CF	50CF/50AF	40CF/60AF	20CF/80AF 20CF/80AF	100AF 100AF	100AF

1. A sealant composition comprising

(1) a urethane prepolymer having an isocyanate functionality of at least 2.0 and a weight average molecular weight of at least 2,000.

(2) a catalytic amount of a tin compound which catalyzes the reaction of isocyanate moieties with water or an active hydrogen containing compound; and

(3) a stabilizing amount of an organophosphite which has an alkaryl ligand or both an aliphatic ligand and an aromatic ligand.

2. Sealants according to Claim 1 wherein the organophosphite corresponds to one of the formulas

$$P\text{-}(OR^1)_3 \text{ or}$$

$$(R^1O)_2\text{–}P\text{-}OR^2O\text{-}P\text{-}(OR^1)_2$$

wherein

R^1 is independently in each occurrence alkyl, alkaryl or aryl; and

R^2 is independently in each occurrence alkylene, alkarylene or arylene;

With the proviso that R^1 and R^2 were selected such that each phosphite has at least one alkaryl group or has at least one aryl and at least one alkyl group.

3. Sealants according to Claim 2 wherein R^1 is independently in each occurrence $C_{6\text{-}18}$ alkyl; $C_{7\text{-}30}$ alkaryl or $C_{6\text{-}20}$ aryl; and R^2 is independently in each occurrence $C_{6\text{-}18}$ alkylene; $C_{7\text{-}30}$ aralkylene or $C_{6\text{-}20}$ arylene.

4. Sealants according to Claim 2 or 3 wherein R^1 is independently in each occurrence $C_{6\text{-}18}$ alkylene, and R^2 is independently in each occurrence $C_{7\text{-}30}$ aralkylene or $C_{6\text{-}20}$ arylene.

5. Sealants according to any of Claims 1 to 4 which comprise.

(1) from 30 to 99.8 percent by weight of polyurethane prepolymer based on the weight of the sealant;

(2) from 60 parts per million to 1 percent by weight of a catalyst based on the weight of the sealant; and

(3) from 0.1 to 1.0 percent by weight of an organic phosphite based on the weight of the sealant.

6. Sealants according to any of Claims 1 to 5 wherein the polyurethane prepolymer further comprises silane functionality or a compound or polymer containing silane moieties.

7. Sealants according to Claim 6 which further comprise from 0.5 to 20 percent by weight of a compound or prepolymer containing silane moieties;

8. A method of bonding glass to a substrate which comprises applying a sealant according to anyone of Claims 1 to 6 to the glass surface or the substrate surface; contacting the glass and substrate such that the sealant was located between the glass and the substrate; allowing the sealant to cure so as to bond the glass to the substrate.

9. A process for bonding glass to a substrate which further comprises prior to contacting the sealants with the glass o the substrate applying a primer to the surface of the substrate, and applying a primer to the surface of the glass;

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/03055

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K3/10 C08G18/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 198834 Derwent Publications Ltd., London, GB; Class A25, AN 1988-240176 XP002137967 & JP 63 175016 A (ASAHI GLASS CO LTD), 19 July 1988 (1988-07-19) abstract ---	1-3,5
A	US 4 374 237 A (BERGER MITCHELL H ET AL) 15 February 1983 (1983-02-15) cited in the application the whole document ---	1,5,8
A	US 4 687 533 A (RIZK SIDKY D ET AL) 18 August 1987 (1987-08-18) cited in the application the whole document --- -/--	1,5-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 18 May 2000	Date of mailing of the international search report 29/05/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Puetz, C

1

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/US 00/03055

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 340 901 A (WANG CHIA L) 23 August 1994 (1994-08-23) the whole document ---	1,2,8
A	US 4 546 166 A (NIINOMI MASAHIRO ET AL) 8 October 1985 (1985-10-08) the whole document ---	1,8
A	DE 34 16 773 A (TOGO MANAGEMENT AG) 8 November 1984 (1984-11-08) claims; examples ---	1
A	DE 32 21 655 A (POLYCHEMIE GES MBH) 8 December 1983 (1983-12-08) claims; example 3 ---	1,8
A	EP 0 516 110 A (TREMCO INC) 2 December 1992 (1992-12-02) claims; example ---	1
A	DATABASE WPI Section Ch, Week 199338 Derwent Publications Ltd., London, GB; Class A14, AN 1993-297398 XP002137968 & JP 05 171128 A (SEKISUI CHEM IND CO LTD) , 9 July 1993 (1993-07-09) abstract -----	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ional Application No
PCT/US 00/03055

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 63175016 A	19-07-1988	NONE	
US 4374237 A	15-02-1983	AT 19525 T	15-05-1986
		AU 559164 B	26-02-1987
		AU 9175682 A	30-06-1983
		CA 1195797 A	22-10-1985
		DE 3270909 D	05-06-1986
		EP 0082528 A	29-06-1983
		JP 1403330 C	09-10-1987
		JP 58109529 A	29-06-1983
		JP 62007210 B	16-02-1987
US 4687533 A	18-08-1987	US 4625012 A	25-11-1986
		AU 562732 B	18-06-1987
		AU 5653786 A	05-03-1987
		BR 8603631 A	10-03-1987
		CA 1278640 A	02-01-1991
		DK 349386 A	27-02-1987
		EP 0219185 A	22-04-1987
		ES 552356 D	16-04-1987
		ES 8704989 A	01-07-1987
		FI 860409 A	27-02-1987
		JP 62050319 A	05-03-1987
		KR 9405871 B	24-06-1994
		MX 168254 B	14-05-1993
		NO 860457 A	27-02-1987
		NZ 214950 A	30-06-1988
		PT 82491 A,B	01-05-1986
		ZA 8600674 A	24-09-1986
US 5340901 A	23-08-1994	US 5175228 A	29-12-1992
		CA 2084181 A,C	10-06-1993
		DE 69224466 D	26-03-1998
		DE 69224466 T	06-08-1998
		EP 0546771 A	16-06-1993
		ES 2114919 T	16-06-1998
		JP 2673480 B	05-11-1997
		JP 5247431 A	24-09-1993
		KR 9611841 B	03-09-1996
		MX 9207138 A	01-06-1993
		US 5354609 A	11-10-1994
US 4546166 A	08-10-1985	JP 1608341 C	28-06-1991
		JP 2034998 B	07-08-1990
		JP 60090284 A	21-05-1985
DE 3416773 A	08-11-1984	CH 662126 A	15-09-1987
DE 3221655 A	08-12-1983	NONE	
EP 0516110 A	02-12-1992	US 5196455 A	23-03-1993
		AT 158610 T	15-10-1997
		AU 650537 B	23-06-1994
		AU 1723092 A	03-12-1992
		CA 2069051 A	01-12-1992
		DE 69222353 D	30-10-1997
		DE 69222353 T	26-03-1998
		DK 516110 T	04-05-1998

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int tional Application No
PCT/US 00/03055

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0516110 A		ES 2109289 T GR 3025619 T	16-01-1998 31-03-1998
JP 5171128 A	09-07-1993	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)