

A METHOD OF ACCELERATING THE CURE OF AN ISOCYANATE MONOMER OR
ISOCYANATE-TERMINATED ADDUCT OR PREPOLYMER

This invention relates to a method of accelerating the cure of an isocyanate monomer or isocyanate-terminated adduct or prepolymer.

Urethane resins, because of their excellent toughness, chemical resistance, adherence and gloss, find wide application in paints, printing inks, adhesives, etc.

The urethane resins to be used in these fields are normally available in a one-can type or two-can type formulation. The former consists of a compound having a molecular weight of 500 to 10,000 and having not less than two isocyanate groups per molecule, and cures through polymerization and cross-linking by the reaction of its isocyanate groups with the moisture in the air, etc., after it has been applied to a substrate. The latter comprises two components, namely a polyol containing not less than two hydroxyl groups per molecule as a resin and a polyisocyanate having not less than two isocyanate groups per molecule as a curing agent. Both components are mixed in predetermined ratios and the mixture is applied to a substrate where it cures through polymerization and cross-linking by the reaction of the isocyanate groups with the hydroxyl groups.

The reaction between isocyanate groups and water or hydroxyl groups is regarded as relatively fast. In cases where the resin is applied continuously as in continuous painting or printing, which involve continuous application, curing and drying for a short period of time, nevertheless, the urethane resins which are used exhibit, in practice, an unsatisfactory rate of curing, and are, in practice, caused to cure at higher speeds by the addition of catalysts and further baking at temperatures exceeding 100°C., or 200°C., as the case may be. The addition of a catalyst to a resin composition reduces its storage stability and, in the case of a two-can type resin, furthermore shortens the pot life after mixing of two components, and also deleteriously affects the operation. Drying, by baking at elevated temperatures, requires large quantities of energy and can cause thermal deterioration of substrates, so that it cannot be applied to plastics substrates in particular.

Aliphatic isocyanates are used in urethane resins to prevent them from yellowing and such resins are used more and more especially for paints. However, these isocyanates have a reactivity which is inferior to that of aromatic isocyanates and are more difficult to
5 cure at high speeds.

A high-speed method for curing urethane resins at ambient temperature has been proposed and comprises coating a polyisocyanate prepolymer on a substrate and treating the prepolymer with an amine in a vapour-phase state (the specification of United States Patent
10 No. 3,874,898). According to this method it is also possible to use amines having active hydrogen atoms such as ammonia, monoethylamine and ethylenediamine, which react with isocyanate groups and act as a chain extender or cross-linking agent.

Since amino groups have a much higher rate of reaction with
15 isocyanate groups than water or hydroxyl groups, this method enables high-speed curing to be accomplished even with urethane resins based on aliphatic isocyanates. Nevertheless, the method involves the formation of cured coating films through cross-linking, due to the capture of such amines by isocyanate groups on the surface to form
20 coating films, thus inhibiting the diffusion of amine vapours into the inside of the coating. Thus, the method can be applied only to the formation, as by painting or printing, of coating films of a reduced thickness. In addition, the method encounters difficulties in providing the stoichiometric amount of amine to react with the
25 isocyanate groups.

On the other hand, triethylamine has been described as an amine in the above-mentioned United States Patent. Triethylamine, because it has no active hydrogen atoms, acts as a reaction catalyst but not as a cross-linking agent. Therefore, it is not necessary
30 to use triethylamine in a stoichiometric amount relative to isocyanate groups contained in a urethane resin, and, as it is not captured by isocyanate groups on the surface layers of paints, it can diffuse smoothly into the inside of the resin.

We have carried out extensive investigations on the curing of various isocyanate monomer compounds and isocyanate-terminated adducts or prepolymers obtained therefrom using triethylamine, and have discovered that, when aromatic isocyanates are employed as an isocyanate compound, triethylamine accelerates the reaction between isocyanate groups and water or hydroxyl groups and allows the curing to proceed uniformly and quickly. However, it was found that with aliphatic isocyanates such as 1,6-hexamethylene diisocyanate and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, triethylamine displays no catalytic action on the reaction between isocyanate groups and water or hydroxyl groups. Further investigation revealed that triethylamine and other tertiary amines have a catalytic action on specific isocyanate compounds.

Accordingly, the present invention provides a method of accelerating the cure of a isocyanate monomer or isocyanate terminated adduct or prepolymer containing isocyanate groups, wherein an isocyanate monomer compound having per molecule not less than two isocyanate groups linked to an aromatic nucleus through a methylene group or an isocyanate-terminated adduct or prepolymer obtained by the reaction of such an isocyanate monomer compound with a non-phenolic active hydrogen-containing compound, or a mixture of said isocyanate monomer compound or said isocyanate-terminated adduct or prepolymer and a non-phenolic active hydrogen-containing compound, is treated with the vapour of a tertiary amine.

Isocyanate group-containing monomer compounds which are cured by the present method are compounds having at least two isocyanate groups linked to an aromatic nucleus through a methylene group, such as diisocyanates exemplified by 1,2-bis(isocyanatomethyl)-benzene, 1,3-bis(isocyanatomethyl)-benzene, 1,4-bis(isocyanatomethyl)-benzene, 1,3-bis(isocyanatomethyl)-5-methylbenzene, 1,3-bis(isocyanatomethyl)-5-ethylbenzene, 1,4-bis(isocyanatomethyl)-2-methylbenzene and 1,5-bis(isocyanatomethyl)naphthalene, and triisocyanates exemplified by 1,3,5-tris(isocyanatomethyl)benzene and dimers, trimers and biurets of the above diisocyanates or triisocyanates.

These isocyanate compounds themselves may be cured by the

present method as may be isocyanate-terminated adducts and prepolymers obtained by the reaction of such isocyanate compounds with, for example, active-hydrogen containing compounds.

The isocyanate-terminated adducts and prepolymers may include, for example, those compositions which are referred to as moisture-curing and are presented as one-can type formulations. These compositions are prepolymers having free isocyanate groups which are obtained by the reaction of an excess of isocyanate monomer compound with a non-phenolic active hydrogen-containing compound. The non-phenolic active hydrogen-containing compounds are polyether polyols, polyester polyols, polyether ester polyols and others which preferably have a molecular weight of 300 to 10,000 and 2 to 4 hydroxyl groups. The non-phenolic active hydrogen-containing compound may also be an acrylic resin polyol.

Examples of suitable polyether polyols include those obtained by the ring opening addition polymerization of, for example, ethylene oxide, propylene oxide or a mixture thereof, and for example, ethylene glycol, propylene glycol, glycerol, pentaerythritol, etc., used as an initiator, or polytetramethylene ether glycol obtained for example by the ring-opening polymerization of tetrahydrofuran, and others.

Suitable polyester polyols can be obtained by the condensation of a dibasic or tribasic acid, such as maleic acid, fumaric acid, succinic acid, adipic acid, sebacic acid, azelaic acid, phthalic acid, isophthalic acid, terephthalic acid or trimellitic acid, with a dihydric to tetrahydric alcohol, examples of suitable dihydric to tetrahydric alcohols including ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, decamethylene glycol, 2,4,4-trimethyl-1,3-pentanediol, cyclohexanediol, cycloheanedimethanol, xylene glycol, trimethylolpropane,

glycerol, 1,2,6-hexanetriol, pentaerythritol, castor oil etc. Higher fatty acids such as coconut oil fatty acids, linseed oil fatty acids, soybean oil fatty acids, cottonseed oil fatty acids,

tung oil fatty acids and castor oil fatty acids may be incorporated into the acid component to make oil-modified polyester polyols.

Polyether ester diols, polybutadienediol, polyisoprenediol, castor oil, etc., can also be used as polyols.

5 Alternatively, the isocyanate-terminated adducts or prepolymers may be so-called two-can type formulations.

These two-can type formulations consist of two components, namely, a resin comprising a polyol having not less than two hydroxyl groups per molecule and a curing agent comprising a
10 polyisocyanate having not less than two isocyanate groups per molecule.

The polyols which are used include polyether polyols, polyester polyols and others having a molecular weight of 300 to 20,000 and 2 to 10 hydroxyl groups. Such polyethers and polyesters
15 can be obtained by the same procedure as described above for the aforesaid one-can type formulations. Acrylic resin polyols are also suitable polyols and can be obtained by the copolymerization of an ester of acrylic acid, such as ethyl acrylate, butyl acrylate and octyl acrylate, an ester of methacrylic acid, such as methyl
20 methacrylate, butyl methacrylate and hexyl methacrylate, or a vinyl monomer, such as styrene, with a hydroxyl-containing acrylic monomer, such as β -hydroxyethyl acrylate or β -hydroxyethyl methacrylate. Such acrylic resin polyols include polyols having a molecular weight of 1,000 to 30,000 and 5 to 50 hydroxyl groups.

25 The polyisocyanates which constitute the curing agent component are obtained by the reaction of the above isocyanate monomer compounds with polyfunctional alcohols, such as diethylene glycol and trimethylolpropane, or water. The curing agent component for moisture-curing or two-can type formulations is normally
30 obtained by known reaction procedures. Generally, the reaction temperature is about 10 to 120°C., and the reaction time is about 1 to 10 hours. The reaction may be conducted without a solvent or in the presence of an organic solvent having no active hydrogen atoms.

Where an isocyanate compound or isocyanate-terminated adduct

or prepolymer thereof obtained by the above procedures is utilized as a paint or printing ink, it is normally and desirably in the form of a solution in an organic solvent, although it can be used in a solvent-free state. Examples of suitable organic solvents having no active hydrogen atoms include esters, such as ethyl acetate, butyl acetate and 2-ethoxy ethanol acetate, and ketones, such as acetone, methyl ethyl ketone and methyl isobutyl ketone, which are particularly preferred in that they not only dissolve urethane resins readily but also promote the permeation and diffusion of tertiary amines into the solution.

When solutions of these isocyanate compounds or isocyanate-terminated adducts or prepolymers thereof are used as paints or printing ink, they may be compounded with conventional additives, such as, for example, pigments, levelling agents, antifoaming agents, stabilizers against weathering, etc.

In carrying out the present method, the isocyanate compounds or said adducts or prepolymers may be applied to a substrate by such means as coating and printing at a rate of application of about 1 g./m.² to 200 g./m.² on a dry weight basis, and then treated with the tertiary amine in the vapour-phase. This may be carried out by allowing the substrate, on which the isocyanate compound or adduct or prepolymer has been applied, to stand in a room filled with tertiary amine vapour.

The substrate may be made of any suitable material, for example, wood, iron, steel, aluminium, slate, flexible board, perlite board, asbestos, slate, plastics or composite materials thereof. Furthermore, it may have the shape of any sheet, board, moulded article, etc.

Examples of suitable tertiary amines which may be employed in the present method include aliphatic tertiary amines, such as trimethylamine, triethylamine, tripropylamine, tributylamine and triamylamine; aromatic tertiary amines, such as dimethylaniline, diethylaniline and tribenzylamine; N-methylmorpholine, N-ethylmorpholine, etc., alkanolamines having a tertiary nitrogen atom,

such as triethanolamine, methyldiethanolamine, dimethylethanolamine, diethylethanolamine, dibutylethanolamine, diisopropylethanolamine, di(2-ethylhexyl)ethanolamine, ethyldiethanolamine, triisopropanolamine, dibutylisopropanolamine and dimethylisopropanolamine, and the like. Dimethylethanolamine is particularly preferred.

The concentration of the tertiary amine in the vapour-phase may be in the range of about 10 to 100,000 ppm, more preferably in the range of about 100 to 20,000 ppm. The temperature may be room temperature but may be adjusted to a suitable temperature within the range of about 0 to 100°C., preferably about 10 to 60°C., to allow curing and drying to be accomplished. The treatment time varies in dependence upon the composition, the thickness of the coating film, and the type and concentration of the tertiary amine, and is normally in the range of about 1 to 10 minutes.

The present method can be advantageously employed in fields such as continuous painting and printing etc., where continuous coating, along with curing and drying have to be accomplished within a short period of time. In addition, it can be applied for outdoor use where weatherability is particularly required, because the cured and dried coating films are non-yellowing.

The invention will now be illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

A mixture of 592 parts of phthalic anhydride, 560 parts of coconut oil fatty acid and 805 parts of trimethylolpropane was heated up to 220°C. While nitrogen gas was blown into the reaction system so that the water produced in the reaction system was removed along with the nitrogen gas, the reaction was allowed to proceed to give a polyester polyol having an acid value of 5 and a hydroxyl value of 187. Butyl acetate was added to the thus obtained polyester polyol so as to yield a 75% solution of the said polyester polyol.

Separately, 400 parts of 1,4-bis(isocyanatomethyl)benzene

5 were heated with 45 parts of trimethylolpropane at 70-75°C., for 4 hours to allow the reaction to take place. Then the unreacted 1,4-bis(isocyanatomethyl)benzene was removed by extraction with a solvent mixture comprising n-hexane and ethyl acetate (weight ratio = 9:1), and the remainder was dissolved in ethyl acetate to give a polyisocyanate solution (NCO content: 11.5%, solids content: 75%).

10 400 parts of the above polyester polyol and 385 parts of titanium oxide were mixed together and then mixed with 370 parts of the above polyisocyanate solution. The resultant composition was applied onto an aluminium plate to give a coating film 50 μ thick and, upon standing for 5 minutes at 25°C., in a room containing 100 ppm of dimethylethanolamine, yielded a completely dried, glossy white coating film.

15 The 400-hour accelerated weathering test with a sunshine type "Weather-O-Meter" (W-O-M) indicated that nothing abnormal was observed.

Comparative Example 1

Four compositions (NCO/OH=1.0; PWC=40%) each prepared from the same polyester polyol as in Example 1 and, instead of the polyisocyanate solution employed in Example 1, (a) tolylene diisocyanate (2,4-isomer/2,6-isomer=80/20)-trimethylolpropane adduct (NCO content: 12.9%, solids contents: 75%), (b) diphenylmethane diisocyanate-trimethylolpropane adduct (NCO content: 14.2%, solids content: 75%), (c) 1,6-hexamethylene diisocyanate-trimethylolpropane adduct (NCO content: 12.6%, solids content: 75%) and (d) 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate-trimethylolpropane adduct (NCO content: 11.0%, solids content: 75%), respectively, were each applied onto an aluminium plate to give a coating film 50 μ thick and, after standing for 5 minutes at 25°C., in a room containing 100 ppm of dimethylethanolamine, and the state of drying of each film was tested. Those films which were tack-free were subjected to the weathering test. The results are shown in Table 1.

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Table 1:

	Poly-isocyanate	a)	State of Drying	Weatherability, 400 hours in W-O-M Gloss retention ratio	b
5	1,4XDI based		Good	98%	2
	TDI based		Good	17	8
	MDI based		Good	15	10
	HDI based		Poor (Tacky)	-	-
	IPDI based		Poor (Tacky)	-	-
10	a)	1,4XDI based:	1,4-Bis(isocyanatomethyl)benzene-trimethylolpropane adduct		
		TDI based :	Tolylene diisocyanate-trimethylolpropane adduct		
		MDI based :	Diphenylmethane diisocyanate-trimethylolpropane adduct		
15		HDI based :	1,6-Hexamethylene diisocyanate-trimethylolpropane adduct		
		IPDI based :	3-Isocyanatomethyl-3,5,5-trimethyl-cyclohexylisocyanate-trimethylolpropane adduct.		

Example 2

20 A 1128 parts portion of 1,3-bis(isocyanatomethyl)-benzene was reacted with 268 parts of trimethylolpropane and 1000 parts of polybutylene adipate (molecular weight 1000) in 3594 parts of ethyl acetate to give a polyisocyanate solution (solids content: 40%, NCO content: 2.8%).

25 The solution was painted on an iron-phosphate treated iron plate to give a coating film 50μ thick and, after standing for 5 minutes at 20°C. in a room containing 200 ppm of dimethylethanolamine, yielded a completely dried coating film. The properties of the coating film were as follows:

30	Pencil hardness	:	2H
	Cross-hatch adhesion	:	100/100
	Erichsen cupping test	:	8mm.
	Impact test (DuPont type)	:	1/2" x 500g x 50cm.
35	Mandrel bending test	:	2mm.

Solvent resistance

Ethyl acetate : Satisfactory
Xylene : Satisfactory
Ethanol : Satisfactory

5 Elongation : 121%
Tensile strength : 485 kg./cm².

When an amine vapour was not employed, the coating film took 3 hours 30 minutes to dry.

Example 3

10 A 400 parts portion of the same polyester polyol as was used in Example 1 and 91 parts of titanium oxide were mixed together and then mixed with 81 parts of 1,3,5-tris(isocyanatomethyl)benzene. The resulting composition was applied on to an aluminium plate to give a coating film 50 μ thick and, upon standing for 5 minutes at 25°C.,
15 in a room containing 100 ppm of dimethylethanolamine, yielded a completely dried, glossy white coating film.

The 400-hours accelerated weathering test with a sunshine type "Weather-o-Meter" indicated that nothing abnormal was observed.

Example 4

20 400 parts of 1,3-bis(isocyanatomethyl)benzene were reacted with 27 parts of trimethylolpropane by heating at 70 to 75°C., for 4 hours. Then unreacted 1,3-bis(isocyanatomethyl)benzene was removed by extraction with the same solvent as in Example 1, and the remainder was dissolved in ethyl acetate to give a polyisocyanate solution
25 (NCO content: 11.5%, solids content: 75%).

According to a conventional method, 46.8 parts of styrene, 30 parts of n-butyl acrylate and 23.2 parts of 2-hydroxyethyl methacrylate were copolymerized in a solvent mixture comprising xylene and butyl acetate, and there was obtained an acrylic polyol
30 solution (hydroxyl value: 50, solids content: 50%).

1122 parts of the above acrylic polyol solution and 556 parts of titanium oxide were mixed together and then mixed with 365 parts of the above polyisocyanate solution mixture. The resulting composition was applied on to an aluminium plate to give a coating film 50 μ thick and, upon standing the thus-coated plate for 3 minutes at 25°C., in a room containing 10,000 ppm of dimethylethanolamine, a completely dried, glossy white coating film was obtained.

The properties of the coating film were as follows:

	Pencil hardness	:	2H
10	Cross-hatch adhesion	:	100/100
	Erichsen cupping test	:	8mm.
	Impact test	:	1/2" x 500g. x 50cm.
	Mandrel bending test	:	2mm.
	Solvent resistance	:	
15	Ethyl acetate	:	Satisfactory
	Xylene	:	Satisfactory
	Ethanol	:	Satisfactory
	Weatherability		
	(400 hours in W-O-M)		Nothing abnormal was observed.
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When an amine vapour was not employed, the coating film took 4 hours to dry.

Example 5

1,000 parts of polypropylene glycol (molecular weight 1,000), 268 parts of trimethylol propane and 406 parts of ethyl acetate were mixed, and the mixture was further mixed with 2,920 parts of the polyisocyanate solution obtained in Example 4. The resulting composition was applied onto an aluminium plate to give a coating film 50 μ thick and, upon standing the thus-coated plate for 7 minutes at 20°C., in a room containing 20,000 ppm of dimethylethanolamine, a completely dried coating film was obtained.

When an amine vapour was not employed, the coating film took more than 10 hours to dry.

CLAIMS:

1. A method of accelerating the cure of a isocyanate monomer or isocyanate terminated adduct or prepolymer containing isocyanate groups, wherein an isocyanate monomer compound having per molecule not less than two isocyanate groups linked to an aromatic nucleus
5 through a methylene group or an isocyanate-terminated adduct or prepolymer obtained by the reaction of such an isocyanate monomer compound with a non-phenolic active hydrogen-containing compound or a mixture of said isocyanate monomer compound, or said isocyanate-terminated adduct or prepolymer and a non-phenolic active hydrogen-
10 containing compound, is treated with the vapour of a tertiary amine.
2. A method as claimed in Claim 1, wherein the isocyanate-terminated adduct or prepolymer is a moisture-curing one having free isocyanate groups and obtained by the reaction of an excess of said isocyanate monomer compound with said non-phenolic
15 active hydrogen-containing compound.
3. A method as claimed in Claim 1, wherein the isocyanate-terminated adduct or prepolymer is one comprising a non-phenolic active hydrogen-containing compound which is a polyether polyol, a polyester polyol, a polyether ester polyol or an acrylic resin
20 polyol having not less than two hydroxyl groups per molecule and a polyisocyanate having not less than two isocyanate groups per molecule obtained by the reaction of said isocyanate monomer compound with a non-phenolic polyfunctional alcohol.
4. A method as claimed in Claim 3, wherein the
25 isocyanate-terminated adduct or prepolymer is one comprising a polyester polyol or an acrylic resin polyol and a polyisocyanate obtained by the reaction of 1,3-bis(isocyanatomethyl)benzene or 1,4-bis(isocyanatomethyl)benzene with trimethylolpropane.
5. A method as claimed in any one of Claims 1 to 4, wherein the
30 concentration of the tertiary amine in the vapour phase is in the range of 10 to 100,000 ppm.
6. A method as claimed in any one of Claims 1 to 5, wherein the tertiary amine is an alkanolamine having a tertiary nitrogen atom.



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7. A method as claimed in Claim 6, wherein the alkanolamine having a tertiary nitrogen atom is dimethylethanolamine.

8. A method in accordance with Claim 1 of accelerating the cure of an isocyanate monomer or isocyanate-terminated adduct or prepolymer substantially as hereinbefore described in any one of Examples 1 to 5 of the foregoing Examples.

9. A cured isocyanate, wherein the isocyanate has been derived from an isocyanate monomer compound having per molecule not less than two isocyanate groups linked to an aromatic nucleus through a methylene group, and wherein the curing of the isocyanate has been accelerated by the method claimed in any preceding claim.
