

TWO-COMPONENT WATERBORNE POLYURETHANE COATING

This invention relates generally to two component aqueous polyurethane dispersions that have a reduced solvent content. More particularly, this invention relates to two component aqueous polyurethane dispersions, containing low viscosity polyisocyanates, that can be cured at ambient temperature, or, if desired, at higher temperature. The coatings prepared therefrom have improved hardness, gloss and solvent resistance compared to conventional aqueous polyurethane dispersions.

One component or two component solvent based polyurethane compositions have been known for many years to produce high quality coatings. However, due to the increasingly strict regulations on the allowable amount of volatile organic compounds emitted during the application of coatings, water based polyurethane have become very important in recent years.

One component aqueous polyurethane dispersions are well known and are used in the production of a variety of useful polyurethane products, including, for example, coatings, adhesives, sealants, and the like. Such dispersions are typically produced by dispersing a water-dispersable, isocyanate-terminated polyurethane prepolymer in an aqueous medium together with an active hydrogen containing chain-extender.

The prepolymers used in the preparation of these one component dispersions are generally substantially linear, that is to say difunctional, and are typically obtained by reacting an excess of a diisocyanate with an isocyanate-reactive component comprising a polymeric diol in the presence of a reactive compound, for example a diol, containing an

ionic or non-ionic hydrophilic group or site.

Even though the one component water based polyurethane dispersions have reduced amounts of organic solvent relative to comparable solvent-based coating compositions, for many applications, they do not exhibit similar coating performance similar to solvent based coating compositions, especially with respect to the properties of gloss, hardness and solvent resistance. This difference is mainly attributable to the lack of chemical crosslinking during the formation of films using the one component, water based systems.

Solvent based two component polyurethane compositions achieve the desired chemical crosslinking by using multifunctional polyisocyanates, such as those containing isocyanurate groups. Multi-functional polyisocyanates have high viscosities and are hydrophobic in nature. They cannot be dispersed in aqueous dispersions, and hence are unsuitable for water based polyurethane compositions.

Previous attempts to carry out the crosslinking of two-component aqueous polyurethane dispersions using hydrophilic polyisocyanates have been reported, as described, for example, in U.S. Patent 5,200,489 and 5,252,696. These patents disclosed the preparation of a water dispersable polyisocyanate, employing an internal emulsifier, that can be used to prepare two component polyurethane compositions. However, this internal emulsifier renders the coating resulting from the polyisocyanates sensitive to water. Among the disadvantages of such prior art two-component water

based polyurethane coating compositions, prepared using water dispersable polyisocyanates, are a shorter pot life, a higher amount of needed isocyanate crosslinker, and a lower gloss (if the amount of co-solvent is not increased) than otherwise might be desired.

Accordingly, there is a need in the polyurethane coatings industry for no solvent, and low solvent, water-based polyurethane coating compositions that provide coatings characterized by good physical properties, and high gloss and solvent resistance, as compared to solvent-based polyurethane compositions.

In one aspect, the present invention relates to a two-component aqueous polyurethane coating composition that is curable at 25 degrees Centigrade (or at a higher temperature if desired) into a coating exhibiting enhanced hardness, gloss, and solvent resistance, said coating composition comprising:

(I) a polyisocyanate which is dispersible in an aqueous polymer resin dispersion, has an average functionality of at least 2.0 and contains:

(A) 25% to 95% by weight of a polyisocyanate adduct selected from the group consisting of cyclodimers or allophanates of 3,3,5-trimethylhexamethylene diisocyanate, 2-methylhexamethylene diisocyanate, isophorone diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, and combinations thereof, and

(B) 5% to 75% by weight of another polyisocyanate adduct selected from the group

consisting of cyclotrimers or biurets of 3,3,5-trimethylhexamethylene diisocyanate, 2-methylhexamethylene diisocyanate, isophorone diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, and combinations thereof, and,

(C) 0% to 30% (preferably 0% to 20%) by weight of an organic solvent that is inert to isocyanate; and,

10 (II) an isocyanate reactive hydroxyl-terminated, water dispersable polymer resin having a hydroxyl number of between 10 and 450 (preferably between 28 and 350), with the proviso that if component (B) consists essentially of cyclotrimerized isophorone diisocyanate, then component (C) is present in an amount of at least 10% by weight, based upon the weight of said coating composition.

In other aspects, the present invention relates to a process for preparing the above-described coating composition, and to a coated substrate containing a coating prepared from the coating composition. The process comprises contacting component (I) and component (II) of said two-component aqueous polyurethane coating composition to provide a mixture, and admixing said mixture to provide a mixed coating composition. The coated substrate is prepared by contacting a substrate with the mixed coating composition.

These and other aspects will become apparent upon reading the following detailed description of the invention.

It has now been surprisingly found, in accordance with the present invention, that

combinations of a select group of water-dispersable polyisocyanate adducts enable the preparation of no solvent (or very low solvent) two-component, coating compositions characterized by good physical properties. These physical properties are comparable to the physical properties only achievable heretofore using high solvent-based, two-component polyurethane coating compositions. Moreover, coatings on a substrate made in accordance with the present invention have been found to be "mar-resistant" over a wide range of pencil lead hardnesses, and the coatings tend to exhibit a "self-healing" characteristic inasmuch as scratches in the coating tend to disappear upon standing at room temperature. Thus, the "mar" in the coating caused by a pencil lead scratch is no longer observable after a short period of time. These surprising mar-resistance and self-healing characteristics would provide a commercial advantage in top-coat and clear-coat applications, for example, in automotive coatings.

In the preparation of the coating compositions of the present invention, suitable polyisocyanate adducts are specified hereinabove. The cyclodimerized polyisocyanates contain uretdione moieties and are commonly referred to as "dimers", whereas the cyclotrimerized polyisocyanates contain isocyanurate moieties and are commonly referred to as "trimers". The allophanates useful in this invention are suitably made by reacting an alcohol with the designated polyisocyanate to form a carbamate intermediate, which then further reacts with additional polyisocyanate to form the desired

allophanate. Methodology for forming allophanates is disclosed, for example, in U.S. Patent Nos. 5,461,135 and 5,124,427.

5 Other polyisocyanate adducts are suitably additionally employed in the coating compositions of the present invention. Suitable additional polyisocyanate adducts include isocyanurates, allophanate, uretidione or biurets prepared from organic diisocyanates represented by the formula:

10
$$R(NCO)_2$$

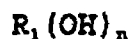
wherein the R represents an organic group having a molecular weight of 24 to 2100, preferably 56 to 1000. Preferred diisocyanates according to this invention are those represented by the above
15 formula wherein R represents a divalent aliphatic hydrocarbon group having from 4 to 25 carbons, a divalent cycloaliphatic hydrocarbon group having from 4 to 20 carbons, or a divalent araliphatic hydrocarbon group having from 6 to 20 carbons.

20 Examples of the organic diisocyanates which are particularly suitable for the process include 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,10-decanemethylene diisocyanate,
25 1,12-dodecanemethylene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, isophorone diisocyanate, bis-(4-isocyanatocyclohexyl)-methane, 1,3- and/or 1,4-bis-(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl,
30 1,3-and/or 1,4-xylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4-and/or

2,6-hexahydrotolylene diisocyanate, 4,4'-
dicyclohexylmethane diisocyanate, m- and p-
tetramethylxylene diisocyanates, p-xylene
diisocyanate, 1,4-phenylene diisocyanate, 2,4-
5 toluene diisocyanate, 2,6-toluene diisocyanate,
4,4'-diphenylmethane diisocyanate, 2,4'-
diphenylmethane diisocyanate, polymethylene
polyphenyl polyisocyanates, 5-naphthalene
diisocyanate. Mixtures of polyisocyanates can also
10 be used and also polyisocyanates which have been
modified by the introduction of urethane,
allophanate, urea, biuret, carbodiimide, uretonimine
or isocyanurate residues.

The organic solvent optionally employed in the
15 coating compositions of the present invention are is
suitably a solvent that does not contain isocyanate
reactive groups. Examples of suitable solvents are
acetone, methylamyl ketone, methylethyl ketone,
methyisobutyl ketone, n-methylpyrrolidone,
20 dimethylformamide, dimethylacetamide, n-
butylacetate, dipropylene glycol dimethyl ether,
propylene glycol methylethylacetate, propylene
glycol methylether, and other such water-compatible
solvents. Mixtures of the solvents may also be
25 used.

The isocyanate reactive hydroxyl terminated
aqueous dispersable resin polymer employed in the
coating composition of the present invention
suitably has a hydroxyl number of between 10 to 450.
30 Preferably, the hydroxyl number is between 28 to
350. Illustrative hydroxyl-terminated polymers are
represented by the formula:



wherein R_1 represents (a) a polyester, or (b) a polyether, or (c) a polyurethane, or (d) a polyacrylate, or (e) a copoly(urethane-acrylate), or
5 a combination thereof, having a molecular weight between 200 to 8,000, preferably between 230 to 6,000. The functionality of the hydroxyl terminated polymer represented in the formula by n can be between 1.8 and 8, preferably between 2 and 6.

10 The hydroxyl-terminated, water dispersible polymer resin according to this invention also has 1% to 20% by weight of non-ionic and/or ionic hydrophilic groups, preferably between 2 to 10%. The suitable non-ionic groups are polymeric ethylene
15 oxides with 3 to 30 repeating ethylene oxide units. The suitable ionic groups are carboxylic, sulfonic, sulfate and quaternary ammonium groups.

Specific examples of the polyesters are the reaction products of one or more kinds of
20 polycarboxylic acids such as saturated aliphatic carboxylic acids, and/or aromatic carboxylic acid and one or more kinds of polyhydric alcohols. Examples of aliphatic acids are oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic
25 acid, suberic acid, sebacic acid, isosebacic acid, and azelaic acid. Examples of aromatic acids are phthalic acid, isophthalic acid, terephthalic acid and their anhydrides. Examples of the polyhydric alcohols are ethylene glycol, 1,2-propylene glycol,
30 1,3-propylene glycol, diethylene glycol, triethylene glycol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,4-pentanediol, 1,6-

hexanediol, 1,5-hexanediol, 1,4-hexanediol, 1,3-hexanediol, 2,3-hexanediol, 2,4-hexanediol, 2,5-hexanediol, 3,4-hexanediol, 1,7-heptanediol, 1,6-heptanediol, 1,5-heptanediol, 1,4-heptanediol, 1,3-heptanediol, 2,3-heptanediol, 2,4-heptanediol, 2,5-heptanediol, neopentyl glycol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 1,4-cyclohexanedimethanol, trimethylolpropane, and glycerol. The polyesters in according to this invention have molecular weight range between 150 to 8,000, preferably between 450 to 4,000. They have functionality between 1.5 to 8, preferably between 1.8 to 4.

Specific examples of the polyethers are the polymers obtained by the reaction of starting compounds which contain reactive hydrogen atoms with alkylene oxides such as propylene oxide, butylene oxide, styrene oxide, tetrahydrofuran, epichlorohydrin or mixtures of these alkylene oxides. Certain proportions of ethylene oxide may also be included. Suitable starting compounds containing at least one reactive hydrogen atom include the polyols set forth as suitable for preparing the polyhydroxy polyesters and, in addition, water, methanol, ethanol, 1,2,6-hexanetriol, 1,2,4-butanetriol, trimethylol ethane, pentaerythritol, mannitol, sorbitol, methyl glycoside, sucrose, phenol, isononyl phenol, resorcinol, hydroquinone and 1,1,1- or 1,1,2-tris(hydroxylphenyl)ethane. The polyethers in according to this invention have molecular weight between 150 to 8,000, preferably between 200 to 6,000. They have functionality between 1.5 to 8.

Preferably between 1.8 to 4.

Specific examples of the polyurethanes are the reaction products of a diisocyanate and a polyol. The diisocyanates suitable for this invention are
5 organic diisocyanates represented by the formula:



wherein the R represents an organic group having a molecular weight of 24 to 2100, preferably 56 to 1000. Preferred diisocyanates according to
10 this invention are those represented by the above formula wherein R represents a divalent aliphatic hydrocarbon group having from 4 to 25 carbons, a divalent cycloaliphatic hydrocarbon group having from 4 to 20 carbons, or a divalent araliphatic
15 hydrocarbon group having from 6 to 20 carbons. Examples of the organic diisocyanates which are particularly suitable for the process include ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,10-decanemethylene diisocyanate, 1,12-dodecanemethylene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1, isocyanato-2-isocyanatomethyl cyclopentane, isophorone
25 diisocyanate, bis-(4-isocyanatocyclohexyl)-methane, 1,3- and/or 1,4-bis-(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl, 1,3-and/or 1,4-xylene diisocyanate, 1-isocyanato-1-methyl-4(3)-
30 isocyanatomethyl cyclohexane, 2,4-and/or 2,6-hexahydrotoluylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, m- and p-tetramethylxylene diisocyanates, p-xylene

diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, polymethylene polyphenyl polyisocyanates, 5-naphthalene diisocyanate. Suitable polyols include those described above as polyesters and polyethers, as well as hydroxyl terminated polylactones, and hydroxyl terminated polycarbonates.

10 Suitable hydroxyl terminated polylactones are polymeric products of valeratelactone, or ϵ -caprolactone having molecular weight between 400 and 6000, preferably between 650 and 3,000.

15 Suitable hydroxyl terminated polycarbonates are reaction products obtained from reaction of the polydydric alcohols previously set forth for preparing the polyhydroxyl polyesters with phosgene, diaryl carbonates such diphenyl carbonate or cyclic carbonates such as ethylene or propylene carbonate. Also suitable are polyester carbonates or polyether carbonates obtained by the reaction of lower molecular weight oligomer of the above-mentioned polyesters, polylactones, or polyethers with phosgene, diaryl carbonates or cyclic carbonates. 20 The hydroxyl terminated polycarbonates suitable for this invention have molecular weight between 250 to 8,000, preferably between 650 and 3,000.

25 Specific examples of hydroxyl group-containing polyacrylates are the polymers obtained by polymerization of one or more kinds of unsaturated hydroxylacrylic monomers (e.g. 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyacrylate), unsaturated acrylic acid amide

monomers (e.g. acrylamide, N-methylolacrylamide, methacrylamide), unsaturated carboxylic acid monomers (e.g. acrylic acid, methacrylic acid, itaconic acid, crotonic acid), unsaturated acid anhydride monomers (e.g. itaconic anhydride, maleic anhydride), unsaturated glycidyl monomers (e.g. glycidyl acrylate, glycidyl methacrylate), acrylic ester monomers (e.g. ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate), methacrylic ester monomers (e.g. methyl methacrylate, n-lauryl methacrylate, isobutyl methacrylate), maleic ester monomers (e.g. dibutyl maleate, diethyl maleate), fumaric ester monomers (e.g. dibutyl fumarate, diethyl fumarate), styrene and its derivatives (e.g. α -methylstyrene, β -chlorostyrene, α -bromostyrene, p-bromostyrene), nitriles (e.g. acrylonitrile, methylacrylonitrile, ethylacrylonitrile) and the like.

Specific examples of copoly(urethane-acrylate) are copolymers prepared as described for component (c), except between 2 to 50 percent by weight of component (d) was used as the polyol.

The two component coating compositions according to this invention are prepared by mixing of the polyisocyanate, component (I), into the isocyanate reactive aqueous solution and/or dispersion of hydroxyl terminated polymer, component (II). Mixing of the two components is suitably carried out by simple stirring or shaking at room temperature without high energy. The quantity of the polyisocyanate component is selected to provide an NCO/OH equivalent ratio, based on the isocyanate groups of component (I), and the hydroxyl groups of

component (II), of about 1 to 5, preferably about 1.2 to 2.0. The mixtures prepared according to this invention have good pot-life and spray viscosity of more than two hours.

5 Before polyisocyanate component (I) is mixed into isocyanate reactive component (II), the auxiliaries and additives typically used in coating technology may be incorporated into the isocyanate reactive component (II). The auxiliaries and
10 additives include foam inhibitors, leveling aids, pigments, dispersion aids for solid pigments, surface active agents, etc.

 The two-component coating compositions according to this invention thus obtained are
15 suitable for virtually any applications solvent-containing, solventless, or other aqueous paint and coating systems on substrates are currently used. Examples of the applications include the painting and coating of metal surfaces, the painting and
20 coating of plastic surfaces, the painting, coating, or sealing of wood and wood based materials such as particle board, fiber board and paper, the painting, coating, or sealing of mineral material surfaces such as lime- and/or cement-bound building material
25 and concrete, and the painting and coating of bitumen-containing pavements. They are also suitable for the bonding of various materials wherein the materials of two surfaces may be the same or different.

30 The aqueous coating compositions according to the present invention may be applied to substrates using any of the various techniques known in the art, such as spraying, roll-on, brush-on and so on.

They can also contain pigments, levelling agents, catalysts, and other auxiliaries known in the art.

The invention is further illustrated in, but is not intended to be limited by, the following
5 examples in which all parts and percentages are by weight unless otherwise specified.

EXAMPLE 1 - Preparation of a Coating Containing HDI Dimer Plus HDI Trimer With Solvent.

Step 1

10 Preparation of Low Viscosity HDI Dimer/HDI Trimer Isocyanate Crosslinker

The HDI dimer/HDI trimer isocyanate crosslinker was prepared by blending: (a) 100 parts of low viscosity hexamethylene diisocyanate (HDI) dimer;
15 (b) 100 parts of HDI trimer; and (c) 35.29 parts of dipropylene glycol dimethyl ether (commercially available as PROGLYDE DMM, a product of Dow Chemical Company). These materials were stirred for 30 minutes at room temperature.

20 Step 2

Preparation of the Polyurethane Ionomer and the Aqueous Dispersion of Polyurethane Resin

To an appropriate sized reaction vessel, namely a 3-neck round bottom flask, equipped with a
25 stirrer, a temperature control, a condenser, and a nitrogen purge, the following five ingredients were charged: (1) polyester polyol in an amount of 110.92 parts (OH equivalent weight=270.75)]; (2) isophorone

diisocyanate (IPDI) monomer in an amount of 45.48 parts; (3) dimethylol propionic acid (DMPA) in an amount of 13.60 parts; (4) N-methyl pyrrolidinone (NMP) in an amount of 30.00 parts; and, (5) T-12 (dibutyltin dilaurate) catalyst in an amount of 0.10 parts.

This reaction mixture was heated to 80°C and maintained until the NCO peak was no longer apparent by IR. 185 parts of said ionomer was weighed into an 800mL disposable beaker and set aside for preparation of dispersion as follows.

To neutralize the carboxyl concentration in the ionomer, 8.78 parts of dimethylethanolamine (DMEA) was added to a 250mL disposable beaker along with tap water, in an amount of 199.76 parts. This mixture was manually stirred into solution with a spoonula. The ionomer was placed under moderate agitation using a Premier Mill dispersator equipped with a "hi-vis" mix head. To this ionomer, the above water/amine solution was charged and dispersed to provide the desired aqueous dispersion of ionomer.

Step 3

Preparation and Testing of Two-Component (2K)

25 Polyurethane-HDI Dimer/HDI Trimer coating

Crosslinking of the two-component composition was effected by first adding to an eight ounce glass bottle the following ingredients: isocyanate crosslinker (from Step 1 of the present Example) in an amount of 18.17 parts; dispersion of ionomer (from Step 2 of the present Example) in an amount of 66.23 parts; OSI Specialties, Inc.'s SILWET L-7604

(10% aqueous) in an amount of 0.80 parts; OSi
Specialties, Inc.'s SILWET L-7605 (10% aqueous) in
an amount of 0.80 parts; dipropylene glycol dimethyl
ether (as Dow Chemical Company's PROGLYDE DMM) in an
5 amount of 12.53 parts; and, water in an amount of
12.40 parts. Standard tests were conducted on the
resulting coating, and the results are give in Table
1 below.

10 The coated test panels were allowed to cure at
ambient temperature and humidity conditions for two
weeks before testing for appearance, mechanical
properties, and chemical resistance. Pencil
hardness was determined according to ASTM D3363-92a.
The conical mandrel bend tests were performed using
15 a one-eight inch tester from BYK-Gardner, Inc.
according to ASTM D522-92. Direct and reverse
impact values were determined according to ASTM
D2794-92 using a variable height impact tester from
BYK-Gardner, Inc. Gloss was determined using a
20 micro-TRZ-gloss, multi-angle glossmeter from BYK-
Gardner. Cross-hatch adhesion was determined using
a cross-hatch cutter from BYK-Gardner according to
ASTM D3359-92a. Chemical Resistance was determined
according to ASTM D1308-87.

TABLE 1

	<u>Physical Property</u>	<u>Result</u>	<u>Chem. Property</u>	<u>Result</u>
	Thickness (mils)	2.85	CHEMICAL RESISTANCE	
	Mandrel Bend (1/4")	PASS	(10% in water [1/2 hour	
5	20° Micro-Gloss	84.95	test])	
	60° Micro-Gloss	92.30	Acetic Acid	PASS
	Impact (direct)	+160	Sodium Hydroxide	PASS
	Impact (reverse)	+160	Hydrochloric Acid	PASS
	Cross-Hatch	PASS	SOLVENT RESISTANCE	
10	Max. Pencil Hard.	>9H*	(1/2 hour test under 2"	
	MEK Rub (100 cycles)	PASS	watch glass)	
			Xylene	PASS
			Methyl Ethyl Ketone	PASS

* Coating provided "mar-resistance" in 2B-9H Pencil
 15 Hardness tests.

EXAMPLE 2 - Preparation of a Coating Composition
 Containing HDI Dimer Plus HDI Trimer With No
 Solvent.

Step 1

20 Preparation of 100% Solids HDI Dimer/HDI Trimer Isocyanate Crosslinker

To an appropriate reaction vessel, namely a 3-
 neck round bottom flask equipped with stirring and a
 nitrogen purge, the following two ingredients were
 25 charged: (1) low viscosity hexamethylene
 diisocyanate (HDI) dimer in an amount of 35.00
 parts; (2) HDI trimer in an amount of 35.00 parts.
 These materials were stirred for 30 minutes at room
 temperature.

Step 2

Preparation of the Coating Composition

Crosslinking followed the procedure as set out in Example 1 above, using ingredient weights that follow: isocyanate crosslinker (see Example 1, Step 1) in an amount of 18.40 parts; dispersion (see Example 1, Step 2) in an amount of 66.23 parts; SILWET L-7604 (10% aqueous) in an amount of 0.80 parts; SILWET L-7605 (10% aqueous) in an amount of 0.80 parts; dipropylene glycol dimethyl ether (as PROGLYDE DMM) in an amount of 12.53 parts; and, water in an amount of 12.40 parts, thus forming the desired coating composition having physical and chemical properties as shown in Table 2.

15

TABLE 2

<u>Physical Property</u>	<u>Result</u>	<u>Chem. Property</u>	<u>Result</u>
Thickness (mils)	2.65	CHEMICAL RESISTANCE	
Mandrel Bend (1/4")	PASS	(10% in water [1/2 hour test])	
20° Micro-Gloss	85.0		
20 60° Micro-Gloss	81.5	Acetic Acid	PASS
Impact (direct)	+160	Sodium Hydroxide	PASS
Impact (reverse)	+160	Hydrochloric Acid	PASS
Cross-Hatch	PASS	SOLVENT RESISTANCE	
Max. Pencil Hard.	>9H*	(1/2 hour test under 2" watch glass)	
25 MEK Rub (100 cycles)	PASS	Xylene	PASS
		Methyl Ethyl Ketone	PASS

* Coating provided "mar-resistance" in 2B-9H Pencil Hardness tests.

EXAMPLE 3 - Preparation of a Coating Composition
Containing Allophanate Plus HDI Trimer
With No Solvent.

Step 1

5 Preparation of HDI Trimer/Allophanate Isocyanate
Crosslinker

The following trimer/allophanate variation was prepared using the procedure of Example 1, Step 1, but without solvent:

10	HDI Trimer	35.00 parts
	ALLOPHANATE	35.00 parts

Step 2

Preparation of the Coating Composition

Crosslinking followed the procedure as set out
15 in Example 1 above, using ingredient weights that follow: isocyanate crosslinker (see Example 1, Step 1) in an amount of 18.86 parts; dispersion (see Example 1, Step 2) in an amount of 66.23 parts; SILWET L-7604 (10% aqueous) in an amount of 0.80
20 parts; SILWET L-7605 (10% aqueous) in an amount of 0.80 parts; dipropylene glycol dimethyl ether (as PROGLYDE DMM) in an amount of 12.53 parts; and, water in an amount of 12.40 parts, thus forming the desired coating composition.

EXAMPLE 4 - Preparation of a Coating Containing
Allophanate Plus IPDI Trimer.

Step 1

Preparation of IPDI Trimer/Allophanate Isocyanate
5 Crosslinker

The following trimer/allophanate variation was
prepared using the procedure of Example 1, Step 1:

	IPDI Trimer	35.00 parts
	ALLOPHANATE	35.00 parts
10	DMM	17.50 parts

Step 2

Preparation of the Coating Composition

Crosslinking followed the procedure as set out
in Example 1 above, using ingredient weights that
15 follow: isocyanate crosslinker (see Example 1, Step
1) in an amount of 22.88 parts; dispersion (see
Example 1, Step 2) in an amount of 66.23 parts;
SILWET L-7604 (10% aqueous) in an amount of 0.80
parts; SILWET L-7605 (10% aqueous) in an amount of
20 0.80 parts; dipropylene glycol dimethyl ether (as
PROGLYDE DMM) in an amount of 12.53 parts; and,
water in an amount of 12.40 parts, thus forming the
desired coating composition.

While the invention has been described above
25 with reference to specific embodiments thereof, it
is apparent that many changes, modifications and
variations can be made without departing from the
inventive concept disclosed herein. Accordingly, it

is intended to embrace all such changes,
modifications and variations that fall within the
spirit and broad scope of the appended claims.

WHAT IS CLAIMED IS:

1. A two-component aqueous polyurethane coating composition that is curable into a coating exhibiting enhanced hardness, gloss, and solvent resistance, said coating composition characterized by:

(I) a polyisocyanate which is dispersible in an aqueous polymer resin dispersion, has an average functionality of at least 2.0 and contains:

10 (A) 25% to 95% by weight of a polyisocyanate adduct selected from the group consisting of cyclodimers or allophanates of 3,3,5-trimethylhexamethylene diisocyanate, 2-methylhexamethylene diisocyanate, isophorone
15 diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, and combinations thereof, and

(B) 5% to 75% by weight of another polyisocyanate adduct selected from the group
20 consisting of cyclotrimers or biurets of 3,3,5-trimethylhexamethylene diisocyanate, 2-methylhexamethylene diisocyanate, isophorone diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, and combinations
25 thereof, and,

(C) 0% to 30% by weight of an organic solvent that is inert to isocyanate; and,

(II) an isocyanate reactive hydroxyl-terminated, water dispersable polymer resin having a
30 hydroxyl number of between 10 and 450 (preferably between 28 and 350),

with the proviso that if component (B) consists



essentially of cyclotrimerized isophorone diisocyanate, then component (C) is present in an amount of at least 10% by weight, based upon the weight of said coating composition.

5 2. A two-component aqueous polyurethane coating composition that is curable into a coating exhibiting enhanced hardness, gloss, and solvent resistance, said coating composition characterized by:

10 (I) a polyisocyanate which is dispersible in an aqueous polymer resin dispersion, has an average functionality of at least 2.0 and contains:

 (A) 25% to 95% by weight of a polyisocyanate adduct selected from the group consisting of
15 cyclodimerized 1,4-tetramethylene diisocyanate, cyclodimerized 1,6-hexamethylene diisocyanate, 1,4-tetramethylene diisocyanate allophanate, 1,6-hexamethylene diisocyanate allophanate, and combinations thereof, and

20 (B) 5% to 75% by weight of another polyisocyanate adduct selected from the group consisting of cyclotrimerized hexamethylene diisocyanate, hexamethylene diisocyanate biuret, cyclotrimerized isophorone diisocyanate, isophorone
25 diisocyanate biuret, and combinations thereof, and,

 (C) 0% to 30% by weight of an organic solvent that is inert to isocyanate; and,

 (II) an isocyanate reactive hydroxyl-terminated, water dispersable polymer resin having a
30 hydroxyl number of between 10 and 450, with the proviso that if component (B) consists essentially of cyclotrimerized isophorone



* C L M S *

diisocyanate, then component (C) is present in an amount of at least 10% by weight, based upon the weight of said coating composition.

3. The composition of claim 1 characterized in that said polyisocyanate adduct of component (A) is an uretidione or an allophanate, or a combination thereof, prepared from hexamethylene diisocyanate.

4. The composition of claim 3 characterized in that the aliphatic diisocyanate are 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, and combinations thereof.

5. The composition of claim 3 characterized in that the adduct has an average isocyanate content of between 16 to 25, preferably between 18 to 23.

6. The composition of claim 1 characterized in that the polyisocyanate additionally contains isocyanurates, allophanates, uretidiones or biurets prepared from organic diisocyanates represented by the formula:

$$R(NCO)_2$$

wherein R represents a divalent aliphatic hydrocarbon group having from 4 to 25 carbons, a divalent cycloaliphatic hydrocarbon group having from 4 to 20 carbons, or a divalent araliphatic hydrocarbon group having from 6 to 20 carbons.



7. The composition of claim 5 characterized in that said diisocyanate is selected from the group consisting of 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 4,4'-diisocyanatodicyclohexylmethane,
5 3,3,5-trimethylhexamethylene diisocyanate, 2-methylhexamethylene diisocyanate, isophorone diisocyanate, and combinations thereof.

8. A coated article prepared by contacting a substrate with the coating composition of claim 1.

10 9. The composition of claim 1 characterized in that said organic solvent is selected from the group consisting of acetone, methylamyl ketone, methylethyl ketone, methyisobutyl ketone, n-methylpyrrolidone, dimethylformamide,
15 dimethylacetamide, n-butylacetate, dipropylene glycol dimethyl ether, propylene glycol methylethylacetate, propylene glycol methylether, xylene, and combination thereof.

10. The composition of claim 1 characterized
20 in that the hydroxyl-terminated, water dispersable polymer resin is selected from the group of resins represented by the formula:



wherein R_1 represents a moiety selected from the
25 group consisting of polyester, a polyether, a polyurethane, a polyacrylate, a copoly(urethane-acrylate), and combinations thereof.



11. The composition of claim 9 characterized in that the molecular weight of the hydroxyl-terminated, water dispersable polymer resin is between 150 and 8,000.

5 12. The composition of claim 10 characterized in that the molecular weight of the hydroxyl-terminated, water dispersable polymer resin is between 650 and 5,000.

10 13. The composition of claim 10 characterized in that the functionality of the hydroxyl-terminated, water dispersable polymer resin is between 1.8 and 8.

15 14. The composition of claim 10 characterized in that the functionality of the hydroxyl-terminated, water dispersable polymer resin is between 2 and 6.

15. The composition of claim 10 characterized in that said R_1 is polyurethane.

20 16. The composition of claim 10 characterized in that said R_1 is copoly(urethane-acrylate).

25 17. A process for preparing a coating composition characterized by contacting component (I) and component (II) of said two-component aqueous polyurethane coating composition of claim 1 to provide a mixture, and admixing said mixture.

