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(57) Abrégé/Abstract:
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(57) Abstract

The present invention relates to a film forming composition, a method of forming the composition, and application of the composition to coating formulations which provide a cured coating having acid rain resistance. A film-forming polyurethane polyol composition comprises a reaction product of an n-functional isocyanate (wherein n is a number ranging from about 2 to about 5) with at least one diol or triol or mixtures thereof and a compound containing isocyanate-reactive functional groups, preferably a monofunctional alcohol or thiol. The low viscosity polyurethane polyol of the present invention is typically cross-linked/cured using a melamine to produce a cured coating which is highly acid etch resistant as well as having other desirable physical-mechanical properties. The coating compositions have improved flow characteristics compared to compositions containing polyurethane polyols prepared without the monofunctional alcohols or thiols.

POLYURETHANE POLYOLS AND COATINGS THEREOF HAVING REDUCED VISCOSITY

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the use of a particular class of oligomeric polyols to form high solids coatings having reduced viscosity as well as resistance to environmental factors such as acid rain and ultraviolet light. Polyurethane polyols are prepared by reacting a polyisocyanate with both a compound having a single functional group reactive with isocyanate, such as a monofunctional alcohol or monofunctional thiol, and with a diol or triol which reacts substantially only single-endedly with an isocyanate.

2. Background of the Invention

Many of the high-performance automotive high-solids coatings presently in use are based on polymeric systems containing polyester or acrylic polyols. In typical single-component coatings, wherein all of the coating ingredients are combined into one storage stable mixture, the polyester or acrylic-polyol component is typically crosslinked with melamine (aminoplast resin) under heat cure conditions of about 250 degrees F or above to provide a thermally cured coating. In typical two-component systems, such polyols are combined with a suitable isocyanate shortly before application to the surface to be coated and the combination is cured at temperatures ranging from about 70 degrees F to about 280 degrees F.

Currently, the automotive industry is using basecoat/clearcoat coatings in ever increasing amounts. In such systems, a pigmented coating is applied over appropriate primers and the coating system is completed by applying an unpigmented, clear topcoat over the pigmented basecoat. It is also desirable that such coating systems comply with VOC regulations, which typically require that the clearcoat have volume solids in excess of 50 percent (for a high solids type). Simultaneously, due to the deterioration of our environment, the automotive industry has been searching for coatings systems which, after curing/drying, are acid rain resistant.

To obtain high solids while maintaining acceptable coating formulation viscosity for spray application, the industry has tended to decrease the number average molecular weight (Mn) of the film forming polymers and to increase the amount of crosslinker, thereby obtaining a cured coating having adequate hardness, gloss, impact strength, appearance and exterior durability. Typical coating formulations use a melamine or other amino resin as the crosslinker. Increased amounts of monomeric melamine crosslinkers reduce the formulation viscosity. As the amount of amino resin is increased, the acid rain resistance of these coatings is compromised. At this time the automobile manufacturers consider improved resistance of automotive finish coatings to environmental etching (acid rain) to be a high priority. It is believed that ester bonds in an acrylic melamine or polyester melamine coating are weak points in the crosslinked resin network, susceptible to acid catalyzed hydrolysis.

Current high solids automotive topcoats, whether they be monocoats or the more modern basecoat/clearcoats, are predominantly oligomeric acrylic polyols crosslinked with melamine-formaldehyde resins. Modern topcoats of this type form visually appealing, high gloss films and are designed to retain high levels of gloss after extensive accelerated weathering and Florida exposure. In recent years, further improvement in durability has been obtained by the use of basecoat/clearcoat systems, where the clearcoat acts as a screen to protect the pigmented film.

There has been a general reduction in the pH, and an increase in the concentration of electrolytes, in rain water, creating "acid rain". Probably as a result of the combination of these factors, a new problem has evolved in automotive topcoat technology which is generally referred to as acid or environmental etching. The defect appears as a grainy water spot pattern seen predominantly on horizontal surfaces. An in depth study of the problem by General Motors workers indicates that acidic components in a wetting event (dew or rainfall) react with calcium, a common constituent of dirt. As droplets evaporate, calcium sulfate precipitate forms on horizontal surfaces around the droplet perimeters. Subsequent washing removes the precipitate, but scars remain. It is generally observed that the problem is most conspicuous on dark, freshly painted surfaces in warmer and more polluted environments. The normal crosslinking at the surface of a coating induced by exposure to UV radiation and oxygen may eventually protect the film. Thus, the problem is largely one that occurs on automobile dealers' lots. Frequently, etched cars must be repainted before they can be sold. One major U.S. manufacturer estimates the cost of environmental etching to exceed 50 million per year.

A considerable amount of work has been done related to coatings containing polyurethane polyols. One way to make polyurethane polyols is to react a diisocyanate or a multifunctional isocyanate with a significant stoichiometric excess of a diol. After the reaction is complete, the excess of diol is removed, preferably by distillation. The obvious disadvantage of this method of making low molecular weight polyurethane polyols is that the distillation of the diols is inconvenient and it is not possible to use diols of high molecular weight (which cannot be distilled off) unless they are later recrystallized. Also, molecular weight control is difficult in such processes because even at the stoichiometric excess, a limited number of hydroxyl groups on the same diol molecules will react with the isocyanate, giving chain extensions beyond the intended low molecular weight polymers. This results in broad molecular weight distributions. U.S. Patents describing the production of polyurethane polyols by using stoichiometric excess of diols include: U.S. Patent

4,543,405 to Ambrose, et al.; issued September 24, 1985; and =U.S. Patent 4,288,577 to McShane, Jr., issued September 8, 1981.

Crosslinked coatings based on polyurethane polyols of this type have been described in U.S. Patents 4,548,998 to Chang, et al., issued October 22, 1985; 4,540,766 to Chang et al., issued September 10, 1985; and 4,485,228 to Chang et al., issued November 27, 1984. The coatings based on these compositions offer good flexibility and hardness balance.

Another class of similar coating polymeric systems is based on urethane-modified polyesters. The polymeric systems are prepared by reacting a polyisocyanate with an excess of diol and then using this resulting mixture as a polyol reactant for carrying out a conventional polyester condensation involving acids, diols, triols and so on. Alternatively, hydroxyl terminated conventional polyesters can be extended with isocyanates.

Typical U.S. patents describing such polymeric systems include: U.S. Patent 4,605,724 to Ambrose et al., issued August 12, 1986; U.S. Patent 4,540,771 to Ambrose et al., issued September 10, 1985; U.S. Patent 4,530,976 to Kordomenos et al., issued July 23, 1985; U.S. Patent 4,533,703 to Kordomenos et al., issued August 6, 1985; U.S. Patent 4,524,192 to Alexander et al., issued June 18, 1985; and U.S. Patent 4,533,704 to Alexander et al., issued August 6, 1985. These patents describe methods of making the polymers and their use in coatings.

Japanese Patent 82-JP-115024, assigned to ASAHI Chemical IND KK, discloses a method of preparing an isocyanate terminated prepolymer wherein the isocyanate termination groups have different reactivity. The isocyanate terminated prepolymer is prepared by reacting two types of polyisocyanate having different reactivities with diols having two kinds of hydroxyl groups of different reactivity. The resulting prepolymer is subsequently crosslinked/cured using moisture or another source of hydroxyl groups.

U.S. Patent No. 3,576,777 discloses the use of polyurethanes prepared from organic diisocyanates and glycols in conjunction with unsaturated oil-modified alkyd resins for preparing thixotropic paints. Small quantities of monoisocyanates and monoalcohols can optionally be concurrently used with these reactants. Since the polyurethanes are described as retaining their thixotropic properties, they are believed to have relatively broad molecular weight distributions.

European Patent EP 0 001 304 of Akzo N.V. discloses coating compositions comprising physical blends in organic solvents of polyhydroxy compounds, and polyisocyanates and tertiary alcohols
which have prolonged pot life but rapid curing when applied.

U.S. Patent No. 2,873,266 discloses polyurethane prepared by reacting mixtures of primary and secondary glycols, each containing at least 4 carbon atoms between the hydroxyl groups with a aliphatic diiso compound containing two groups of the formula -N=C=X separated by at least 4 carbon atoms, where X is oxygen or sulfur.

U.S. Patent No. 4,619,955 discloses isocyanate functional urethanes useful as flexibilizing additives for polymeric vehicles, comprising reaction products of (a) aliphatic polyisocyanates, (b) at least one monofunctional alcohol containing an ether or carboxyl oxygen and (c) at least one diol.

U.S. Patent No. 4,631,320 discloses thermosettable coating compositions comprising hydroxy group-containing polyurethanes, amino cross-linkers and optional catalysts and/or solvent. The hydroxypolyurethanes can be prepared by either self-condensing certain polyhydroxyalkyl carbonate compounds or by condensing same with polyols.

U.S. Patent No. 5,155,201 of Akzo N.V. discloses polyurethane polyols comprising reaction products of n-functional polyisocyanates (n=2-5) and substantially monomeric diols having hydroxyl groups separated by 3 carbon atoms or less.

U.S. Patent No. 5,175,227 of Akzo N.V. discloses acid etch resistant coating compositions comprising polyurethane polyols and hydroxyl group-reactive crosslinkers. The polyurethane polyols comprise reaction products of substantially monomeric asymmetric diols with hydroxyl groups separated by 3 carbon atoms or less and n-functional polyisocyanates (n=2-5).

Additionally, U.S. Patent No. 5,130,405 of Akzo N.V. discloses acid etch resistant coatings comprising (1) polyurethane polyols prepared from symmetric 1,3-diol components and polyisocyanates and (2) hydroxyl group-reactive crosslinking agents.

Using any given multifunctional isocyanate starting material, none of the references cited above discloses a composition or process for making a composition having a controlled molecular weight which permits high solid coatings with exceptionally low application viscosity, of the kind possible using the present invention, without resorting to the employment of large molar excesses of diol components.

The preparation of polyurethane polyols is also possible without using isocyanate reactants. The preparation involves the reaction of an amine with a cyclic carbonate, leading to a urethane with a hydroxyl group in a beta position to the urethane group. For example, the reaction of a diamine with two moles of ethylene or propylene carbonate will lead to a polyurethane diol. Various embodiments of this method of producing polyurethane polyols are found in the following patents: U.S. Patent 3,248,373 to Barringer, issued April 26, 1966; European Patent 0257848 to Blank, published March 2, 1988; U.S. Patent 4,631,320 to Parekh, et al., issued December 23, 1986; U.S. Patent 4,520,167 to Blank et al., issued May 28, 1985; U.S. Patent 4,484,994 to Jacobs III et al., issued November 27, 1984; U.S. Patent 4,268,684 to Gurgiolo, issued May 9, 1981; and U.S. Patent 4,284,750 to Ambirsakis, issued August 18, 1981. Most of the patents listed directly above describe the use of such polyurethane polyols in crosslinked coatings. The polymer systems comprising these coatings do not provide exceptional chemical resistance nor acid-rain resistance.

European patent application 0 530 806 A1 (Mitsubishi Kasei) discloses linear polyurethane polyols obtained by the reaction of various hydrocarbon diols (having from 7 to 20 carbon atoms) with isophorone diisocyanate, reportedly having Mn from 500 to 20,000. Since both reactants are difunctional, the final molecular weight and viscosity should be predominantly determined by the OH/NCO ratio and the non-symmetric nature of the diisocyante. No modifications with monofunctional reactants are disclosed.

European patent application 0 537 900 A2 (Rohm & Haas) disclosed <u>thickening</u> agents for non-aqueous solvent-containing compositions, based upon reaction products of polyols containing at least two hydroxyl groups with polyisocyanates containing at least two isocyanato groups and an active hydrogen compound. The active hydrogen compound can contain hydroxyl groups or primary or secondary amino groups. The reaction of isocyanates with amines to form urea compounds for rheology control (i.e., thickening) is a well-known technique which teaches away from the present invention.

An Abstract of JP 0 5,043,644A discloses polyurethane resins prepared by reacting glycols (A) with polyisocyanates (B) in the presence of monofunctional active hydrogen compounds (C) (such as monothioalcohols), then reacting the urethane prepolymers obtained (D) with chain extenders (E) to obtain polyurethane resins of very high molecular weight (Mn > 200,000). The use of α,β-diols and α,γ-diols is not disclosed.

An Abstract of JP 0 4,117,418A (Hitachi) discloses the preparation of urethane resins in the presence of acrylic monomers to reduce solvent emissions from coatings containing same. The resins contain (A) copolymers containing hydroxyl group-containing ethylenically unsaturated monomers as comonomers, (B) polyisocyanates and (C) reactive diluents consisting of 100-60 wt% of a polyhydric alcohol and 0-40 wt% of a monohydric alcohol.

Recently it has become increasingly important, for environmental compliance, to develop polymeric systems with low solution viscosities, which permit formulation of high solids coatings with low application viscosities. High solids (greater than about 50 weight percent solids) coatings decrease the amount of volatile organic compounds (VOC) which pass into the ambient atmosphere upon drying/curing of the coating.

To achieve acceptable solution viscosities (20-30 seconds, #4 Ford Cup at about 25 degrees C) for typical high solids coating systems, it is necessary that the film-forming polymer have a weight average molecular weight (Mw) lower than about 5,000. To achieve good film properties in such systems after crosslinking, it is also necessary that the number average molecular weight (Mn) should exceed about 800, and that each number average molecule should contain at least two reactive hydroxyl groups. These general principles apply to polyester polyols, acrylic polyols, and also to urethane polyols when crosslinked with melamine resins or with isocyanates. As is evident from the above discussion, the requirements for acceptable solution viscosities and good film properties lead to contradictory molecular weight requirements - for low solution viscosities the Mw should be low, but for good film properties the Mn should be high.

Currently used high solids one-component clearcoats are based on low molecular weight acrylic polyols and melamines, typically hexamethoxymethyl melamine. Acid rain resistant and high solids coating systems have been achieved using two component systems such as the polyol-isocyanate systems previously discussed. These coating systems can be used at an overall weight percent solids of greater than about 50 percent. However, the presence of reactive isocyanate groups necessitates the use of a two-component system which must be mixed shortly before use. The two component systems require additional handling and storage operations as well as provide a source of error in relative quantity of ingredients used. Errors in mixing can adversely affect the quality of the finished coating. The use of reactive isocyanate crosslinkers requires the use of special safety equipment to avoid toxic effects resulting from human exposure to isocyanate. Unfortunately this technology is substantially more expensive than current one component coatings, both in terms of raw material cost and the expense involved in retrofitting an existing automotive assembly line to handle two component coatings. Thus, it would be advantageous to have a single component isocyanate-free system which can be applied at a high weight percent solids and which exhibits acid rain resistance.

SUMMARY OF THE INVENTION

In accordance with the present invention, a polyurethane polyol composition useful as a film-forming material comprises the reaction product of:

(a) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5;

(b) x moles of at least one component diol or triol or mixtures thereof, selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon atoms; and

(c) y moles of a compound containing from 1 to 18 carbon atoms and a single functional group capable of reacting with an isocyanate, wherein the sum of x+y is about 0.6 to 1.4 and y = about 0.01x to about 75x, provided that the NCO/OH equivalent ratio does not exceed unity.

These ingredients are preferably combined in a sequence that produces reaction products having low polydispersity, e.g. Mw/Mn ≤ 3, or preferably ≤ 2.5, or most preferably ≤ 2.

The compounds of (c) can be selected from a group of single active hydrogen-containing compounds containing from 1 to 18 carbon atoms. As stated in U.S. Patent No. 4,394,491, such compounds can be described as "monoahls", i.e. organic compounds containing single hydrogen moieties capable of reacting with the isocyanate moieties of unsaturated isocyanates via a urethane reaction. This class includes monoalcohols and thiols, primary and secondary amines and heterocyclic nitrogen compounds containing an active hydrogen attached to a nitrogen atom within the ring. The monoalcohols and thiols are presently preferred. Some of these compounds can be represented by the formulas R-OH, R-SH, $R-NH_2$, R^1-NH-R^2 and $(CH_2)_2-NH$, where R is a hydrocarbyl group having 18 carbon atoms or less and can be an alkyl, alkenyl, aryl, alkaryl group or the like, and R^1 and R^2 are selected from the same family of groups, with the sum of the carbon atoms in R^1 and R^2 being 18 or less. The nitrogen-containing heterocyclic rings can contain from 4 to about 7 members selected from carbon atoms, nitrogen atoms and other compatible atoms such as sulfur and oxygen. Preferably, the ring contains only nitrogen and from 4 to about 6 carbon atoms, i.e., z=4 to 6 in the formula.

It should be noted that, as used herein, the term "polyurethane polyol" refers to a reaction product wherein the principal reactants (diol component and polyisocyanate component) are linked substantially only via urethane linkages. This is in contrast, for example, to the aforementioned polyesterurethane and urethane-modified polyester polyols, in which the reactants are linked via urethane as well as ester linkages. Furthermore, these products include hydroxyl groups as their principal functional groups.

Optionally, the monofunctional alcohols, thiols, or other active hydrogen compounds (c) can contain additional polar groups which are substantially nonreactive with the isocyanate groups of the n-functional polyisocyanates (a), or at least less reactive than the isocyanate-reactive functional groups under typical reaction conditions, as described later and in the examples. Such groups can include nitro groups, carboxylate groups, urea groups, fluoro groups, silicon-containing groups and the like. The presence of such functional groups in alcohols/thiols (c), and thus in the finished polyurethane polyol, is believed to make such resins better pigment dispersants and also to improve the adhesion to certain substrates of the coating compositions containing same.

Further in accordance with the invention, the polyurethane polyols can be reacted with a suitable diisocyanate to form an adduct having a molar ratio of isocyanate:OH equivalents of no more than about 0.5:1. Such adducts can be used in coating compositions in the same manner as the polyurethane polyols themselves.

Further in accordance with the invention, the n-functional isocyanate (a) is reacted with the diol or triol or mixture thereof (b) and said isocyanate - reactive compound (c) in a manner such that substantially all of the isocyanate groups of said n-functional isocyanate (a) are reacted with one hydroxyl group on said diol or triol molecules or with said isocyanate-reactive compound (c), whereby the less reactive hydroxyl groups on said diol or triol remain substantially unreacted.

Further in accordance with the invention, the above coating film-forming materials can be used in combination with compounds having crosslinking functional groups and (optionally) with catalysts to provide a high solids coating material which is cured and dried to a film having excellent weathering characteristics, including acid rain resistance and non-yellowing behavior relative to other known film-forming materials. In accordance with one embodiment of the invention, a high solids, thermosetting coating composition comprises from about 20 to about 80 weight percent of a polyurethane polyol as described above, optionally up to about 80 weight percent of another polyol selected from the group consisting of polyester polyols, polyacrylate-polyols and alkyd polyols and from about 10 to about 50 weight percent of an at least partially alkylated melamine resin which acts as a crosslinker for the other components, all weight percentages being based on total vehicle solids.

While the composition of the present invention is particularly useful in automotive coatings, it can also be used for other transportation industry coatings, with plastics and for general industrial and decorative applications. The process of the present invention allows exceptionally good molecular weight control of the polyurethane polyol, which permits the formulation of high solids coatings with exceptionally low application viscosity. An unexpected

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beneficial feature of polyurethane polyols produced using this particular class of polyols is that for automotive coatings they provide good acid rain resistance when cured with melamine in a one-component coating. Other outstanding features of polyurethane polyols of the present invention are that they can be used to produce coatings having good UV durability, good chemical resistance, and other properties desirable not only for the automotive industry, but potentially for other applications such as appliances, metal furniture and business machines, for example.

As also indicated above, the diol component is selected from substantially monomeric diols wherein the hydroxyl groups are separated by 2 or 3 carbon atoms. The diol component may comprise a single such monomeric diol or combinations thereof.

For the purposes of the present description, this class of diols can be divided into two groups: (i) asymmetric diols - possessing hydroxyl groups of a different order, for example, one primary and one secondary hydroxyl group, and (ii) symmetric diols, in which both hydroxyl groups are of the same order, preferably primary.

Suitable triols can be used as additions or alternatives to the diols described above, as discussed below, but are generally not preferred because they lead to products of higher viscosity.

The n-functional isocyanate is substantially monomeric and is at least difunctional, with a functionality of 3 to 4 being most preferred. The isocyanate can be an isocyanurate of a monomeric diisocyanate; for example, the isocyanurate of 1,6-hexamethylenediisocyanate. The isocyanate can also be a biuret of a monomeric isocyanate; for example, a biuret of 1,6-hexamethylenediisocyanate. In addition, the isocyanate can be the reaction product of a diisocyanate and a polyhydroxy compound, such as the product of meta-tetramethylxylelenediisocyanate with trimethyolpropane. In the present invention, isocyanurates are preferred. The amount of isocyanate is chosen so that the ratio of the number of isocyanate equivalents to the number of moles of the monofunctional alcohol (or other isocyanate-reactive compound) and the diol or triol molecules is in the range of about 0.6 to about 1.4, preferably from 0.9 to 1.1. Typically the Mw/Mn of the reaction product ranges from about 1.1 to about 2.5 or about 3, wherein Mn ranges from about 300 to about 3,000, with the most preferred Mn being less than about 2,500.

Coatings comprising the above-described polyurethane polyol film-forming composition can be clear coatings wherein the overall coating weight percent solids ranges from about 40 percent to about 80 percent, and wherein the coating material (film-forming composition in a suitable solvent system) viscosity over the above solids range is from about 25 cps to about 300 cps at 25 degrees C.

The polyurethane polyol film-forming compositions of the present invention can also be used in pigmented paint or coating formulations. The overall coating weight percent solids ranges from about 40 percent to about 80 percent wherein the coating material viscosity over the above solids range is from about 25 cps to about 300 cps at about 25 degrees C. It has been found that single layer pigmented coatings made using the composition have a lower tendency to yellow when overbaked upon curing than do conventional acrylic and polyester enamels.

The use of the monofunctional alcohols/thiols or other compounds of (c) in place of a portion of the diol/triol component (b) results in polyurethane polyols having lower hydroxyl functionality than those prepared with the diols/triols alone. Such polyurethane polyols, as described in U. S. Patents Nos. 5,155,201; 5,130,405 and 5,175,227, all assigned to Applicants' Assignee, have been found to produce coating compositions which cure to films having many advantageous features, including acid etch resistance. Surprisingly, the coating compositions of the present invention which incorporate polyurethane polyols having lower hydroxyl functionality have been found to have equivalent acid etch resistance and reduced viscosity. The combination of acceptable acid etch resistance (of cured films) with reduced viscosities (of the polyurethane polyols and coatings containing same) is advantageous, since it permits the formulation of coatings compositions having higher solids contents which have the lower volatile organic contents (VOC) increasingly demanded by the marketplace.

To reduce the viscosity of such coating compositions while retaining similar acid etch resistance in the cured coatings (compared with products of these previous patents) is considered surprising and unexpected because the substitution of monofunctional species for diols reduces the hydroxyl content in the resulting resin, and thus the crosslink density of the network formed when the polyurethane polyol is cured with melamine. A polymer chemist would normally expect such effects to diminish chemical resistance properties of the cured coatings, which are normally enhanced by increasing crosslink density.

DETAILED DESCRIPTION OF THE INVENTION

The Polyurethane-Polyol Compositions

The polyurethane-polyol composition of the present invention can be synthesized using either isocyanates or polyisocyanates. The isocyanates are n-functional, wherein n is a number ranging from 2 to about 5, with a functionality of 2 to 4 being preferred, and a functionality of about 3 to 4 being most preferred. Due to variations in the preparation of such isocyanates, the n-values may be either integral or have intermediate values in the numerical ranges indicated. Preferred isocyanates are either biurets or isocyanurates of hexamethylenediisocyanate. Isocyanurates are typically obtained by cyclotrimerization of three moles of a diisocyanate. Biurets are typically obtained by the reaction of three moles of diisocyanate per mole of water.

The more preferred polyurethane-polyol compositions have a number average molecular weight (Mn) ranging from about 300 to about 3,000, with the ratio of weight average molecular weight (Mw) to number average molecular weight ranging from about 1.1 to about 3. Preferably, this ratio (polydispersity index) ranges from about 1.1. to about 2.5, and most preferably from about 1.1 to about 2.

Examples of isocyanates which can be used to synthesize the composition of the present invention include:

DIISOCYANATES such as 1,6-hexamethylenediisocyanate, available for example, as HMDI from Miles, formerly Mobay Chemical Corp.;

isophorone diisocyanate, available as IPDI from, for example, Huls America Inc.;

tetramethylxylylene diisocyanate, available for example, as TMXDI(meta) from Cytek;

2-methyl-1,5-pentane diisocyanate; 2,2,4-trimethyl-1,6-hexamethylene diisocyanate; 1,12-dodecane diisocyanate and methylene bis(4-cyclohexyl isocyanate) available for example, as Desmodur W (Trade-mark) from Miles; and

POLYISOCYANATES such as the biuret of HMDI, available for example, as Desmodur (Trade-mark) N from Miles; the isocyanurate of HMDI, available for example, as Desmodur (Trade-mark) N-3390 from Miles; the isocyanurate of IPDI, available for example, as Desmodur (Trade-mark) Z-4370 from Miles.; and the triisocyanate product of m-TMXDI and trimethylolpropane, available for example, as Cythane (Trade-mark) 3160 from Cytek.

The isocyanurates and biurets of each diisocyanate listed above can also be used to synthesize the compositions of the present invention. There are numerous n-functional isocyanates commercially available which can be used in the present invention, as indicated above.

Preferred asymmetric diols are those having from 3 to 18, more preferably 4 to 18, and especially 5 to 12 carbon atoms.

Examples of such asymmetric diols include: 2-ethyl-1,3-hexanediol (EHDO), available for example, from Union Carbide Corp.; 1,2-propanediol; 1,3-butanediol; 2,2,4-trimethyl-1,3-pentanediol, available for example, from Eastman Chemical Products, Inc.; and 1,12-octadecanediol, as well as 1,2-hexanediol, 1,2-octanediol and 1,2-decanediol. Preferred of these are 2-ethyl-1,3-hexanediol, 1,2-hexanediol, 1,2-octanediol, 1,2-decanediol and 2,2,4-trimethyl-1,3-pentanediol. Such asymmetric diols can be classified as 1,2-(α,β) and 1,3-(α,γ) diols. When such diols are reacted with the isocyanates under conditions favoring the reaction of substantially all available isocyanate groups with the more active hydroxyl groups of the diols, the remaining hydroxyl groups on the diols (or triols) will become sterically hindered toward further reactions.

If the synthesis temperature is higher than desired, the reactivity of the second hydroxyl group on the (former) diol molecule that has already reacted once with isocyanate increases relative to the hydroxyl groups on the unreacted diol. When this happens, the selectivity of the reaction between the isocyanate functional groups and the preferred hydroxyl group is reduced. The Mw/Mn ratio of the polyurethane-polyol compound is thereby detrimentally increased. Thus, in the method of synthesis of the polyurethane polyols of the present invention using asymmetric diols, the synthesis reaction temperature is typically controlled between about 15 degrees C and about 120 degrees C.

Preferred symmetric diols include those having from 2 to 18, more preferably 5 to 18 carbon atoms, and especially 5 to 12 carbon atoms. Specific examples include ethylene glycol, neopentyl glycol, 2,3-butanediol, 2,4-pentanediol, 1,3-propanediol, 2,2-diethyl-1,3-propanediol and 2-butyl-2-ethyl-1,3-propanediol. Preferred of these are neopentyl glycol, 2,3-butanediol, 2,2-diethyl-1,3-propanediol and 2-ethyl-2-butyl-1,3-propanediol.

Suitable triols having from 3 to about 18 carbon atoms can be used as alternatives to or in addition to the diols described above. The hydrocarbyl groups to which the hydroxyl groups are attached can be alkyl, alkenyl or alkaryl, with either symmetric or asymmetric molecular structure and arrangement of the hydroxyl groups (i.e., primary or secondary). Typical triols which are suitable include 2-ethyl-(2-hydroxymethyl)-1,3-propanediol, glycerol and 1,1,1-tris(hydroxymethyl)ethane.

The monofunctional compounds used as component (c) in synthesizing the polyurethane polyols can preferably be selected from alcohols and thiols having 18 carbon atoms or less. Such compounds can be represented by the formulas R-OH and R-SH, where R is a hydrocarbyl group having 18 carbon atoms or less and can be an alkyl, aklenyl, alkaryl group or the like. The R group can be linear or branched, cyclic or acyclic, and the alcohols and thiols can thus be primary, secondary or tertiary. The species presently preferred are the linear primary alcohols and thiols, with the most preferred being the short chain aliphatic species having from 2 to about 12 carbon atoms.

It is generally preferred that the components should be reacted at a temperature of about 125 degrees C or less, preferably ranging from about 15 degrees C to about 125 degrees C. If the reaction temperature is too high or too low, the molecular weight properties of the resulting polyurethane polyols may be undesirably compromised. Low temperature effects may be due to solubility effects, and are thus dependent upon the solvent(s) optionally employed. The time period can range from about 30 minutes to about 24 hours.

As mentioned above, the components may optionally be reacted in the presence of a polyurethane catalyst. Suitable polyurethane catalysts are conventional and may be utilized in conventional amounts. Of course, the particular choice of

catalyst type and amount will be dictated based upon a number of factors such as the particular components and reaction conditions. These and other factors are well-known to those skilled in the art, who can make the proper choices accordingly.
Presently preferred catalysts include tin and tertiary amine-containing compounds, such as organometallic tin compounds and tertiary alkylamines.

The principal reactants can be combined in any suitable sequence which produces reaction products having low polydispersity, some variations of which will produce preferred versions of the polyurethane polyols. For example, (i) the monofunctional isocyanate-reactive component (c) can be reacted with the n-functional isocyanate (a) and then the resulting intermediate can be reacted with the diol or triol component (b). (This is designated "Method 1".) Alternatively, (ii) the n-functional isocyanate (a) can be reacted with a mixture of the diol component (b) and the monofunctional component (c), preferably in the presence of a catalyst. (This is designated "Method 2".) Additionally, (iii) a portion of n-functional isocyanate (a) can be reacted with the monofunctional isocyanate-reactive component (c), the resulting intermediate can then be mixed with the remainder of the n-functional isocyanate (a) and the mixture reacted with the diol or triol component (b). (This is designated "Method 3".)

As is common in the preparation of polyurethanes, a variety of reaction products can be formed in such reactions, depending upon the reactants, their proportions and the reaction sequences employed. For purposes of the present invention, it is desired to obtain substantially homogeneous products having low polydispersity, preferably lower than about 2. In some cases it is advantageous to utilize a small proportion of nonfunctional polyurethanes in conjunction with the polyurethane polyols, whether generated in situ or added from a separate source.

Generally the reaction products of the processes used to prepare the polyurethane polyols will comprise species which can be represented by the following structure:

$$[HO{-}R^2{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}]_{x'}{-}R^1{-}{-}[{-}{-}NH{-}\overset{O}{\overset{\|}{C}}{-}R^3]_{y'}$$

wherein R^1 is the portion of an n-functional polyisocyanate, with n ranging from 2 to about 5, from which the isocyanate groups have been abstracted;

R^2 is the portion of a substantially monomeric diol having 2 or 3 carbon atoms between the hydroxyl groups from which at least one hydroxyl group has been abstracted,

R^3 is the portion of a monofunctional active hydrogen-containing, isocyanate group-reactive compound from which the active hydrogen has been abstracted, and

$X^1 + y^1$ = from 2 to about 5.

Preferably the diols of R^2 are selected from α,ß-diols and α,γ-diols.

As stated above, a variety of reaction products can be formed in these reactions. For example, polyisocyanates which are at least difunctional can be joined together by diols which have reacted di-endedly. The degree to which that occurs depends upon the selectivity of the particular diols and isocyanates employed, and on the degree of functionality of the precursor isocyanates.

Further in accordance with the invention, the polyurethane polyols described above can be reacted with a diisocyanate to form an adduct, the diisocyanate being combined with the polyol in amounts such as to result in isocyanate:OH equivalents ratios of no more than about 0.5:1 in the adducts formed. suitable diisocyanates include those described above for component (a).

Crosslinkers

Two melamine crosslinkers are illustrated in the examples below as useful with the polyurethane polyol compositions of the present invention to provide cured crosslinked coatings. There are numerous kinds of hydroxyl group-reactive crosslinkers which can be used with these polyurethane polyol compositions, such as polyisocyanates, blocked polyisocyanates and/or aminoplast resins. The blocking agents for the blocked polyisocyanate can be ketoximes, alcohols, phenolic compounds, malonic esters or acetoacetates. Presently preferred are the aminoplast resins, which generally speaking are aldehyde condensation products of melamine, urea, benzoguanamine or similar compounds. The most commonly used aldehyde is formaldehyde. These condensation products contain methylol or similar alkylol groups, and these alkylol groups are commonly at least partly etherified with an alcohol, such as methanol or butanol, to form alkylated ethers. The crosslinker resin can be substantially monomeric or polymeric depending on the desired final properties of the polyurethane-polyol cured coating. Monomeric melamine resins are preferred because they allow the formulation of coatings with higher solids contents. Polymeric melamines are useful in coatings where the use of a strong acid catalyst should be avoided.

Examples of readily available amino crosslinkers of the kind described above include: Hexamethoxymethylmelamine, such as Cymel (Trade-mark) 303, available from Cytek Industries, Inc.; mixed ether methoxy/butoxy methylmelamine, such as Cymel (Trade-mark) 1135, also available from Cytek; polymeric butoxy methylmelamine, such as M-281-M, available from Cook Composites and Polymers; and high imino polymeric methoxy-methylmelamine, such as Cymel (Trade-mark)325, available from Cytek. This list could include many other crosslinkers which differ by degree of polymerization, imino content, free methylol content, and ratios of alcohols used for etherification.

These aminoplast crosslinking agents can be utilized in widely varying weight ratios of polyurethane polyol to aminoplast, generally ranging from about 90:10 to 40:60, preferably from about 90:10 to 50:50.

Suitable isocyanate crosslinking agents include any of a number of those known for use in similar systems. Specific examples include the previously described n-functional isocyanates, especially the biuret and isocyanurate versions. Blocking of such isocyanates is well known to those skilled in the art and need not be detailed here.

As with the aminoplast crosslinking agents, the isocyanate crosslinking agents may also be utilized in widely varying amounts, but generally in an equivalents ratio of hydroxyl to isocyanate groups ranging from about 0.7 to about 2.2.

Crosslinkinc Catalyst

The crosslinking catalyst used in the examples below was a blocked dodecyl benzene sulfonic acid, such as Nacure (Trade-mark) 5226, available from King Industries. Other acid catalysts can be used as well. Acid catalysts are used to increase the rate of the crosslinking reaction in melamine-cured compositions. Generally, 0.1 to 5 percent by weight of the active catalyst is used, based on the coating formulation nonvolatile content. These acids may be blocked by a suitable compound, so that the catalyst is inactive until the coating is baked. Optionally, the catalyst may be used in an unblocked form, which may necessitate the formulation of a two-component coating. Since a single component coating is preferred for the reasons previously discussed, the work below was done using a blocked acid catalyst in a one component system. Examples of acids which may be used include phosphoric acid, alkyl acid phosphates, sulfonic acid and substituted sulfonic acids, and maleic acid or alkyl acid maleates. Examples of readily available catalysts include: para-toluenesulfonic acid (PTSA) such as Cycat 4040, available from Cytek; dodecylbenzene sulfonic acid (DDBSA) such as Bio-Soft 5-100, available from Stepan; phenyl acid phosphate (PAP); amine blocked DDBSA, such as Nacure 5226 and Nacure XP-158, available from King Industries; amine blocked PTSA, such as VP-451, available from Byk-Mallinckrodt; dinonylnaphthalene disulfonic acid (DNNDSA); and maleic acid.

This list could include numerous additional catalysts (blocked and unblocked) known to those skilled in the art. The type of catalyst used is determined by the desired bake schedule. Depending on the type of catalyst used, the bake conditions are typically from about 80 degrees C to about 200 degrees C.

The clear coatings described herein can be modified to produce pigmented coatings or paints. The paint formulas frequently contain a number of additives for flow, surface tension adjustment, pigment wetting, or solvent popping. Some typical additives follow: Flow aids such as A-620-A2 polybutylacrylate, available from Cook; Byk-320 silicone, available from Byk-Mallinckrodt; pigment wetting aids such as Disperbyk (Trade-mark), available from Byk-Mallinckrodt; UV absorbers, such as Tinuvin (Trade-mark) 900 from Ciba; and hindered amine light stabilizers, such as Tinuvin (Trade-mark) 292 from Ciba. Other additives may also be used. The coatings can contain from 0 to 400 weight percent of suitable pigments and/or extenders based upon the combined weights of the polyurethane polyol and the crosslinker and from 0 to 15 weight percent additives for improvement of coating properties, based upon total solids content of the coating.

These coating compositions may be applied to any number of well known substrates by any of a number of conventional application methods. Curing of the coatings may be conducted under a variety of conditions, although curing of the above-described one-component systems is preferably carried out under baking conditions, typically from about 80 degrees C to about 200 degrees C.

The foregoing general discussion of the present invention will be further illustrated by the following specific but nonlimiting examples.

EXAMPLES

Synthesis of the Polyurethane Polvols

COMPARATIVE EXAMPLES I, II AND III

For use as controls, polyurethane polyols based upon isocyanates and diols(only) without the monofunctional species of the invention, were prepared according to the methods of Example 1 of co-assigned U.S. Patent No. 5,155,201. Representative ingredients and properties of the polyols are shown in Table I below.

Examples IV and V are nonfunctional polyurethanes prepared by Method 2, with sufficient isocyanate employed to react with all available hydroxyl groups. As such, it is equivalent to complete replacement of the diol reactant by a monofunctional species such as an alcohol.

Coatings Formulated Using the Polyurethane-Polyol Composition

TABLE I

Polyurethane Polyols Prepared with Monofunctional Alcohols

Ex/Method	HDT LV	Des 3300	EHDO	Mono-functional Alcohol	BEPD	%NV	Visc. 20C	Mn	Mw/Mn
I		1.0 eq	1.0m			72.7	4470	1778	1.56
II	1.0 eq		1.0m			68.4	1330	1642	1.37
III		1.0 eq			1.0m	74.6	6100	1598	1.33
IV	1.0 eq			1.00m sBUT		75.1	1020	963	1.25
V		1.0 eq		1.00m sBUT		69.9	400	1093	1.32
1/1		1.0 eq	0.67m	0.33m sBUT		69.4	940	1378	1.48
2/1		1.0 eq	0.60m	0.40m sBUT		73.9	3025	1500	1.84
3/1		1.0 eq	0.50m	0.40m sBUT		69.9	700	1390	1.47
4/1		1.0 eq	0.33m	0.67m sBUT		70.9	580	1284	1.44
5/1		1.0 eq		0.33m sBUT	0.67m	72.2	1040	1442	1.37
6/2		1.0 eq	0.73m	0.27m EH		66.7	1360	1912	2.06
7/2	1.0 eq		0.65m	0.35m OCDA		70.0	N/A	1926	1.62
8/2	1.0 eq		0.65m	0.35m DDA		67.2	1500	1857	1.57
9/2	1.0 eq		0.73m	0.27m DA		68.2	1440	2031	1.64
10/2		1.0 eq	0.80m	0.20m DA		66.9	1600	2182	1.92
11/3		1.0 eq	0.67m	0.33m sBUT		74.0	3085	1528	1.84

HDT LV = trimer containing isocyanurate ring of HMDI
EHDO = 2-ethyl,1,3-hexanediol

EH = 2-ethylhexanol
OCDA = octadecanol
sBUT = secondary butanol

BEPD = 2-butyl-2-ethyl,1,3-propanediol
Des 3300 = (Desmodur 3300) = isocyanurate of HMDI
DA = decyl alcohol
DDA = dodecanol
HMDI = hexamethylene diisocyanate

EXAMPLES 1 to 5
(Method 1, monoalcohol reacted with NCO, then intermediate added to diol)

In these examples, the monofunctional alcohol is added to all of the isocyanate component and the resulting intermediate is then added to the diol component for reaction. Representative reaction procedures are outlined below.

Example 1:

Polyurethane polyol made by the reaction of secondary butanol and 2-ethyl-1,3-hexanediol (EHDO) with Desmodur 3300. (isocyanurate of hexamethylene diisocyanate)

REAGENTS:

Reagent	Eq.Wt.	Grams	Eq's	Wt%
Kettle Charge (A)				
sec. butanol	74.12	146.0	1.97	5.409
10% DBTDL (in butyl acetate)		1.3		0.048
Feed-(B)				
Des3300	194.0	1.158.2	5.97	42.907
Methyl amylketone		809.2		29.978
Kettle Charge (C)				
EHDO	146.0	584.0	8.0	21.635
10% DBTDL (in Butyl acetate)		0.6		0.022

DBTDL = Dibutyl tin dilaurate

Into a 5L 4NRB flask fitted with a reflux condenser, mechanical stirrer, thermometer, monomer inlet adapter, and maintained under a nitrogen atmosphere, kettle charge (B) was placed. After heating the mixture 70 degrees C, feed (A) was added to 1.3 ml/min (2hrs), maintaining the temperature at 70 degrees C. This mixture (AB) was held at 70 degrees C for 1.5 hr, cooled down to room temperature and transferred to 1 gallon can. Kettle charge (C) was placed in the original 5L

4NRB (which prior to that was rinsed with solvent). After heating (C) to 70 degrees C, feed (AB) was added at 14.5 ml/min (2 hr). After completion of the feed addition, the temperature was held at 70 degrees C for an additional 1.5 hr, after which the resin was cooled and transferred to a 1 gal container.

% Non-volatiles were measured on ca. 0.5 g samples, diluted with ca. 1.0 g MAK, stirred with a tared paper clip, and heated for 1 hr at 110 degrees C. Brookfield Viscosity was measured using a #4 spindle, 10 rpm, at 25 degrees C. Molecular weights are by GPC, using polyethylene glycol/polystyrene standards.

CHARACTERIZATION

% Non-volatiles: 70.0 (theory); 69.4 (measured)
Hydroxyl equivalent weight: 473
Viscosity: 940 mPa.s
Mn: 1378
Mw: 2035
Mw/Mn: 1.5

The remaining Examples 2 to 5 were prepared using similar reaction procedures. The proportions of reactants and results are shown in Table I.

Examples 6 to 10

(Method 2, NCO added to mixture of diol and monoalcohol.)

Example 6

Polyurethane polyol made by the reaction of secondary butanol and 2-ethyl-1,3-hexanediol (EHDO) with Desmodur 3300.

Reagents	Molecular Weight	Equivalent Weight	Amount(g)	Equivalents/ Moles	Weight %
A: Kettle Charge					
2-ethyl-1-hexanol	130.00	130.00	228.20	1.75	7.32%
2-ethyl-1,3-hexanediol	146.00	73.00	692.80	4.75	22.21%
2-heptanone			467.40		14.99%
10% DBTDL Solution in n-butyl acetate			2.20		0.07%
B: Isocyanate Feed					
Desmodur N-3300 isocyanurate		194.00	1261.00	6.50	40.43%
2-heptanone			467.40		14.99%
			3119.00		100.00%

Characterization:

% non-volatiles:	Theoretical:	70.00%	70.00%
	Actual:	67.00%	67.00%
OH Equivalent weight:	Theoretical:	459.4	459.4
Brookfield Viscosity:	1360 mPa.s		
Mn: 1912			
Mw: 3935			
Mw/Mn: 2.06			

Into a 5L, 4 neck roundbottom flask fitted with a ref lux condenser, mechanical stirrer, thermocouple, thermowatch, heating mantle, monomer inlet adapter, and maintained under a nitrogen atmosphere, kettle charge (A) was placed. After heating the mixture to 70 degrees C, the isocyanate feed (B) was added over a 2.5 to 3 hour period at a rate of approximately 11.5 ml/minute with a Masterflex peristaltic pump and #16 Viton (Trade-mark) tubing, maintaining the temperature at 70 degrees C throughout. The resin was held an additional 1.5 hours at 70 degrees C then cooled to room temperature and decanted into a 1 gallon metal can.

% Non-volatiles were measured on ca. 0.5 g samples, diluted with ca. 1.0 g 2-heptanone, stirred with a tared wire paper clip, and heated for 1 hour at 110 degrees C. Brookfield Viscosity was measured on a 25 degree C resin sample using a #4 spindle at 10.0 rpm. Molecular weights were determined by Gel Permeation Chromatography using polyethylene glycol/polystyrene standards.

The remaining Examples 7 through 11 were prepared using similar reaction procedures. The proportions of reactants and results are shown in Table I.

Example 12

(Method 3, Reaction product of alcohol and part of isocyanate is mixed with remainder of isocyanate and the mixture is then added to the diol.)

Polyurethane polyol made by the reaction of secondary butanol and 2-ethyl-1,3-hexanediol (EHDO) with Desmodur (Trade-mark) 3300.

REAGENTS:

Reagent	Eq.Wt.	Grams	Eq's	Wt%
Kettle Charge (A)				
sec. butanol	74.12	224.1	3.023	5.800
Methyl amyl ketone		257.9		6.672
10% DBTDL (in butyl acetate)		0.9		0.023
Feed-(B)				
Des3300	194.0	1.777.0	9.160	45.971
Methyl amyl ketone		450.0		11.641
Kettle Charge (C)				
EHDO	146.0	896.0	12.274	23.179
Methyl amyl ketone		257.8		6.669
10% DBTDL (in Butyl acetate)		1.8		0.047

DBTDL = Dibutyl tin dilaurate

Into a 5L 4NRB flask fitted with a reflux condenser, mechanical stirrer, thermometer, monomer inlet adapter, and maintained under a nitrogen atmosphere, kettle charge (A) was placed. After heating the mixture to 70 degrees C, 40% of feed (B) was added at 8.1 ml/min (2 hrs), maintaining the temperature at 70 degrees C. The remaining 60% of feed (B) was added over 10 minutes, still maintaining the temperature at 70 degrees C. This mixture (AB) was transferred to 1 gal can and cooled to room temperature. Kettle charge (C) was placed in the original 5L 4NRB (which prior to that was rinsed with solvent). After heating (C) to 70 degrees C, feed (AB) was added at 17.0 ml/min (2.5 hr).

After completion of the feed addition, the temperature was held at 70 degrees C for an additional 1.5 hr. after which the mixture was cooled and transferred to a 1 gal container.

% Non-volatiles were measured on ca. 0.5 g samples, diluted with ca. 1.0 g MAK, stirred with a tared paper clip, and heated for 1 hr at 110 degrees C. Brookfield viscosity was measured using a #4 spindle, 10 rpm, at 25 degrees C.

Molecular weights are by GPC, using polyethylene glycol-/polystyrene standards.

CHARACTERIZATION:

% Non-volatiles: 75.0 (theory); 74.0. (measured)
Hydroxyl equivalent weight: 472
Viscosity: 3085 mPa.s Mn: 1526
Mw: 2807 Mw/Mn: 1.84

ACID ETCH SPOT TESTING

The following Table II illustrates the acid etch properties of polyurethane polyol resins, modified with monofunctional alcohol (sec. Butanol). All resins were incorporated into formulations consisting of 35 wt% melamine (Cymel (Trade-mark) 303), 11% MPL-200 (a polyurethane polyol, prepared from as in Example II from HDTLV and 2-ethyl-1,3-hexanediol) (which entered the formula in a fumed silica dispersion for rheology control), 3% resin from commercial additives and 51% PUPO resin of interest. All formulas contained (based on resin solids) 0.4% Nacure (Trade-mark) 5226 acid catalyst, 2.7% Sanduvor 3206 UV absorber, 1.34% Tinuvin (Trade-mark) 440 hindered amine light stabilizer, 10.6% Aerosil (Trade-mark) R972 fumed silica, and 0.4% Coroc(Trade-mark)A-620-A2 flow agent. Substitution of the diol with monofunctional alcohol was done at 1/3, 1/2 and 2/3 molar replacement either by blending MPL-200 (the polyurethane polyol of Example I) with a non-functional polyurethane of Example III (MPL-457) or by using resins which were prepared by reacting monoalcohol/diol combinations with Desmodur (Trade-mark) 3300 multifunctional isocyanate, utilizing the method previously described. The clearcoats were sprayed over a black acrylic/melamine basecoat, wet on wet, and baked for 17 min at 290 degrees F (metal temperature). All dry films were measured to be between 1.8 and 2.1 mils. The films were tested for acid etch resistance by the acid spot test disclosed in U.S. Patent No. 5,130,405, column 11.

A simulated acid rain solution was formulated by mixing 1 normal aqueous solutions of sulfuric, nitric and hydrochloric acids at a volume ratio of 65/30/5, respectively. The resulting acid mixture had a pH of 0.2 units.

Panels prepared in Examples were tested for acid resistance. Each panel was spotted with 0.5 ml of the acid solution mentioned above, and was left standing uncovered at room temperature. Evaporated water was replaced with more acid solution at regular intervals (2 hours) so that the spot size remained the same throughout testing. At the end of the exposure time, the panel was rinsed with distilled water and allowed to dry overnight. The panels were inspected for damage the following day. The exposure times required to damage the various systems are shown below in Table II.

TABLE II
Acid Etch Spot Testing of Coatings

Example /Preparation method	Blend Ratio (based on resin solids)	Diol Type	Diol Level (moles)	sec-Butanol Level (moles)	Time to form a ring (hours)
Comparative Example II	---	EHDO	1.0	0.0	9
5/1	---	BEPD	0.67	0.33	10
1/1	---	EHDO	0.67	0.33	8
Blend II & V	0.67 : 0.33	EHDO	0.67	0.33	8
3/1	---	EHDO	0.5	0.5	7
Blend II & V	0.5 : 0.5	EHDO	0.5	0.5	10
4/1	---	EHDO	0.33	0.67	10
Blend II & V	0.33 : 0.67	EHDO	0.33	0.67	10
Commercial acrylic control*	---	---	---	---	3

* A commercially produced melamine crosslinked acrylic clearcoat.

Several important conclusions can be reached from these data:

1) Polyurethane polyols can be prepared from mixtures of monofunctional alcohols and diols to give coatings with acid etch resistance. However, as seen in Table I, the viscosities of these "modified" polyurethane polyols were lower than those of the conventional polyurethane polyols such as Comparative Examples I, II and III.

2) There is no large difference between the acid etch resistance properties of coatings based on blending non-functional polyurethane polyols and fully diol-derived polyurethane polyols, and coatings based on polyurethane polyols having the same level of monofunctional alcohol reacted into the polyol in a statistically random manner.

3) Polyurethane polyols prepared from 2-butyl-2-ethyl-1,3 propanediol (BEPD) are better than those prepared from 2-ethyl-1,3-hexanediol. The species prepared from BEPD produce coatings having greater acid etch resistance. While not wishing to be bound by theory, it is believed that this is due to steric hindrance provided by the bulky butyl groups.

COMPARATIVE EXAMPLES VI TO X

The resin solution from Example I (a conventional polyurethane polyol) was used to formulate melamine crosslinked clear coatings at 30 and 45% by weight hexamethoxymethyl melamine, based on total resin solids. For the sake of comparison, a typical hydroxy functional polyacrylate was formulated into coatings at the same levels of melamine. All samples were catalyzed, with an acid catalyst such as Nacure 5226 available from King Industries, at 0.38% active catalyst based on resin solids. Samples were reduced to 60% nonvolatile (NV) with butyl acetate and were drawn down at 1.5-1.8 mils dry film thickness on aluminum test panels. The coatings were cured 30 minutes at about 250°F.

The panels produced in these Examples were subsequently tested for acid resistance as described above for the Examples of Table III.

TABLE III

EX/POLYMER	MELAMINE LEVEL	HOURS TO FIRST SPOT	HOURS TO FILM DEGRADATION
VI Hydroxy-functional Polyacrylate	30%	4	Not Degrade after 7 hrs
VII Hydroxy-functional Polyacrylate	45%	2	4
VIII Polyurethane-Polyol	30%	No Spot, 7 hrs.	---
IX Polyurethane-Polyol	45%	No Spot, 7 hrs.	---
X Two Component Acrylic Urethane		No Spot, 7 hrs.	---

The above data suggest that a significant improvement in acid resistance can be obtained by the replacement of an acrylic resin with a polyurethane polyol of co-assigned U.S. Patent No. 5,155,201. The melamine crosslinked polyurethane-polyol coatings displayed acid resistance approaching that of a two component acrylic urethane control, which is known for its acid resistance. The two-component coating was an acrylic urethane based on a hydroxy functional polyacrylate resin, which was crosslinked with Desmodur N-3390 from Miles. The coatings prepared from the polyurethane polyols of the present invention provide comparable acid etch resistance when cured, with the advantage of lower viscosity during application.

HYPOTHETICAL EXAMPLE XI

A single layer pigmented top coat is prepared as follows: About 150 parts by weight of polyurethane-polyol of the type described in the above Examples are placed in a mixing vessel. To this was added about 183 parts of titanium dioxide pigment (Titanox 2160 available from N.L. Chemicals Inc.). The two materials are blended using high speed dispersion equipment. After dispersion of the pigment, the following ingredients are added: About 106 parts by weight of melamine crosslinker (Cymel 303, available from Cytek); about 53 parts by weight of solvent (butyl acetate); about 12 parts by weight of blocked acid-catalyst (Nacure 5226, available from King Industries); about 96 parts by weight of an additional solvent (methyl amyl ketone); and about 150 additional parts by weight of the same polyurethane-polyol.

The nonvolatile content of the resulting white topcoat is about 65.0% by weight. This topcoat is applied to 20 gauge phosphated steel test panels using commercially available atomization spray equipment, to a dry, cured coating thickness of about 2.0 mils. The coating is dried and cured by oven baking at about 250 degrees F for a time period of about 30 minutes.

Only a limited number of preferred embodiments of the invention have been described above. However, one skilled in the art will recognize the numerous substitutions, modifications and alternations which can be made without departing from the spirit and scope of the invention as limited by the following claims.

CLAIMS:

1. A polyurethane-polyol composition comprising the reaction product of:

(a) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5;

(b) x moles of at least one component diol or triol or mixtures thereof, said diol or triol being selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon atoms; and

(c) y moles of a compound containing from 1 to 18 carbon atoms and a single functional group capable of reacting with an isocyanate, wherein the sum of x+y is about 0.6 to 1.4 and y is about 0.01x to about 75x, provided that the NCO/OH equivalent ratio is less than 0.976.

2. The composition of Claim 1 wherein said n-functional isocyanate (a) is selected from the group consisting of the isocyanurates and biurets of monomeric di-isocyanates, and reaction products of diisocyanates and polyhydroxy compounds.

3. The composition of Claim 2 wherein said isocyanate (a) is selected from the group consisting of hexamethylene diisocyanate, isophorone diisocyanate, tetramethyl xylylene diisocyanate, 2-methyl-1,5-pentane diisocyanate, 2,2,4-trimethyl-1,6 hexamethylene-diisocyanate, 1,12-dodecane diisocyanate and methylene-bis(4-cyclohexyl isocyanate).

4. The composition of Claim 1 wherein said diol or triol is asymmetric.

5. The composition of Claim 2 wherein said diol is selected from the group consisting of 2,2,4-trimethyl-1,3-pentanediol,
2-ethyl-1,3-hexanediol, 1,2-propanediol, 1,2-hexanediol, 1,2-octanediol, 1,2-decanediol, 1,2-octadecanediol and 1,3-butanediol.

6. The composition of Claim 1 wherein said diol or triol contains hydroxyl groups which are symmetric.

7. The composition of Claim 6 wherein said hydroxyl groups are all primary.

8. The composition of Claim 1 wherein the isocyanate-reactive compound (c) is a single active hydrogen-containing compound.

9. The composition of Claim 1 wherein said compound (c) is a alcohol or thiol characterized by the formulae

R-OH and R-SH,

wherein R is a hydrocarbyl group containing from 1 to 18 carbon atoms which can be alkyl, alkenyl, aryl or alkaryl.

10. The composition of Claim 9 wherein said compound (c) is an aliphatic alcohol having from about 2 to about 12 carbon atoms.

11. The composition of Claim 1 wherein said compound (c) is an amine selected from the group represented by the formulae $R\text{-}NH_2$ and $R^1\text{-}NH\text{-}R^2$ and $(CH_2)_z\text{-}NH$, wherein each R is a hydrocarbyl group having from 1 to 18 carbon atoms, the sum of the carbon atoms in R^1 and R^2 also being from 1 to 18, and wherein z is from 4 to about 6.

12. The polyurethane polyol composition of Claim 1 wherein the ratio of the weight-average molecular weight (Mw) to the number average molecular weight (Mn) ranges from about 1.1 to about 3, and wherein Mn ranges from about 300 to about 3,000.

13. A polyurethane-polyol composition comprising the reaction product of:

(a) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5;

(b) x moles of at least one component diol or triol or mixtures thereof, said diol or triol being selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon atoms; and

(c) y moles of a compound containing from 1 to 18 carbon atoms, a single isocyanate-reactive functional group capable of reacting with an isocyanate, and at least one additional functional group which is a polar group and is less reactive with isocyanate groups than said isocyanate-reactive functional group under typical reaction conditions, wherein the sum of x+y is about 0.6 to 1.4 and y us about 0.01x to about 75x, provided that the NCO/OH equivalent ratio is less than 0.976.

14. The polyurethane polyol of Claim 13 wherein said polar group is selected from the group consisting of a nitro group, carboxylate group, urea group, fluoro group and silicon-containing groups.

15. A method of preparing a polyurethane-polyol composition comprising the steps of:

(a) providing about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5;

(b) providing about x moles of at least one substantially monomeric diol or triol or mixtures thereof, wherein the hydroxyl groups on each diol or triol molecule are separated by 2 or 3 carbon atoms;

(c) providing about y moles of a compound having from 1 to 18 carbon atoms and a single functional group capable, of reacting with an isocyanate, wherein the sum of x + y is in the range of from about 0.6 to about 1.4 and y is about 0.01x to about 75x, provided that the NCO/OH equivalent ratio is less than 0.976; and

(d) reacting said n-functional isocyanate (a) with said diol or triol or mixture thereof (b) and the isocyanate-reactive compound (c).

16. The method of Claim 15 wherein said n-functional isocyanate
(a) is reacted with said diol or triol or mixture thereof (b) and said isocyanate-reactive compound (c) in a manner such that substantially all of the isocyanate groups of

said n-functional isocyanate (a) are reacted with one hydroxyl group on said diol or triol molecules or with said isocyanate-reactive compound (c), whereby the less, reactive hydroxyl groups on said diol or triol remain substantially unreacted.

17. The method or Claim 15 wherein the step (d) reaction is carried out in the presence of a catalyst, and wherein the concentration of said catalyst ranges from an effective amount from 0.1 to about 5 percent by weight based on nonvolatile solids.

18. The method of Claim 17 wherein said catalyst is selected from the group consisting of organometallic compounds and tertiary alkyl amines.

19. The method of Claim 18 wherein said catalyst is an organometallic tin compound.

20. The method of Claim 15 wherein said n-functional isocyanate (a) is selected from the group consisting of isocyanurates of monomeric diisocyanates, biurets or monomeric diisocyanates and reaction products of diisocyanates and polyhydroxy compounds.

21. The method or Claim 15 wherein reaction step (d) is carried out over a temperature range from about 15 degrees C to about 125 degrees C over a time period ranging from about 30 minutes to about 24 hours.

22. The method of Claim 15 wherein the isocyanate and diol or triol components are linked substantially via urethane linkages.

23. The method of Claim 15 wherein said diol or triol component (b) and said isocyanate-reactive component (c) are admixed and then reacted in the presence of a catalyst with the isocyanate component.

24. The method of Claim 15 wherein said isocyanate-reactive component (c) is reacted with said isocyanate component (a) and the resulting intermediate is then reacted with said diol or triol component (b).

25. The method of Claim 15 wherein a portion of said n-functional isocyanate (a) is reacted with said isocyanate-reactive component (c), the resulting intermediate is then admixed with the remainder of said n-functional isocyanate (a) and the resulting mixture reacted with said diol or triol component (b).

26. The method of Claim 25 wherein said component (c) is an alcohol or thiol characterized by the formulas R-OH and R-SH, wherein R is a hydrocarbyl group containing from 1 to 18 carbon atoms which can be alkyl, alkenyl, aryl or alkaryl.

27. The method of claim 15 wherein said isocyanate-reactive component (c) is a single active hydrogen-containing compound.

28. The method of claim 15 wherein said isocyanate-reactive component (c) is a primary or secondary amine.

29. A method of preparing an adduct of a polyurethane-polyol and a diisocyanate comprising the step of reacting a diisocyanate with the reaction product of the method of Claim 15.

30. A coating composition comprising:

(a) polyurethane-polyol composition comprising the reaction product of:

(1) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5;

(2) x moles of at least one component diol or triol or mixtures thereof, said diol or triol being selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon atoms; and

(3) y moles of a compound containing from 1 to 18 carbon atoms and a single functional group capable of reacting with an isocyanate, wherein the sum of x+y is about 0.6 to 1.4 and y is about 0.01x to about 75x, provided that the NCO/OH equivalent ratio does not exceed unity;

(b) a cross linker selected from the group consisting of aminoplast resins, polyisocyanates, and blocked polyisocyanates;

(c) 0.1 to 5 percent by weight of a suitable catalyst for the crosslinking reaction between the polyurethane polyol of step (a) and the crosslinker of step (b), based on the nonvolatile content;

(d) a solvent or solvent blend compatible with the overall coating composition;

(e) 0-400 percent by weight of suitable pigments and/or extenders based on the combined weights of the polyurethane polyol of step (a) and the crosslinker of step (b); and

(f) 0-15 percent by weight of additives for improvement of coating properties, based on total solids content of the coating, wherein solids refers to the cured coating weight.

31. The coating composition of Claim 30, wherein said crosslinker is an aminoplast resin.

32. The coating composition of Claim 31, wherein the aminoplast resin is selected from the group consisting of aldehyde condensation products of melamine, urea resin, benzoguanamine resin, and partially or fully alkylated ethers thereof.

33. The coating composition of Claim 31, wherein said aminoplast resin is reacted with an alcohol to form an at least partially alkylated ether thereof.

34. The coating composition of Claim 30, wherein said crosslinker is a polyisocyanate or blocked polyisocyanate.

35. The coating composition of Claim 34, wherein the blocking agent for the blocked polyisocyanate is selected from the group consisting of ketoximes,

alcohols, phenolic compounds, malonic esters, and acetoacetates.

36. The coating composition of Claim 30, wherein said polyurethane-polyol has an Mw/Mn ranging from about 1.1 to 3 and an Mn ranging from about 300 to 3,000.

37. The coating composition of Claim 30 wherein said polyurethane polyol is reacted with at least one diisocyanate to form an adduct therewith.

38. A high solids, thermosetting coating composition comprising:

(a) about 20% to about 80% by weight of a polyurethane polyol composition comprising the reaction product of:

(1) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5;

(2) x moles of at least one component diol or triol or mixtures thereof, said diol or triol being selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon atoms; and

(3) y moles of a compound containing from 1 to 18 carbon atoms and a single functional group capable of reacting with an isocyanate, wherein the sum of x+y is about 0.6 to 1.4 and y is about 0.01x to about 75x, provided that the NCO/OH equivalent ratio does not exceed unity;

(b) about 0% to about 80% by weight of a polyol selected from the group consisting of polyester polyols, polyacrylate-polyols and alkyd polyols; and

(c) about 10% to about 50% by weight of an at least partially alkylated melamine resin which acts as a crosslinker for components (a) and (b); with the above weight percentages being based on total vehicle solids.

39. A polyurethane polyol composition comprising reaction products characterized by the structure

$$[HO-R^2-O-\overset{O}{\overset{\|}{C}}-NH-]_{x'}-R^1--[--NH-\overset{O}{\overset{\|}{C}}-R^3]_{y'},$$

wherein R^1 is the portion of an n-functional polyisocyanate, with n ranging from 2 to about 5, from which the isocyanate groups have been abstracted, R^2 is the portion of a substantially monomeric diol selected from the group consisting of α,β-diols and α,γ-diols from which the hydroxyl group have been abstracted, R^3 is the portion of a monofunctional active hydrogen-containing, isocyanate group-reactive compound containing from 1 to 18 carbon atoms, from which the active hydrogen has been abstracted, and x'+y' = from 2 to 5, and the NCO:OH equivalent ratio is less than 0.976.

40. A mixture of the polyurethane-polyol composition of claim 1 with a nonfunctional polyurethane.

41. A mixture of the polyurethane-polyol composition of claim 13 with a nonfunctional polyurethane.

42. The method of claim 15 further comprising the step of

(e) mixing the resulting polyurethane-polyol with a non-functional polyurethane.

43. The coating composition of claim 30 further comprising:

(g) a nonfunctional polyurethane.

44. A high solids, thermosetting coating composition comprising:

(a) about 20% to about 80% by weight of a mixture of:

(i) a polyurethane polyol comprising the reaction product of:

(1) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5;

(2) x moles of at least one component diol or triol or mixtures thereof, said diol or triol being selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon atoms; and

(3) y moles of a compound containing from 1 to 16 carbon atoms and a single functional group capable of reacting with an isocyanate, wherein the sum of x+y is about 0.6 to 1.4 and y is about 0.01x to about 75x, provided that the NCO/OH equivalent ratio does not exceed unity; and

(ii) a nonfunctional polyurethane;

(b) about 0% to about 80% by weight of a polyol selected from the group consisting of polyester polyols, polyacrylate-polyols and alkyd-polyols; and

(c) about 10% to about 50% by weight of an at least partially alkylated melamine resin which acts as a crosslinker for components (a) and (b);
with the above weight percentages being based on total vehicle solids.

45. A mixture of the polyurethane polyol composition of claim 39 with a nonfunctional polyurethane.

46. A polyurethane-polyol composition comprising:
(I) about 33-67% of the reaction product of:
(1) about one mole of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, and
(2) 0.8n to 1.2n moles of at least one component diol or triol or mixtures thereof, said diol or triol being selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon atoms; and
(II) about 33-67% of the reaction product of:
(1) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, and
(2) one mole of a compound containing from 1 to 18 carbon atoms and a single functional group capable of reacting with an isocyanate.

47. A polyurethane-polyol composition comprising:
(I) about 33-67% of the reaction product of:

(1) about one mole of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, and

(2) 0.8n to 1.2n moles of at least one component diol or triol or mixtures thereof, said diol or triol being selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon-atoms; and

(II) about 33-67% of the reaction product of:

(1) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, and

(2) one mole of a compound containing from 1 to 18 carbon atoms, a single functional group capable of reacting with an isocyanate, and at least one additional functional group which is a polar group and is less reactive with isocyanate groups than said isocyanate-reactive functional group under typical reaction conditions.

48. A method of preparing a polyurethane-polyol composition comprising the steps of:

(a) reacting about *one* mole of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, with about 0.8n to 1.2n moles of at least one substantially monomeric diol or triol or mixtures thereof, wherein the hydroxyl groups *on* each diol or triol molecule are separated by 2 or 3 carbon atoms;

(b) reacting about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, with about one mole of a compound having from 1 to 18 carbon atoms and a single functional group capable of reacting with an isocyanate;

(c) mixing about 33-67% of the reaction product of (a) with about 33-67% of the reaction product of (b).

49. A coating composition comprising: (a) a mixture of

(i) about 33-67% of the reaction product of:

(1) about one mole of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, and

(2) 0.8n to 1.2n moles of at least one component diol or triol or mixtures thereof, said diol or triol being selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon atoms; and

(ii) about 33-67% of the reaction product of:

(1) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, and

(2) one mole of a compound containing from 1 to 18 carbon atoms and a single functional group capable of reacting with an isocyanate;

(b) a cross linker selected from the group consisting of aminoplast resins, polyisocyanates, and blocked polyisocyanates;

(c) 0.1 to 5 percent by weight of a suitable catalyst for the crosslinking reaction between the polyurethane polyol of step (a) and the crosslinker of step (b), based on the nonvolatile content;

(d) a solvent or solvent blend compatible with the overall coating composition;

(e) 0-400 percent by weight of suitable pigments and/or extenders based on the combined weights of the polyurethane polyol of step (a) and the crosslinker of step (b); and

(f) 0-15 percent by weight of additives for improvement of coating properties, based on total solids content of the coating, wherein solids refers to the cured coating weight.

50. A high solids, thermosetting coating composition comprising:

(a) about 20% to about 80% by weight of a mixture of

(I) about 33-67% of the polyurethane polyol comprising the reaction product of:

(1) about one mole of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, and

(2) 0.8n to 1.2n moles of at least one component diol or triol or mixtures thereof, said diol or triol being selected from substantially monomeric species wherein the hydroxyl groups are separated by 2 or 3 carbon atoms;

(II) about 33-67% of a polyurethane-polyol composition comprising the reaction product of:

(1) about one NCO equivalent of an n-functional isocyanate compound, wherein n is a number ranging from 2 to about 5, and

(2) one mole of a compound containing from 1 to 18 carbon atoms and a single functional group capable of reacting with an isocyanate;

(b) about 0% to about 80% by weight of a polyol selected from the group consisting of polyester polyols, polyacrylate-polyols and alkyd polyols; and

(c) about 10% to about 50% by weight of an at least partially alkylated melamine resin which acts as a crosslinker for components (a) and (b):

with the above weight percentages being based on total vehicle solids.

51. A polyurethane polyol composition comprising a mixture of

(A) about 33-67% of the reaction product characterized by the structure:

$$[HO{-}R^2{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}]_n{-}{-}R^1 ,$$

and

(B) about 33-67% of the reaction product characterized by the structure:

$$[R^3{-}\overset{O}{\overset{\|}{C}}{-}NH{-}]_n{-}{-}R^1$$

wherein R^1 is the portion of an n-functional polyisocyanate, with n ranging from 2 to about 5, from which the isocyanate groups have been abstracted, R^2 is the portion of a substantially monomeric diol selected from the group consisting of α,β-diols and α,γ-diols from which the hydroxyl groups have been abstracted, and R^3 is the portion of a monofunctional active hydrogen-containing, isocyanate group-reactive compound containing from 1 to 18 carbon atoms, from which the active hydrogen has been abstracted.