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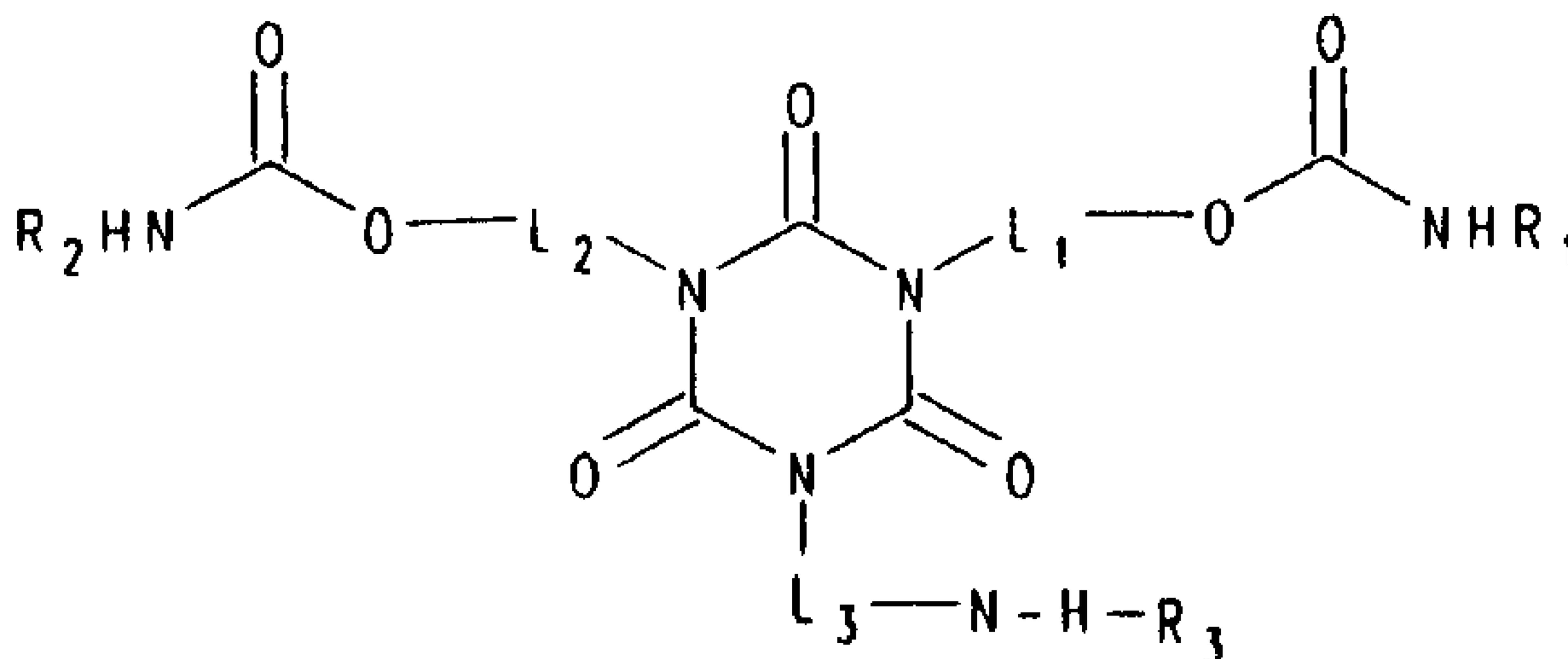
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(54) Titre : ISOCYANURATES DEVELOPPES, AGENTS DE RETICULATION DANS DES COMPOSITIONS DE
REVETEMENT

(54) Title: EXTENDED ISOCYANURATES FOR USE AS CURING AGENTS IN COATING COMPOSITIONS



(57) Abrégé/Abstract:

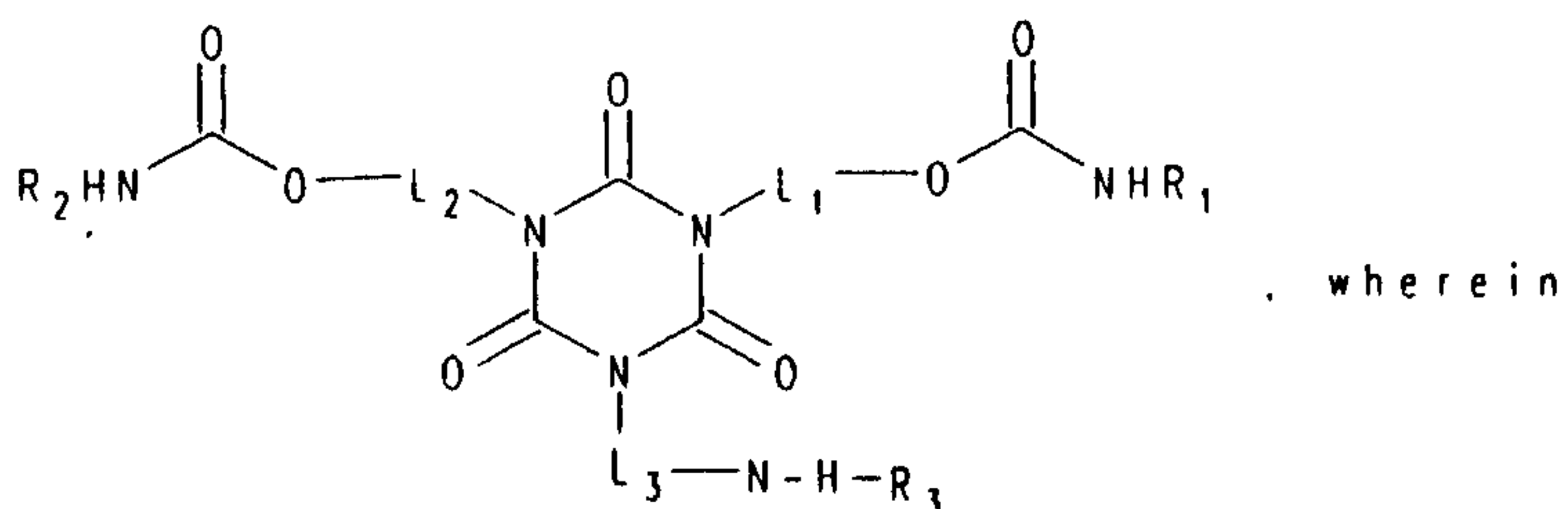
Compounds are prepared from trifunctional isocyanurates by first reacting the isocyanurate with water, monohydric alcohol, diol or diamine. This isocyanurate is subsequently reacted to form a carbamate substituted compound, having the formula: (see above formula) wherein L₁, L₂, and L₃ each independently represents a divalent linking group, and R₁ and R₂, each independently represents H, alkyl, cycloalkyl, or aryl and R₃ is the residue resulting from the reaction of isocyanate and water, monohydric alcohol, diol or diamine. These compounds are useful as crosslinking agents for curable compositions such as coating compositions.



EXTENDED ISOCYANURATES FOR USE AS CURING AGENTS IN COATING COMPOSITIONS

Abstract

Compounds are prepared from trifunctional isocyanurates by first reacting the isocyanurate with water, monohydric alcohol, diol or diamine. This isocyanurate is subsequently reacted to form a carbamate substituted compound, having the formula:



L_1 , L_2 , and L_3 each independently represents a divalent linking group, and

R_1 and R_2 , each independently represents H, alkyl, cycloalkyl, or aryl and R_3 is the residue resulting from the reaction of isocyanate and water, monohydric alcohol, diol or diamine.

These compounds are useful as crosslinking agents for curable compositions such as coating compositions.

EXTENDED ISOCYANURATES FOR USE AS CURING AGENTS IN COATING COMPOSITIONS

Field of the Invention

5 This invention relates to curable compositions, especially curable coating compositions, particularly acrylic compositions.

Background of the Invention

10 Polyurethane compositions based on triisocyanurates for coating and/or molding are well-known in the art. They provide a number of desirable characteristics such as resistance to solvent, salt, and other types of environmental attack.

15 However, these polyurethanes do suffer some disadvantages. An essential building block of these polyurethanes is the triisocyanurate. Triisocyanurates are expensive and difficult to handle. The NCO groups on the triisocyanurate are highly reactive, so they must be chemically blocked if it is desired to use the triisocyanurate in a one-pack coating composition. The use of chemical blocking groups further increases the expense of the material, results in increased VOC
20 during cure, introduces an additional component into the composition that can have the potential for adverse side-effects such as yellowing, and necessitates a high heat curing temperature on the order of 150°C. If the NCO groups are not chemically blocked, the triisocyanurate must be utilized as one
25 part of a two-pack composition. With such a composition, the highly-reactive triisocyanurate must be kept isolated from the surrounding environment and from the other component(s) of the composition until just before application to a substrate or mold, further increasing the expense and complexity of the process.

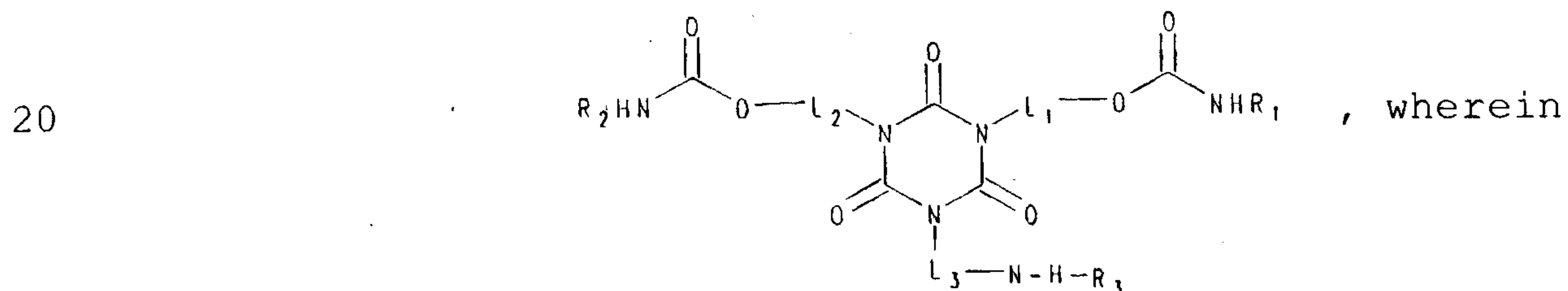
30 It has thus long been desired to produce a composition that exhibits the advantages of triisocyanurate-cured compositions having an optimum mix of characteristics as described above, but without having to use isocyanates groups as the functional groups for the curing reaction.

It is further desired that the coating composition demonstrate good sprayability when applied and good etch performance for the cured film.

Summary of the Invention

According to the present invention, there is provided a curable composition obtained by a process comprising:

- (a) reacting a trifunctional isocyanurate with a compound selected from the group consisting of monohydric alcohol, water, diol or diamine in a ratio of 3:1 respectively, so that, on average, at least one of the isocyanate groups is reacted,
- (b) reacting the compound obtained in step (a), hereinafter called component (a), with at least one compound to form a carbamate containing compound hereinafter called component (b) having the formula



L_1 , L_2 , and L_3 each independently represents a linking group, and

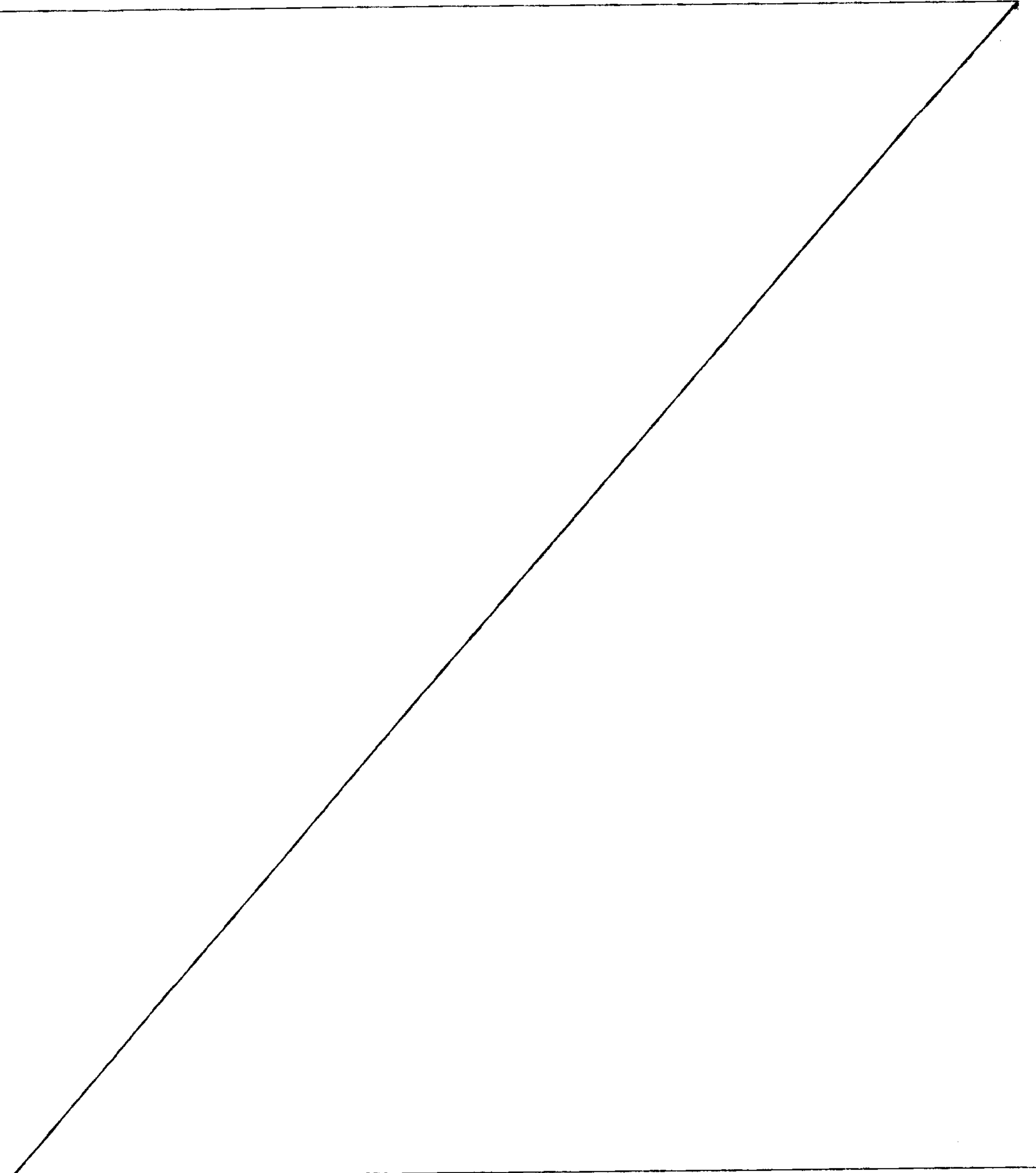
R_1 and R_2 each independently represents H, alkyl, or cycloalkyl and R_3 is a residue resulting from the reaction of isocyanate and water, monohydric alcohol, diamine or diol

- (c) reacting component (b) with a component having a plurality of functional groups that are reactive with carbamate, whereby a component (c) is obtained.
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Description of the Preferred Embodiments

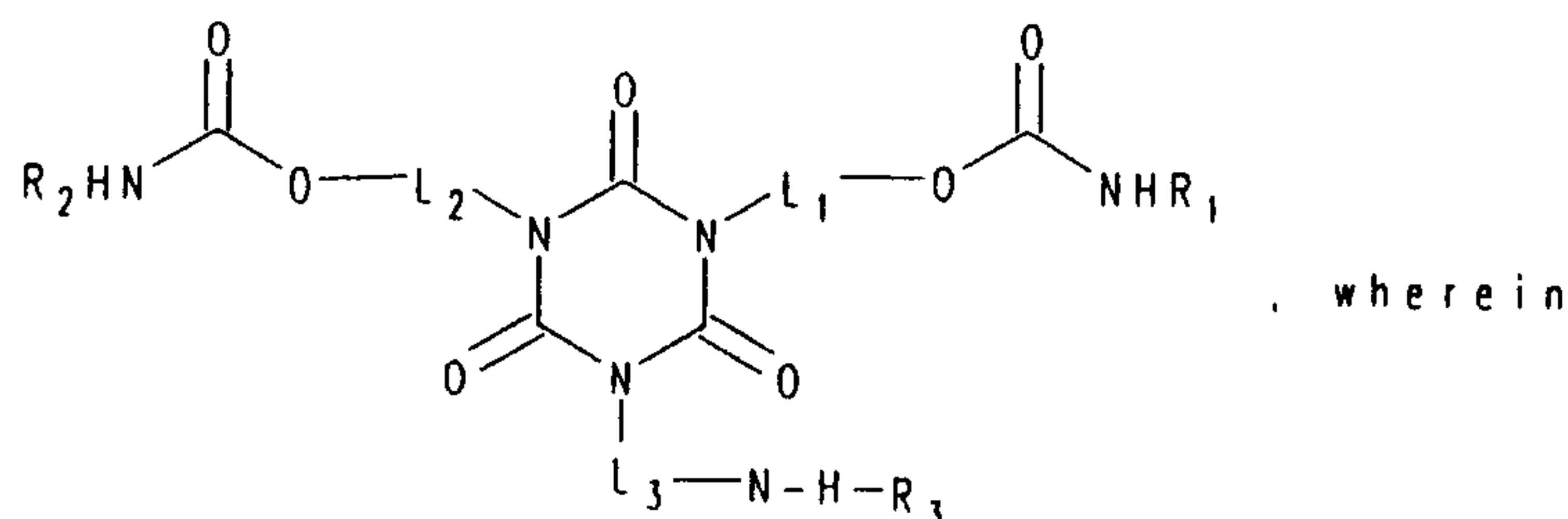
The component (a) used in the practice of the invention is formed by reacting a triisocyanurate with a compound selected from the group consisting of water, diamines, monohydric alcohols and diols, to provide an isocyanurate having one of the isocyanate groups defunctionalized or to provide a chain extended



isocyanurate by reaction of one of the isocyanates. Preferably the isocyanate and water, alcohol, diamine or diol are reacted in a ratio of 3:1 respectively, so that on average, one of the isocyanate groups is reacted prior to formation of the carbamate component. Accordingly, the isocyanurate has only two isocyanate groups, on average, which are available for formation of the carbamate linkage.

For example when the triisocyanurate is reacted with a monohydric alcohol, one isocyanurate group reacts with the -OH group from the alcohol and is defunctionalized and unavailable for further reaction. The isocyanate functionality of the isocyanurate is in effect reduced from 3 to 2. When the triisocyanurate is reacted with water, a diamine or diol, the isocyanurate is chain extended by first reacting one isocyanate group with the -OH group or -NH group and then subsequently reacting the OH or NH substituted isocyanurate with additional triisocyanurate, whereby the isocyanate functionality of the chain extended isocyanurate is increased from 3 to 4.

The isocyanurate obtained from step (a) is subsequently reacted to provide a carbamate substituted compound having the formula



L_1 , L_2 , and L_3 each independently represents a linking group, and

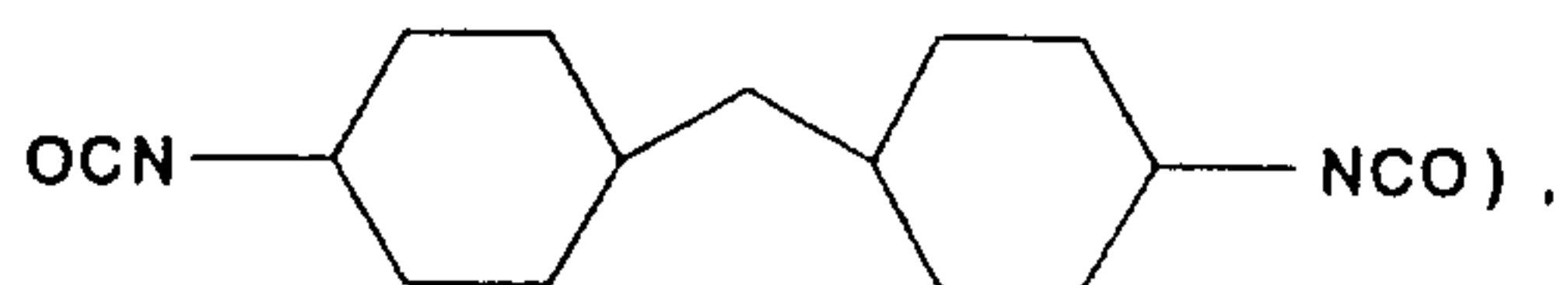
R_1 and R_2 each independently represents H, alkyl, or cycloalkyl. R_3 is a residue resulting from the reaction of isocyanate and water, monohydric alcohol, diamine or diol.

The carbamate substituted compound is formed from the isocyanurate described in (a), having on average two reactive NCO groups, by reaction with a compound containing an isocyanate-

reactive group and a carbamate group, e.g., a hydroxyalkyl carbamate such as hydroxypropyl carbamate or hydroxybutyl carbamate. Alternatively, the isocyanurate may be adducted with substituents that have the capability of forming carbamate groups after reaction with the isocyanurate compound is completed. For example, the isocyanurate can be reacted with a compound having a hydroxyl group and a cyclic carbonate group (e.g., the reaction product of glycidol and CO_2), and the cyclic carbonate groups then reacted with ammonia to form the carbamate functional groups.

The above-described NCO-functional isocyanurates are adducted with compounds containing a carbamate group or group that can be converted to carbamate and a group that is reactive with the -NCO functional group. Carbamate-containing compounds that can be adducted onto the NCO groups of an isocyanurate are preferably hydroxyalkyl carbamates such as hydroxypropyl carbamate or hydroxybutyl carbamate. Compounds containing groups that can be converted to carbamate and groups that are reactive with NCO include hydroxy-containing cyclic carbonate compounds convertible to carbamate by reaction with ammonia (e.g., the reaction product of glycidol and CO_2), monoglycidyl ethers (e.g., Cardura E®) convertible to carbamate by reaction with CO_2 and then ammonia, and monoglycidyl esters (e.g., the reaction product of a carboxylic acid and epichlorohydrin) convertible to carbamate by reaction with CO_2 and then ammonia, allyl alcohols where the alcohol group is reactive with NCO and the double bond can be converted to carbamate by reaction with peroxide, and vinyl esters where the ester group is reactive with NCO and the vinyl group can be converted to carbamate by reaction with peroxide, then CO_2 , and then ammonia.

The composition of the divalent linking group L_1 , L_2 , and L_3 in the above formula may be controlled by the type of cyanuric ring compound or polyisocyanate chosen. The divalent linking groups L_1 , L_2 , and L_3 individually may be either an aliphatic (e.g., hexamethylene), cycloaliphatic (e.g., residue of isophorone diisocyanate or

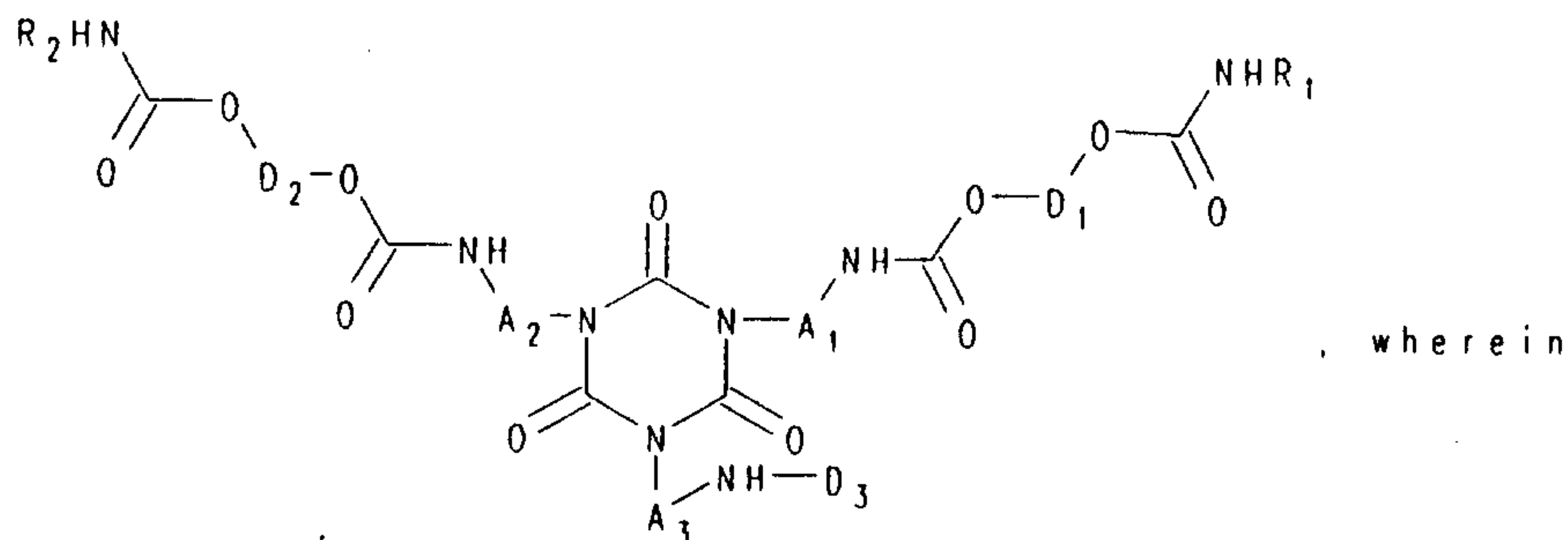


or aromatic group (e.g., residue of tetramethylxylylene diisocyanate), preferably up to 20 carbon atoms with terminal urethane, urea, or ester bonding to the substituent comprising the carbamate group. If resistance to solar degradation is desirable, then the divalent linking groups are preferably all aliphatic or cycloaliphatic. In a preferred embodiment, each of the -L- groups independently represents a group having the formula -A-NH-COO-D- where A and D each represents a divalent linking group as described below.

In the above formulas, R_1 and R_2 each independently represents H, alkyl, preferably of 1 to 6 carbon atoms, or cycloalkyl, preferably up to 6 ring carbon atoms. It is to be understood that the terms alkyl and cycloalkyl are to include substituted alkyl and cycloalkyl, such as halogen-substituted alkyl or cycloalkyl. In a preferred embodiment, R_1 and R_2 are H, allowing for greater flexibility in the choice of the (a) component to react with the carbamate groups during cure. Substituents that will have an adverse impact on the properties of the cured material, however, are to be avoided. For example, ether linkages are thought to be susceptible to hydrolysis, and should be avoided in locations that would place the ether linkage in the crosslink matrix.

Although isocyanurates derived from cyanuric acid are useful in the present invention, isocyanurates formed by condensation of one or more types of diisocyanates, such as hexamethylene diisocyanate, or isophorone diisocyanate are preferred. Examples of preferred isocyanurates include the isocyanurate of hexamethylene diisocyanate, and the isocyanurate of isophorone diisocyanate. If light-fastness is not a critical requirement, then an aromatic isocyanurate such as the isocyanurate of 2,4-toluene diisocyanate may be used.

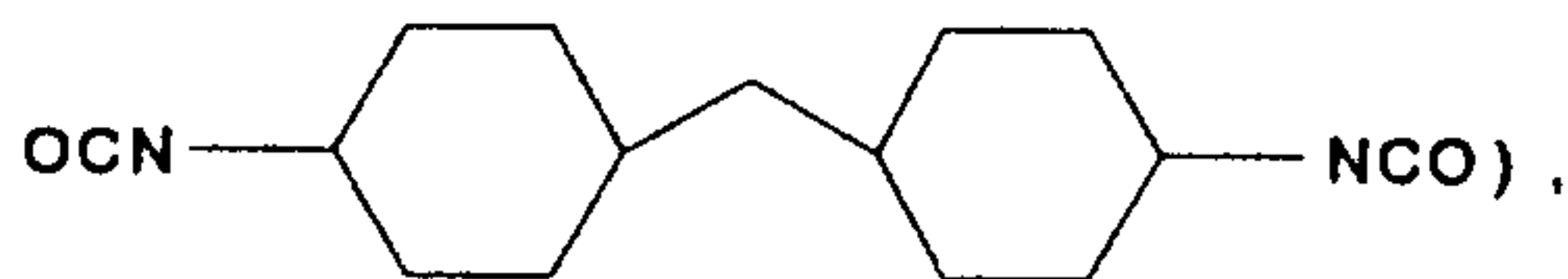
In a preferred embodiment of the invention, component (b) is derived from a trimerized diisocyanate, and has the formula (II):



5 A_1 , A_2 , and A_3 each independently represents a divalent linking group, and

D_1 and D_2 each independently represents a divalent linking group. D_3 represents the residue resulting from the reaction between one isocyanate group and water, alcohol, diamine or diol.

10 In this formula, each A is a divalent linking group as is typically derived from the core of the diisocyanate used to form the isocyanurate, and may be either an aliphatic (e.g., hexamethylene), cycloaliphatic (e.g., residue of isophorone diisocyanate or



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or aromatic group (e.g., residue of tetramethylxylylene diisocyanate), preferably up to 20 carbon atoms. D_1 and D_2 are divalent linking groups, preferably up to 20 carbon atoms, and are typically derived from the compounds having a carbamate group or carbamate-convertible group as described above. D_3 may be a urea linkage when the $-NCO-$ is reacted with water or diamine or a urethane linkage when the $-NCO-$ is reacted with diol.

20

25 The carbamate substituted compound (b) preferably has a molecular weight of 300 to 3000, preferably 450 to 1800. The equivalent weight per carbamate functional group can range from 100 to 1000, and preferably 150 to 600.

The component (c) used in the practice of the present invention has groups that are reactive with the carbamate groups on component (b). Such reactive groups include active methylol or methylalkoxy groups on aminoplast crosslinking agents or on other compounds such as phenol/formaldehyde adducts, isocyanate groups, siloxane groups, and anhydride groups. Examples of (c) compounds include melamine formaldehyde resin (including monomeric or polymeric melamine resin and partially or fully alkylated melamine resin), urea resins (e.g., methylol ureas such as urea formaldehyde resin, alkoxy ureas such as butylated urea formaldehyde resin), polyanhydrides (e.g., polysuccinic anhydride, copolymers of maleic anhydride), and polysiloxanes (e.g., trimethoxy siloxane). Aminoplast resin such as melamine formaldehyde resin or urea formaldehyde resin are especially preferred. Even more preferred are aminoplast resins where one or more of the amino nitrogens is substituted with a carbamate group for use in a process with a curing temperature below 150°C, as described in EP laid-open patent application EP-0,594,142,-A entitled "Carbamate-Defunctionalized Aminoplast Curing for polymer Composition".

A solvent may optionally be utilized in the coating composition used according to the present invention. Although the formulation of the present invention may be utilized, for example, in the form of substantially solid powder, or a dispersion, it is often desirable that the formulation used in the present invention is in a substantially liquid state, which can be accomplished with the use of a solvent. Preferably the solvent is present in an amount effective to substantially solubilize both the (b) component and the (c) component. In general, the solvent can be any organic solvent and/or water. More preferably, the solvent is a polar aliphatic solvents or polar aromatic solvents. Still more preferably, the solvent is a ketone, ester, acetate, aprotic amide, aprotic sulfoxide, aprotic amine, and water. Examples of useful solvents include methyl ethyl ketone, methyl isobutyl ketone, m-amyl acetate, ethylene glycol butyl ether-acetate, propylene glycol monomethyl ether

acetate, xylene, n-methylpyrrolidone, and blends of aromatic hydrocarbons.

The solvent may be present in the coating composition in an amount of from about 0.01 weight percent to about 99 weight percent, preferably from about 10 weight percent to about 60 weight percent, and more preferably from about 30 weight percent to about 50 weight percent.

The above-described coating compositions can be coated on the article by any of a number of techniques well-known in the art. These include, for example, spray coating, dip coating, roll coating, curtain coating, and the like. For automotive body panels, spray coating is preferred.

In one preferred embodiment, the composition of the invention is used as the clear coating composition over a pigmented basecoat as part of a composite color-plus-clear coating. Such composite coatings are popular for their depth of color and liquid glossy surface appearance. They have found particularly wide acceptance in the field of automotive coatings.

Pigmented basecoat compositions for such composite coatings are well-known in the art, and do not require explanation in detail herein. Polymers known in the art to be useful in basecoat compositions include acrylics, vinyls, polyurethanes, polycarbonates, polyesters, alkyds, and polysiloxanes. Preferred polymers include acrylics and polyurethanes. Basecoat polymers are preferably crosslinkable, and thus comprise one or more type of cross-linkable functional groups. Such groups include, for example, hydroxy, isocyanate, amine, epoxy, acrylate, vinyl, silane, and acetoacetate groups. These groups may be masked or blocked in such a way so that they are unblocked and available for the cross-linking reaction under the desired curing conditions, generally elevated temperatures. Useful cross-linkable functional groups include hydroxy, epoxy, acid, anhydride, silane, and acetoacetate groups. Preferred cross-linkable functional groups include hydroxy functional groups and amino functional groups.

Basecoat polymers may be self-cross-linkable, or may require a separate cross-linking agent that is reactive with the functional groups of the polymer. When the polymer comprises hydroxy functional groups, for example, the cross-linking agent
5 may be an aminoplast resin, isocyanate and blocked isocyanates (including isocyanurates), and acid or anhydride functional cross-linking agents.

After the article is coated with the above-described layers according to the invention, the coated article is
10 subjected to conditions so as to cure the coating layers. Although various methods of curing may be used, heat-curing is preferred. Generally, heat curing is effected by exposing the coated article to elevated temperatures provided primarily by radiative heat sources. Curing temperatures will vary depending
15 on the particular blocking groups used in the cross-linking agents, however they generally range between 82°C and 144°C, and are preferably between 110°C and 133°C. The curing time will vary depending on the blocking agents, and physical parameters such as the thickness of the layers, however, typical curing
20 times range from 15 to 60 minutes.

Use of the isocyanurates reacted according to the present invention provides coatings with improved sprayability and improved appearance. Also, the cured films are less brittle and do not crack and demonstrate improved resistance to
25 environmental etch.

The invention is further described in the following examples.

Example 1 -

30 Isocyanurate of Hexamethylene Diisocyanate Reacted with Hydroxy Acid

A reactor was charged with 368.7 parts xylene and 958.1 parts methyl isobutyl ketone and heated to reflux (122°C) under
35 inert atmosphere. Once at reflux, the inert atmosphere was turned off and 24.2 parts of the refluxed solvent was removed. The reaction mixture was then cooled to 40°C under inert

atmosphere and 1224 parts of isocyanurate of hexamethylene diisocyanate (N3300, from Miles Corporation, Pittsburgh, Pa), along with 4.0 parts dibutyl tin dilaurate were added. A slow purge of inert atmosphere was maintained for the rest of the
5 reaction. The reaction mixture was then brought up to 60° C and 736 parts of 2,2-dimethyl-3-hydroxyproipionic acid were added over 1 hour and 45 minutes. The reaction mixture was kept at 60°C for an additional 1 hour and 10 minutes. 63 parts of methyl amyl alcohol were then added over a 10 minute period. After the
10 reaction mixture tested free of isocyanate by infrared spectrometry, 1217.0 parts methyl isobutyl ketone were added. The product had a solids content of 58.4% and a non-volatile acid equivalent weight of 333.6 g/eq.

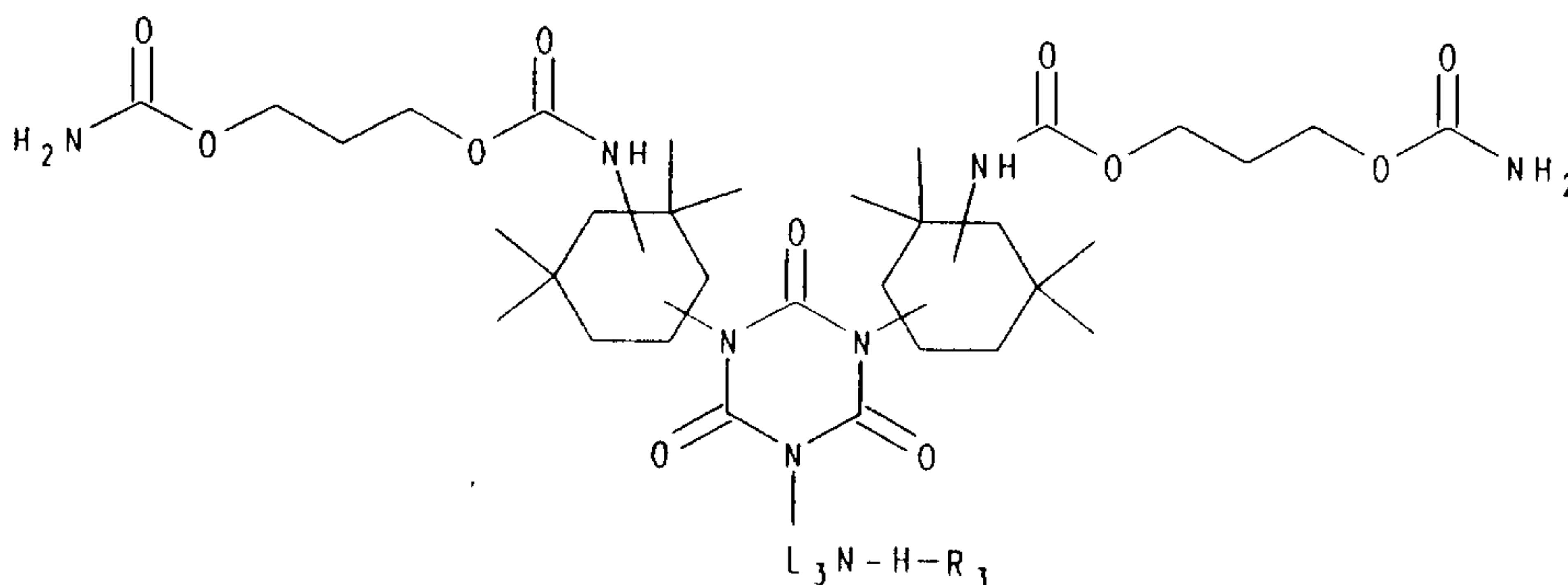
15 Example 2

A reactor was charged with 368 parts xylene and 626.2 parts methyl isobutyl ketone and heated to reflux (122°C) under inert atmosphere. Once at reflux, the inert atmosphere was turned off and 24.1 parts of the refluxed solvent was removed. The reaction
20 mixture was then cooled to 55°C under inert atmosphere and 1411.3 parts of isocyanurate of isophorone diisocyanate (T1890, from HULS America, Inc., Piscataway, NJ), along with 4.2 parts dibutyl tin dilaurate were added. A slow purge of inert atmosphere was maintained for the rest of the reaction. 482.1 parts of 2,2-
25 dimethyl-3-hydroxyproipionic acid were added over 1 hour and 10 minutes, at a reaction temperature of between 51 to 57°C. The reaction mixture was kept at 54 to 60°C for an additional 2 hours and 45 minutes. 45.7 parts of methyl amyl alcohol were then added over a 3 minute period. The product had a solids content
30 of 58.7% and a non-volatile acid equivalent weight of 422 g/eq.

Example 3

Isocyanurate Having Carbamate Functional Group

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A reactor vessel under a nitrogen blanket was charged with 1047.0 g of the isocyanurate obtained from Example 2. (Based on the isocyanurate of isophorone diisocyanate, available from Huls America, Inc., Piscataway, NY), 4.2 g of dibutyltin dilaurate, and 356.7 g of the solvent propylene glycol monomethylether acetate. Temperature control was applied to the reaction mixture until a constant temperature of about 80°C was reached, and 381.1 g of hydroxypropyl carbamate was slowly added. The reaction was maintained until virtually all of the NCO had been consumed. At that point, additional solvent (337.8 g propylene glycol monomethylether acetate and 25.0 g *n*-butanol) was added to the mixture.

Example 4 - Coating Example

A clear coating composition was prepared having the following formulation:

<u>Ingredient</u>	<u>Parts by weight</u>
Example 3	56.70
Dispersion of partially-defunctionalized melamine formaldehyde resin* in xylene (51.9% non-volatiles)	14.19
Tinuvin 348B®	6.84
Tinuvin 123®	0.42

<u>Ingredient</u>	<u>Parts by weight</u>
Dispersion of dodecylbenzene sulfonic acid (33.0% non-volatiles)	0.84
solvent blend (Exxate 800® and butanol)	26.61

* A melamine formaldehyde resin as described in EP-0,594,142-A.

10 This composition was then applied onto a metal test panels that had been precoated with an unbaked high solids solvent-borne acrylic/melamine pigmented basecoat. The basecoat was applied to a primed metallic substrate test panel in two coats with a period of one minute in between coats to allow the first coat to flash dry. After the second basecoat was applied, the basecoat was flash dried, followed by application of the clear coat composition. The clearcoat was applied in two even coats with a flash between coats. The coated substrate was then allowed to dry for a short period, and then bake cured at 140°C for 30 minutes.

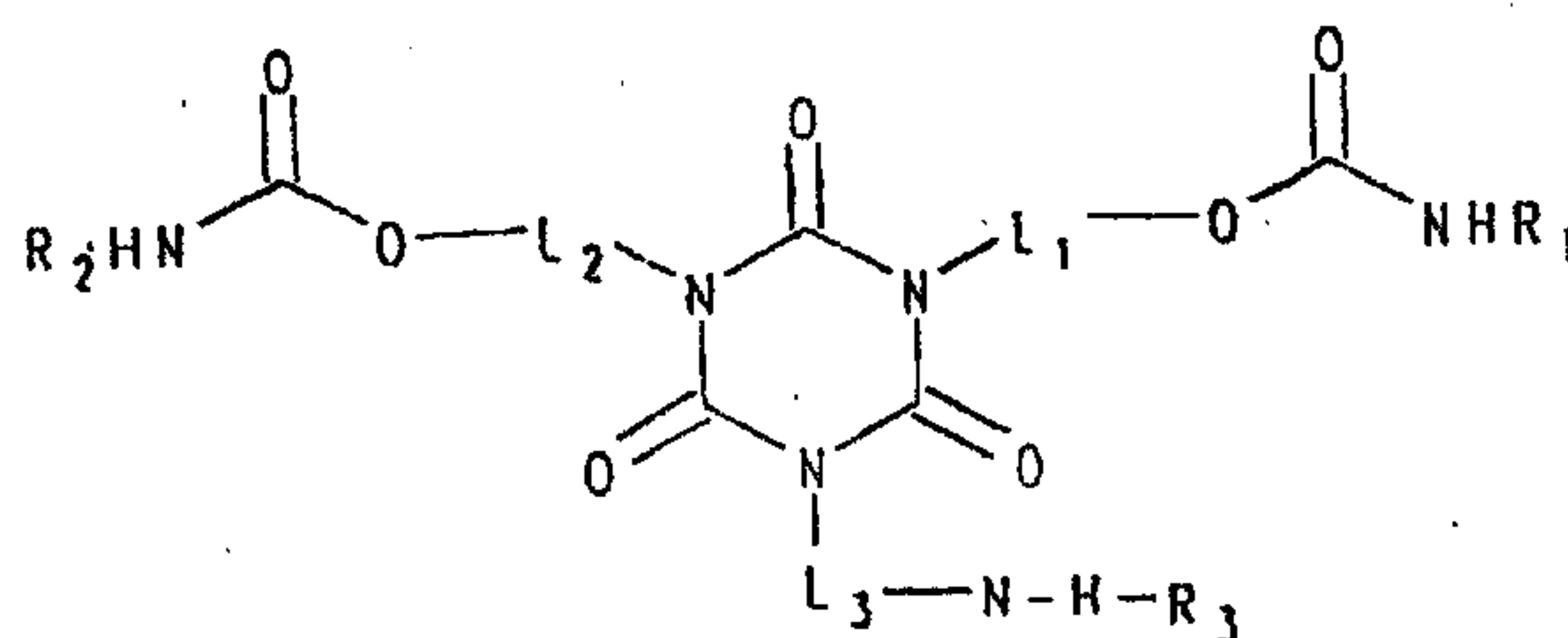
20 The panel was then placed on an outside exposure rack under severe etch-producing conditions for 4 weeks. The test panel coated with the coating of the invention (Example 2) had the most favorable etch rating of 1 on the General Motors etch evaluation scale. By comparison, a test panel coated with a known clearcoat utilizing a hydroxyfunctional acrylic polymer and an alkylated melamine formaldehyde resin had an etch rating of 10 on the General Motors etch evaluation scale. This represents a significant advantage in the etch performance of the coating composition according to the invention.

30 The invention has been described in detail with reference to preferred embodiments thereof. It should be understood, however, that variations and modifications can be made within the spirit and scope of the invention.

CLAIMS

1. A coating composition obtained by the process of:

- (a) reacting a trifunctional isocyanurate with a compound selected from the group consisting of monohydric alcohol, water, diol and diamine in a ratio of 3:1 respectively, so that, on average, at least one of the isocyanate groups is reacted,
- (b) reacting the compound obtained in the previous step, hereinafter called component (a), with at least one compound to form a carbamate containing compound hereinafter called component (b) having the formula



, wherein

L_1 , L_2 , and L_3 each independently represents a linking group, and R_1 and R_2 each independently represents H, alkyl, or cycloalkyl and R_3 is a residue resulting from the reaction of isocyanate and water, monohydric alcohol, diamine or diol

- (c) reacting component (b) with a component having a plurality of functional groups that are reactive with carbamate, whereby a component (c) is obtained.

2. A coating composition obtained by the process of claim 1, wherein component (a) is reacted with an isocyanate reactive group and a carbamate group, to form component (b).

3. A coating composition obtained by the process of claim 1, wherein component (a) is reacted with a substituent having a hydroxy group and a cyclic carbonate group, followed by reaction with ammonia, to form component (b).

4. A coating composition obtained by the process of claim 1, wherein R1 and R2 each independently represents H.

5. A coating composition according to the
10 process of claim 1, where R1 and R2 each independently represents alkyl, cycloalkyl or aryl.

6. A coating composition obtained by the process of claim 1 wherein L1, L2 and L3 each includes a urethane linkage.

7. A coating composition obtained by the process of claim 1, wherein the functional groups on the component (c) are selected from the group consisting of active methylol or methylalkoxy groups, cyclic carbonate groups, anhydride groups, and siloxane groups.

8. A coating composition obtained by the
20 process of claim 1, wherein component (c) is an aminoplast resin.

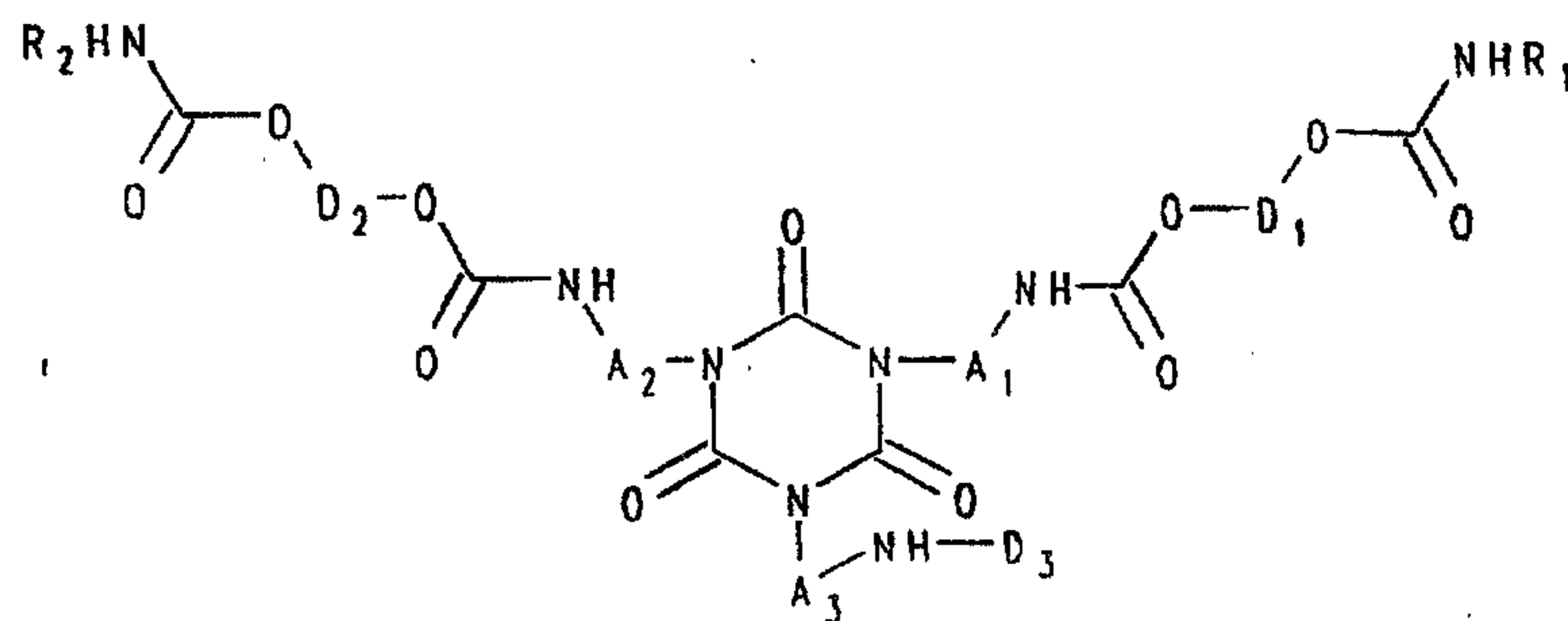
9. A coating composition according to claim 8, wherein the aminoplast resin is melamine formaldehyde or alkylated melamine formaldehyde.

10. A coating composition obtained by the process of claim 1, wherein the component (c) is a polymer or oligomer backbone having said carbamate-reactive functional groups appended thereto.

11. A coating composition obtained by the process of claim 10, wherein said polymeric or oligomeric backbone is derived from acrylic or methacrylic monomers.

12. A coating composition obtained by the process of claim 1 wherein component (b) has the formula:

10



, wherein

A₁, A₂, and A₃ each independently represents a divalent linking group, and

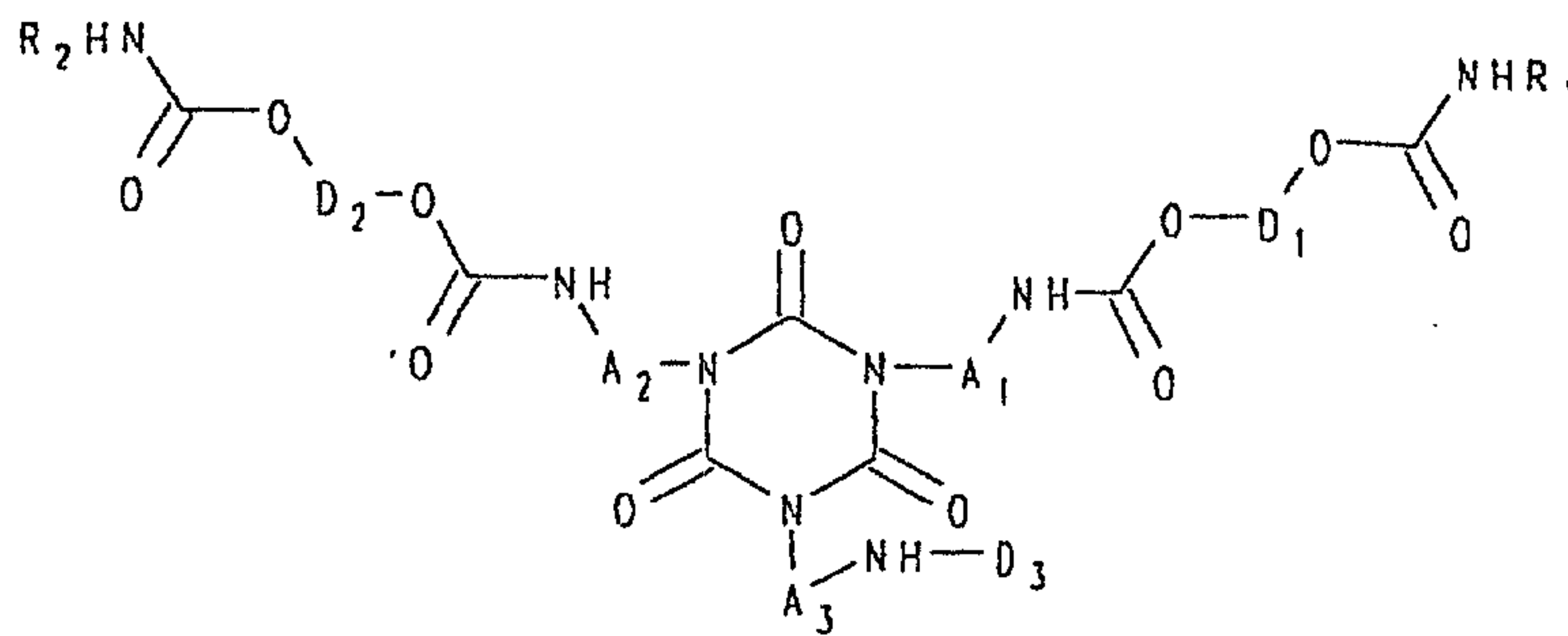
D₁ and D₂ each independently represents a divalent linking group and D₃ represents the residue resulting from the reaction of isocyanate and water, monohydric alcohol, diol or diamine.

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13. A composite color-plus-clear coating comprising a colored base coating and a clear coating, said clear coating being derived from the coating composition prepared by the process as defined in claim 1 or 4.

14. A composite color-plus-clear coating comprising a colored base coating and a clear coating, said clear coating being derived from the coating composition prepared by the process as defined in claim 13, wherein the component (b) has the formula

16



, wherein

A₁, A₂, and A₃ each independently represents a divalent linking group, and

10 D₁ and D₂ each independently represents a divalent linking group and D₃ represents the residue resulting from the reaction of isocyanate and water, monohydric alcohol, diol or diamine.

15. A curable composition obtained by a process as defined in claim 1.

