677313

SPRUSON & FERGUSON

AUSTRALIA

PATENTS ACT 1990

PATENT REQUEST: STANDARD PATENT

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] Applicant(s)/Nominated Person(s):

Ciba-Geigy AG, incorporated in Switzerland, of Klybeckstrasse 141, 4002 Basle, SWITZERLAND

[54] Invention Title:
UV-Absorbing Polyurethanes and Polyesters

[72] Inventor(s):
Juliana Rodgers, Istvan Borsody, Athanasios Karydas, Robert Allan Falk, Karl Friedrich Mueller and Michele Kovaleski

[74] Address for service in Australia:
Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia (Code **SF**)

Details of Basic Application(s):

[31] Appl'n No(s):	[33] Country:	[32] Application Date:
073,227	US	4 June 1993

Basic Applicant(s): Juliana Rodgers, Istvan Borsody, Athanasios Karydas, Robert Allan Falk, Karl Friedrich Mueller and Michele Kovaleski

DATED this THIRTIETH day of MAY 1994

Ciba-Geigy AG

By:

Registered Patent Attorney

S 046699 030694

IRN: 271304 INSTR CODE: 52760

5845/3

SPRUSON & FERGUSON

Australia

Patents Act 1990

Notice Of Entitlement

I, John David O'Connor, of 31 Market Street, Sydney, New South Wales, 2000, Australia, Patent Attorney for the Applicant/Nominated Person in respect of an application entitled:

UV-Absorbing Polyurethanes and Polyesters

state the following:-

The Applicant/Nominated Person has entitlement from the actual inventors as follows:-

The Applicant/Nominated Person is the assignee of the actual inventors.

The Applicant/Nominated Person is entitled to rely on the basic application listed on the Patent Request as follows:

The Applicant/Nominated Person is the assignee of the basic applicants.

The basic application listed on the Patent Request is the first application made in a Convention Country in respect of the invention.

Dated 27 May 1994

John David O'Connor

IRN: 271304

INSTR CODE: 52760

[N:\LIBF]04148:GSA

AU9464523

(12) PATENT ABRIDGMENT (11) Document No. AU-B-64523/94
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 677313

(54) Title
UV-ABSORBING POLYURETHANES AND POLYESTERS

International Patent Classification(s)
(51)[5] **C08G 018/32** **C07C 225/16** **C07D 249/18** **C08G 063/16**

(21) Application No. : **64523/94** (22) Application Date : **03.06.94**

(30) Priority Data

(31) Number	(32) Date	(33) Country
073227	**04.06.93**	**US UNITED STATES OF AMERICA**

(43) Publication Date : **08.12.94**

(44) Publication Date of Accepted Application : **17.04.97**

(71) Applicant(s)
CIBA-GEIGY AG

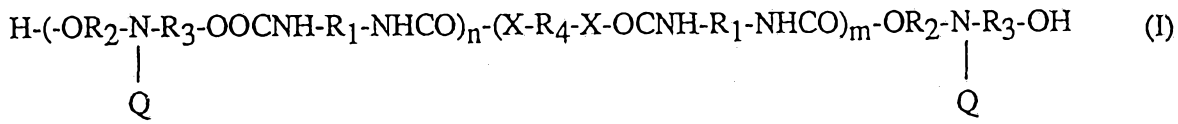
(72) Inventor(s)
JULIANA RODGERS; ISTVAN BORSODY; ATHANASIOS KARYDAS; ROBERT ALLAN FALK; KARL FRIEDRICH MUELLER; MICHELE KOVALESKI

(74) Attorney or Agent
SPRUSON & FERGUSON , GPO Box 3898, SYDNEY NSW 2001

(56) Prior Art Documents
EP 342974
US 4853471

(57) Claim

1. A polyurethane of 1,000 to 15,000 molecular weight of the formula I



(I)

wherein

n is a number from 2 to 20,

m is zero to 5,

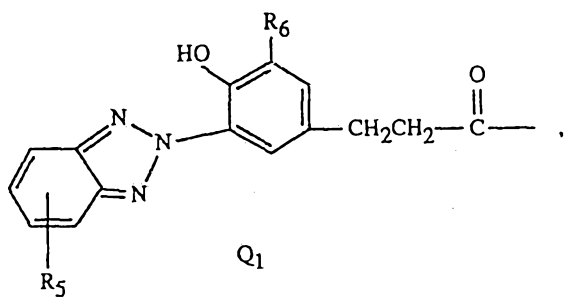
R_1 is the diradical residue of an aliphatic, cycloaliphatic or aromatic diisocyanate

R_2 and R_3 independently of each other are C_2-C_6alkylene,

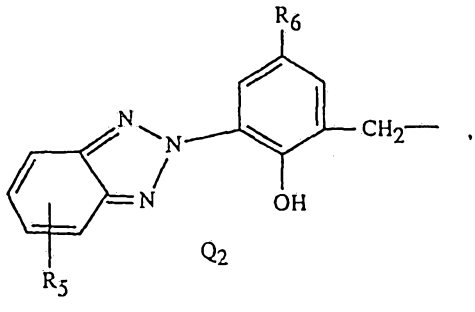
R_4 is the diradical residue of a diol or diamine of 40 to 5000 molecular weight,

X is oxygen or -NH- and

Q is a radical of the formula

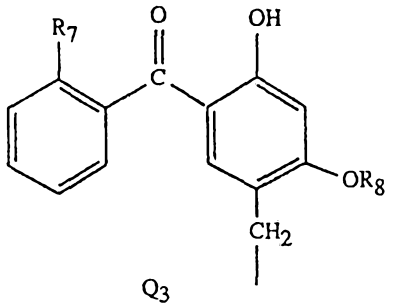


Q_1 ,



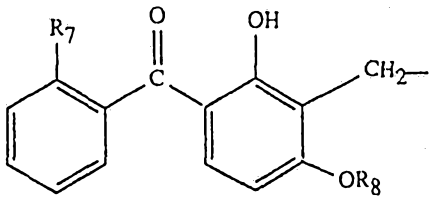
Q_2 ,

. . ./2



Q_3

or



Q_4

in which

R_5 is hydrogen, chlorine or C_1-C_4alkyl,

R_6 is C_1-C_8alkyl,

R_7 is hydrogen or hydroxyl and

R_8 is hydrogen or C_1-C_8alkyl,

with the proviso that the sum of m + n is such that the resulting polymer has an average molecular weight of 1,000 to 15,000.

CT/2-19579/A/CGC 1707

UV-absorbing polyurethanes and polyesters

Background and Prior Art

The present invention relates to protecting porous surfaces from UV degradation. More particularly it relates to novel polymeric compounds useful for this purpose, to intermediates used in their preparation and to methods of applying compositions containing the polymers to porous substrates.

Ultraviolet radiation-absorbing compounds are almost universally present in polymers used in out-door applications. Typically they are molecules of medium molecular weight with specific UV-absorbing moieties, such as benzotriazoles, and are incorporated into the bulk of thermoplastics or rubbers during compounding, extrusion or molding steps. Often they are combined with radical-scavenging molecules, like hindered amines (HALS = "hindered amine light stabilizers") or phenols.

UV absorbers can also be formulated into polymer coating systems in order to protect a substrate, but in this case their effectiveness is greatly influenced by the physical nature of the substrate. If the substrate is a hard surface, such as glass, metal or certain finished wood products, conventional UV stabilizers work quite well in protecting the coating in which they are applied and the underlying substrate. On porous substrates however, such as leather, paper or raw wood, their effectiveness is almost entirely lost because most of the active material diffuses below the surface of the substrate.

Summary of the Invention

It has now been discovered that polyurethanes and polyesters of 1,000 to 15,000 molecular weight and containing at least 5 % and up to 80 % by weight of UV-absorbing moieties can provide excellent protection against fading of dyes or degradation of the substrate, even when this substrate is highly porous.

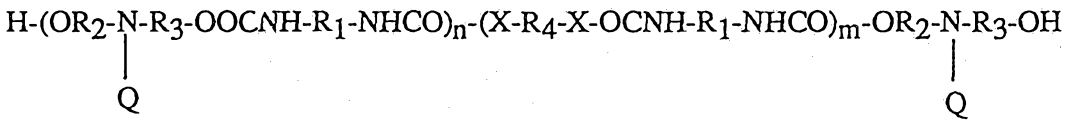
Bis-urethanes obtained by reaction of 2 equivalents of hydroxybenzotriazoles or benzophenones with 1 equivalent of a diisocyanate are described in U.S. Patents 4,061,652 and 4,179,548; as phenol-derived urethanes, they are thermally unstable and reform the UV-absorbing molecule during heat curing.

Bis-ureas obtained from 2 equivalents of aminoalkyl-substituted hydroxybenzotriazoles and 1 equivalent of a diisocyanate are described in U.S. Patent 5,081,258; here the essential doubling of the UV-absorbing molecule's molecular weight serves to make the additive less extractible, less prone to migration and eliminates the formation of colored complexes with iron or copper.

No polyurethanes containing more than two hydroxybenzotriazole or benzophenone units are described in the literature.

Detailed Description

The polyurethanes of the present invention are of the general formula I



(I)

wherein

n is a a number from 2 to 20,

m is zero to 5,

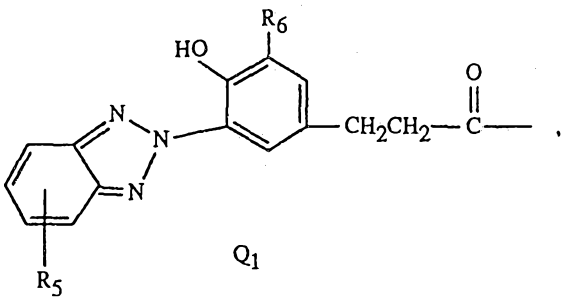
R_1 is the diradical residue of an aliphatic, cycloaliphatic or aromatic diisocyanate

R_2 and R_3 independently of each other are C_2-C_6 alkylene,

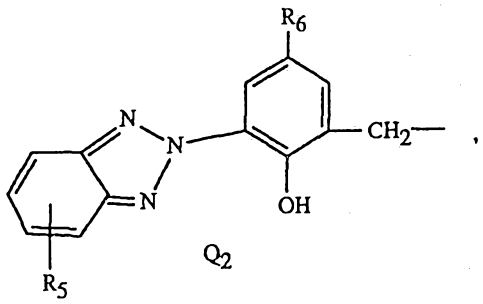
R_4 is the diradical residue of a diol or diamine of 40 to 5000 molecular weight,

X is oxygen or -NH- and

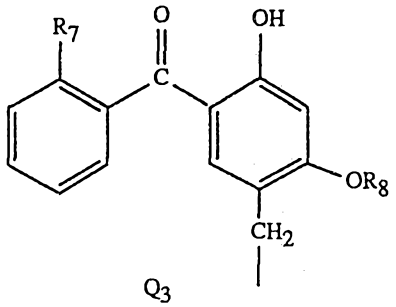
Q is a radical of the formula



Q_1

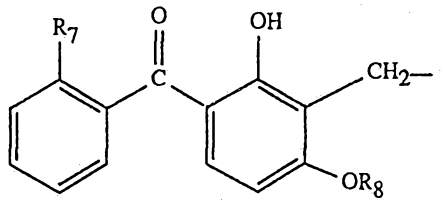


Q2



Q3

or



Q4

in which

R_5 is hydrogen, chlorine or C_1-C_4alkyl,

R_6 is C_1-C_8alkyl,

R_7 is hydrogen or hydroxyl and

R_8 is hydrogen or C_1-C_8alkyl,

with the proviso that the sum of m + n is such that the resulting polymer has an average molecular weight of 1,000 to 15,000.

The subscripts m and n refer to the average number of repeating units; a range of numbers and a correponding distribution of molecular weights is actually obtained. The number average molecular weights of the polymers may be readily determined by gel permeation chromatography.

Diisocyanates useful in preparing polymers of the formula I include 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane (= "isophorone diisocyanate"), hexane-1,6-di-isocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate, bis-(4-isocyanatocyclo-hexenyl)methane, ethylene diisocyanate, 1,2-diisocyanatopropane, 3-diisocyanatopropane, 1,2-diisocyanato-cyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatobenzene, bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatophenyl)-methane, 2,6- and 2,4-toluene diisocyanate, 3,3-dichloro-4,4'-diisocyanatobiphenyl, tris(4-isocyanato-

phenyl)methane, 1,5-diisocyanato-naphthalene, hydrogenated toluene diisocyanate, 1,3,5-tris(6-isocyanatohexyl)biuret, 2,2'-diisocyanatodiethyl fumarate, 1,5-diisocyanato-1-carboxypentane, 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- and 2,3-diisocyanatonapnthalene, 2,4- and 2,7-diisocyanato-1-methylnaphthalene, 4,4'-diisocyanatobiphenyl, 4,4'-diisocyanato-3,3'-diisocyanato-6(7)-methylnaphthalene, 4,4'-diisocyanato-2,2'-dimethylbiphenyl bis-(4-isocyanatophenyl)ethane and bis(4-isocyanatophenyl) ether. All are commercially available.

One preferred group of polymers of formula I are those wherein
R_1 is the diradical residue of a diisocyanate selected from the group above and
m is zero.

Preferred diisocyanates include 1-isocyanato-methyl-5-isocyanato-1,3,3-trimethylcyclohexane (="isophorone diisocyanate"), hexane-1,6-diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanatocyclohexenyl)methane.

Preferred are polymers of formula I wherein
m is zero
n is 2 to 10,
R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanatocyclohexenyl)methane,
R_2 and R_3 are ethylene,
Q is Q_1,
R_5 is hyrogen and
R_6 is tertiary butyl.

Also preferred are polymers of formula I wherein
m is zero
n is 2 to 10,
R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanatocyclohexenyl)methane,
R_2 and R_3 are ethylene,

Q is Q_2,
R_5 is hyrogen and
R_6 is tertiary butyl.

Also preferred are polymers of formula I wherein
m is zero
n is 2 to 10,
R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-di-isocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanato-cyclohexenyl)methane,
R_2 and R_3 are ethylene,
Q is Q_3 or Q_4,
R_7 is hydrogen and
R_8 is methyl.

Another preferred group of polymers of formula I are those wherein
m is 1 or more and
R_4 is the diradical residue of a poly-(C_2-C_4alkyleneoxide), a poly-(dimethylsiloxane)--α,ω-dialkylene of 500 to 3000 molecular weight or a tertiary nitrogen-containing diol residue of 40 to 500 molecular weight.

Within this group, especially preferred are polymers of formula I wherein
m is greater than 1,
n is 2 to 5,
R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-di-isocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanato-cyclohexenyl)methane,
R_2 and R_3 are ethylene,
Q is Q_1,
R_4 is a poly-(tetramethyleneoxide) or a tertiary nitrogen-containing diol residue of 40 to 500 molecular weight,
R_5 is hyrogen and
R_6 is tert-butyl.

Also preferred are polymers of formula I wherein

m is greater than 1,

n is 2 to 5,

R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-di-isocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanato-cyclohexenyl)methane,

R_2 and R_3 are ethylene,

Q is Q_2,

R_4 is a poly-(tetramethyleneoxide) or a tertiary nitrogen-containing diol residue of 40 to 500 molecular weight,

R_5 is hyrogen and

R_6 is tert-butyl.

Also preferred are polymers of formula I wherein

n is 2 to 5,

R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-di-isocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanato-cyclohexenyl)methane,

R_2 and R_3 are ethylene,

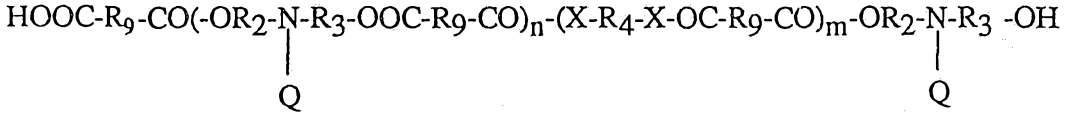
Q is Q_3 or Q_4,

R_4 is a poly-(tetramethyleneoxide) or a tertiary nitrogen-containing diol residue of 40 to 500 molecular weight,

R_7 is hydrogen and

R_8 is methyl.

The polyesters of the present invention are of the general formula II



(II)

wherein

n is a number from 2 to 20,

m is zero to 5,

R_9 is the diradical residue of an aliphatic, cycloaliphatic or aromatic di- or tetra-

carboxylic acid with structure HOOC-R_9-COOH,

R_2 and R_3 independently of each other are C_2-C_6alkylene,

R_4 is the diradical residue of a diol or diamine of 40 to 5000 molecular weight,

X is oxygen or -NH- and

Q is one of the structures Q_1, Q_2, Q_3, or Q_4 as described above,

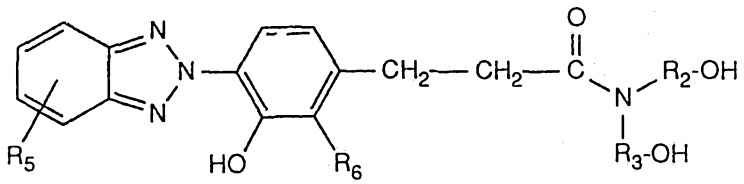
with the proviso that the sum of m + n is such that the resulting polymer has an average molecular weight of 1,000 to 15,000.

As with the polyurethanes, m and n refer to average values.

Preferred di- and tetracarboxylic acids HOOC-R_9-COOH, and reactive derivatives thereof for the preparation of polyesters of the formula II include succinic acid, maleic acid, itaconic acid and phthalic acid as well their corresponding anhydrides, acid chlorides and C_1- C_4-alkyl esters; glutaric and adipic acid, isophthalic and terephthalic acid and their corresponding acid chlorides and C_1-C_4-alkyl esters; also useful are dianhydrides like benzophenone-tetracarboxylic acid dianhydride and pyromellitic dianhydride.

Most preferably, R_9 is the diradical residue of succinic, maleic or adipic acid. Preferred dianhydrides are pyromellitic and benzophenone-tetracarboxylic acid dianhydrides.

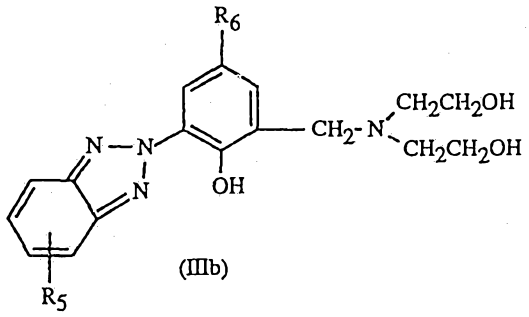
Diols useful in preparing polymers of the formula I or II containing the UV-absorbing benzotriazole moiety Q_1 are of the structure IIIa:



in which

R_2, R_3, R_4, R_5 and R_6 are as described above. Such compounds are described in U.S.patent 4,853,471.

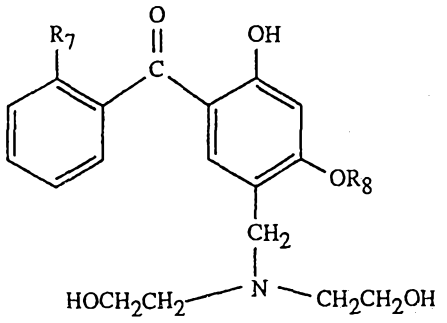
Diols with moieties Q_2 are of the structure IIIb:



(IIIb)

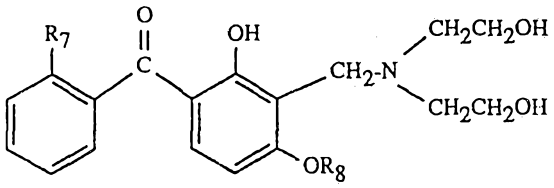
in which R_5 and R_6 are as described above.

Diols containing the benzophenone moieties Q_3 or Q_4 are of the formula IIIc or IIId:



or

(IIIc)



(IIId)

in which R_7 and R_8 are as described above.

The novel intermediates of formulae IIIb, IIIc and IIId are a further object of this invention.

Preferred chain-extending diols and diamines of the structure $HX\text{-}R_4\text{-}XH$ include branched or linear C_3-C_{10}alkyl diols and diamines; tertiary nitrogen-containing diols of 40

to 500 molecular weight like N-methyl-diethanolamine, N-phenyl-diethanolamine, N-toloyl-diethanolamine, N,N'-dihydroxyethyl-piperazine, N,N'-dihydroxypropyl-piperazine, N-C_2-C_{20}-alkyl di(hydroxyethyl)- and di(hydroxy-polyethoxyethyl)-amines; N-methyl-bis(3-aminopropyl)amine; ether-diols like diethyleneglycol and tetraethyleneglycol; di-secondary amines like N,N'-dimethyl-1,3-propanediamine; polyester-diols of 500 to 3000 molecular weight made from saturated or unsaturated dicarboxylic acids and C_2-C_{10}alkylene diols; poly-(alkyleneoxide) diols and diamines, wherein alkylene denotes a branched or linear alkylene group with 2 - 4 carbon atoms; or poly-(dimethylsiloxane)-α,ω-dialkanols or -dialkylene amines of 500 to 3000 molecular weight.

Typical chain-extending poly-(C_2-C_4alkyleneoxide)-moieties are derived from poly-(ethyleneoxide)diol, poly-(propyleneoxide)diol, poly-(tetramethyleneoxide)diols, or poly-(ethyleneoxide)-α,ω-dialkyleneamine and poly-(tetramethyleneoxide)-α,ω-dialkyleneamines, or from ethyleneoxide-propyleneoxide block copolymer diols and diamines; chain-extending polysiloxanes are poly-(dimethylsiloxane)-α,ω-dialkanols, wherein the alkanol group is an aliphatic hydrocarbon group with 3 to 6 carbon atoms and poly-(dimethylsiloxane)-α,ω-dialkyleneamines, wherein the alkyl group is an aliphatic hydrocarbon group with 3 to 6 carbon atoms.

Synthesis

The first step in the synthesis of the inventive polyurethanes and polyesters consists in making the UV-absorbing diol precursor. A benzotriazole-diol of structure IIIa can be made, for instance, from a benzotriazole-ester by transamidification with a dialkanolamine as described in detail in the examples. The reaction can be carried out in bulk or, preferably, in a solvent. Useful solvents include toluene, xylene, high boiling ketones like methyl isobutyl ketone and ethers like ethyleneglycol dimethylether. Benzotriazole-diols of structure IIIb and benzophenone-diols of structure IIIc and IIId can be made by the Mannich reaction, that is aminoalkylation with formaldehyde and diethanolamine, as illustrated in the examples.

Polyurethanes of formula I are subsequently synthesized by reaction of a diol of the formula IIIa, IIIb, IIIc or IIId with a diisocyanate and, optionally, another chain-extending diol or diamine component, using known methods of polyurethane synthesis. The reaction is preferably carried out using a diluting solvent like 2-butanone, xylene, toluene,

ethyleneglycol dimethylether, or a mixture thereof. Useful catalysts include dibutyltin dilaurate, stannous octoate, sodium methoxide or tertiary amines like triethylamine. If the polyurethane of formula I contains no water-solubilizing groups, its solution is then emulsified in water, using a nonionic, anionic or cationic surfactant or a mixture thereof, and the organic solvent is stripped off. The examples describe the process in detail. If the polyurethane contains a sufficient number of polyethylene oxide groups or tertiary amino groups, the polymer may be soluble or dispersible in water at neutral or acidic pH.

Suitable anionic surfactants can be either so-called water-soluble soaps or water-soluble synthetic surface-active ingredients.

Soaps are the alkali metal, alkaline earth metal or substituted or unsubstituted ammonium salts of higher fatty acids (C_{10}-C_{22}), for example the sodium or potassium salts of oleic or stearic acid, or of naturally occurring fatty acid mixtures, which can be obtained, for example, from coconut oil or tallow oil. The fatty acid methyltaurine salts may furthermore also be mentioned.

More often, however, so-called synthetic surfactants are used, in particular fatty alcohol sulfonates, fatty alcohol sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates.

The fatty alcohol sulfonates or sulfates are as a rule in the form of alkali metal, alkaline earth metal or substituted or unsubstituted ammonium salts and contain an alkyl radical having 8 to 22 C atoms, alkyl also including the alkyl moiety of acyl radicals, for example the sodium or calcium salt of ligninsulfonic acid, of dodecylsulfate or of a fatty alcohol sulfate mixture prepared from naturally occurring fatty acids. These also include the salts of sulfuric acid esters and sulfonic acids of fatty alcohol-ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and a fatty acid radical having 8-22 C atoms. Alkylarylsulfonates are, for example, the Na, Ca or triethanolamine salts of dodecylbenzenesulfonic acid, dibutylnaphthalenesulfonic acid or a naphthalenesulfonic acid-formaldehyde condensation product.

Corresponding phosphates, for example salts of the phosphoric acid ester of a p-nonylphenol-(4-14)-ethylene oxide adduct, or phospholipids are furthermore also suitable.

Nonionic surfactants are in particular polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, which can contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols.

Other suitable nonionic surfactants are the water-soluble polyethylene oxide adducts containing 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups, with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol having 1 to 10 carbon atoms in the alkyl chain. The compounds mentioned usually contain 1 to 5 ethylene glycol units per propylene glycol unit.

Examples of nonionic surfactants are nonylphenol polyethoxyethanols, castor oil polyglycol ether, polypropylene-polyethylene oxide adducts, tributylphenoxy-polyethoxy-ethanol, polyethylene glycol and octylphenoxypolyethoxyethanol.

Fatty acid esters of polyoxyethylenesorbitan, such as polyoxyethylenesorbitan trioleate, are furthermore also suitable.

The cationic surfactants are in particular quaternary ammonium salts which contain at least one alkyl radical having 8 to 22 C atoms as the N-substituent and lowerhalogenated or unhalogenated alkyl, benzyl or lower hydroxyalkyl radicals as further substituents. The salts are preferably in the form of halides, methylsulfates or ethylsulfates, for example stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

The optimum amount of surfactant to employ can be determined by routine experimentation.

These surfactants are described, inter alia, in the following publications:

- "McCutcheon's Detergents and Emulsifiers Annual", MC Publishing Corp., Glen Rock, New Jersey, 1988.
- M. and J. Ash, "Encyclopedia of Surfactants", Vol.I-III, Chemical Publishing Co., New York, 1980-1981.
- Dr. Helmut Stache "Tensid-Taschenbuch" (Surfactant Handbook), Carler Hanser Verlag,

The polyesters of formula II are synthesized by any of the known methods of polycondensation, for example by melt condensation from the UV-absorber diols with di-acids or anhydrides, by transesterification with the lower-alkyl esters of dicarboxylic acids or by reaction with diacid chlorides. If dianhydrides are used, the free carboxylic acid groups allow dispersability of the polymer at basic pH. Otherwise they may be dispersed using the same surfactants as the polyurethanes.

Application

The UV-absorbing polyurethanes and polyesters of the present invention, in the form of emulsions or solutions, can be applied to a substrate by various means. If the substrate is leather, the polymer can be applied by a batch exhaustion method, but preferably it is applied to one surface only by spraying. For textiles a padding operation can be used and for paper, addition to wet pulp; but here also, surface application by a spraying or a coating process is preferable. It is possible to mix the inventive UV-absorbing polymers with other finishing agents for paper, leather or textiles, especially filmforming polymers and oil and water repellent fluorochemical polymers. After application the substrate is dried, preferably at a temperature above 50° C.

The UV-absorbing polymers of the present invention can function to protect a substrate itself, or to protect dyes with which the substrate has been colored, or other finishes which have been applied to the substrate. Preferably the substrate is porous.

The following non-limiting examples illustrate various aspects of the invention. Examples 1 and 2 show the synthesis of benzotriazole-diols.

Example 1

2-[Bis(2-hydroxyethyl)amino]carbonyl ethyl)phenyl]-benzotriazole.

2-[2'-Hydroxy-3'-t-butyl-5'-(2-methoxycarbonyl ethyl)phenyl]-benzotriazole (BTZ) (1000 g, 2.83 mol) and diethanolamine (446.18 g, 4.24 mol) are placed in a one-liter jacketed reactor equipped with nitrogen inlet and stirrer. The mixture is blanketed with nitrogen and heated until it melts into a black liquid, and then stirred at 130° C. The reaction's progress is monitored by gas chromatography and is complete after 8 hours. The reaction mixture is then cooled to 65° C where it turns to a green-yellow solid mass.

Two liters of methanol are added and the solid sample turns into a black slurry. The slurry is taken from the reactor and placed in a 4 liter beaker equipped with a mechanical stirrer. The excess diethanolamine is removed by adding 140 g AMBERLYST-15 ion exchange resin (from Rohm and Haas Co.)and stirring for 15 minutes. The resin is removed by vacuum filtration. The removal of diethanolamine from the sample is monitored by gas chromatography. Finally the methanol is stripped off on a vacuum rotary evaporator and a light tan powder is isolated, which is 2-[bis(2-hydroxy ethyl)amino]carbonyl ethyl)phenyl]benzotriazole, or BTZ-diol of the formula IIIa. GC/MS results indicate a purity of 94%, the remainder being unreacted starting material (BTZ). The equivalent weight of the product was found to be 228, compared to a theoretical value of 215.

Example 2

2-(2-Hydroxy-3-(bis(2-hydroxyethyl)aminomethyl-5-methylphenyl)-2H-benzotriazole.

2-(2-Hydroxy-5-methylphenyl)-2H-benzotriazole (25.0 g, 0.11 mol), diethanolamine (17.5 g, 0.167 mol) and paraformaldehyde (5.7 ,0.189 mol) are dissolved in 37 ml of n-butanol. The mixture is heated with agitation at reflux (95 to 100° C) for 16 hours. Since thin layer chromatography (TLC) indicated the reaction was incomplete, it was heated an additional 24 hours at which time TLC indicated complete reaction. The solvent is then removed by vacuum distillation to give a viscous liquid product in high yield. This Mannich base is identified as the above-named compound by ^{1}H-NMR.

Example 3

3(5)-Diethanolaminomethyl-2-hydroxy-4-methoxy-benzophenone.

To a one liter 3-necked flask equipped with condenser, stirring shaft and dropping funnel fitted with a gas inlet tube are added 2-hydroxy-4-methoxybenzophenone (150.0 g, 0.66 mol), formaldehyde (116.3 g, 37.4 % solution in water) and 225 ml ethylene glycol dimethyl ether. Diethanolamine (139.0 g, 1.32 mol) is charged to the dropping funnel and dripped into the reaction vessel with agitation over a period of 10 minutes. Following this addition, the reaction mixture is heated to 80° C and held at this temperature for 16 hours with stirring and introducing a stream of nitrogen gas. After this time, the formation of product is confirmed by thin layer chromatography, using toluene as the mobile phase. The mixture is cooled and poured into a 3-l Erlenmeyer flask; 1.5 l water are added and

the mixture is cooled in an ice bath. The product oils out and the water layer is decanted. The oil is washed once more with 200 ml of water. The oil is dissolved in toluene and the water-toluene azeotrope mixture is distilled off. The remaining solvent is removed in vacuo and 140 g (96 % of theory) of the product is obtained in form of a viscous yellow liquid. ^{1}H- NMR shows that the product is a mixture of compounds IIIc and IIId in molar ratios of approximately 1:1 (BPO-diol). The equivalent weight of the product was found to be 166 compared to a theoretical value of 173.

Example 4

Synthesis of a BTZ-diol-polyurethane.

First 70 g (0.1535 mol) of the diol of Example 1 and 130 g of 2-butanone (MEK) are placed into a flask equipped with stirrer, nitrogen inlet and a thermo-regulator. The mixture is heated to 105° C under nitrogen and approximately 20 % of the 2-butanone is distilled off to remove any water. The reaction mixture is then cooled to 80° C and 22.03 g (0.134 mol) of hexamethylene diisocyanate (HDI) are added together with 0.42 g (0.00067 mol) of dibutyltin dilaurate and 32 g of 2-butanone. The reaction mixture is stirred at 80° C for two hours, after which time the reaction is complete as determined by IR-spectroscopy.

The product is a 40 % solution in MEK of a polyurethane containing the BTZ-diol of Example 1 and HDI in a molar ratio of 8:7.

Example 5

Synthesis of a poly-ether/BTZ-diol co-polyurethane.

First 29.39 g (0.01527 mol) of poly-(butyleneoxide)glycol (POLYMEG 2000, from Quaker Oats Chemical Company) and 44.1 g of 2-butanone (MEK) are placed into a flask equipped with stirrer, nitrogen inlet and a thermo-regulator and heated to 80° C. Then 5.01 g (0.0306 mol) of hexamethylene diisocyanate (HDI) are added along with 7.8 g of 2-butanone and 0.09 g (0.00014 mol) dibutyltin dilaurate. The mixture is stirred for 45 min. at 80° C and is monitored by NCO titration. After the NCO-value has dropped to approximately one half of its original value - indicative of an isocyanate capped poly-(butyleneoxide) glycol prepolymer - 2.5 g (0.0153 mole) of HDI are added along

with 13.97 g (0.0305 mol) of the diol of Example 1. The mixture is heated for an hour following this addition, after which time the reaction is complete, as determined by IR-spectroscopy.

The product is a 40% solution in MEK of a polyurethane, containing the BTZ-diol of Example 1, poly-(butyleneoxide) glycol and HDI in mole ratios 2:1:3.

Examples 6 - 9

Following the procedure of Example 4, the polyurethanes listed in the following table are synthesized as 40 % solutions in 2-butanone.

Example Nr.	Mol Ratio BTZ-diol/HDI
6	3 / 2
7	4 / 5
8	5 / 4
9	6 / 5.

Examples 10 - 13

Example 8 is repeated using the diisocyanates listed below to make 40% solutions in MEK of polyurethanes containing the BTZ-diol of Example 1 and the diisocyanate in a mol ratio of 5/4.

Example Nr.	Diisocyanate
10	isophorone diisocyanate, MW: 222
11	3,3,4(4,3,3)-trimethylhexane-1,6-diisocyanate, MW: 213
12	DIMER ACID diisocyanate (General Mills Co.), MW: 594
13	4,4'-diisocyanato-diphenylmethane; MW: 258.

Example 14

Synthesis of a cationic BTZ-diol-co-polyurethane.

First 100 g (0.25 mol) of the BZT-diol of Example 1 and 30 g of toluene are added to a 1-liter jacketed reactor equipped with a nitrogen sparge, condenser and stirrer. The mixture is stirred at 110° C until it becomes a clear amber liquid; then cooled to 72° C and 120 g 2-butanone (MEK) are added. To the slightly hazy amber liquid 34.6 g (0.201 mol) of hexamethylene diisocyanate (HDI) are added along with 51.9 g of MEK and 0.27 g (0.015 mol) of dibutyltin dilaurate catalyst. The mixture is stirred at 72° C for 45 minutes; then 6.85 g (0.0575 mol) of N-methyldiethanolamine (NMDA) are added along with 10.3 g of 2-butanone and the mixture is kept at 60° C for 15 minutes. The reaction is complete as determined by IR spectroscopy.

The product is a 40 % polyurethane solution in toluene and 2-butanone. It contains the BTZ-diol of Example 1, HDI and NMDA in a mol ratio of a 6:7:2.

Upon drying, a clear, hard, brown polymer is obtained which is dispersible in aqueous acetic acid solution.

Example 15

First 100 g (0.25 mol) of the diol of Example 1, 250 g of 2-butanone (MEK) and 30 g of xylene are placed into a flask equipped with a stirrer, nitrogen inlet and a thermo-regulator. The mixture is heated to reflux under nitrogen and, after dissolution of the diol, 64.9 g (0.375 mol) of hexamethylene diisocyanate (HDI) is added, followed by 22.35 g (0.187 moles) of N-methyldiethanolamine (NMDA). The mixture is kept at reflux

for five hours, after which time no free isocyanate can be detected by IR.

The product is a 40 % solution in MEK of a polyurethane containing the BTZ-diol of Example 1, HDI, and NMDA in a mol ratio of 1.3:2:1.

The polymer solution dries to a very hard, glossy, brown film, which is soluble in dilute acetic acid.

Example 16

Synthesis of a BPO-diol-polyurethane.

First 60 g (0.181 mol) of the BPO-diol of Example 3 and 111 g of 2-butanone (MEK) are placed into a flask equipped with stirrer, nitrogen inlet and a thermo-regulator. The mixture is heated at 105° C under nitrogen and approximately 20 % of the 2-butanone is distilled off to remove any water. The reaction mixture is then cooled to 80° C and 27.32 g (0.158 mol) of hexamethylene diisocyanate (HDI) are added together with 0.49 g of dibutyltin dilaurate and 41 g of 2-butanone. The reaction is stirred at 80° C for two hours, after which time the reaction is complete as determined by IR-spectroscopy.

The product is a 40 % MEK solution of a polyurethane containing the BPO-diol of Example 3 and HDI in a mole ratio of 8:7.

Example 17

Emulsification of an inventive polyurethane.

First 200 g of the polyurethane solution of Example 4 (46.21% solids) is added to a 400 ml beaker along with 31 g of 2-butanone. The mixture is covered to prevent the loss of solvent and stirred and heated to 65° C. This phase is the organic phase and is a clear amber liquid.

Then to a 800 ml beaker are added 1.11 g of Ethomeen S/12® (bis(2-hydroxyethyl)soy amine) and 5.91 g of Arquad 2 C/75® (dimethyldicocoammonium chloride), both from Akzo Chem. Inc. Next 370 g distilled water are added with agitation. This mixture, the aqueous phase, is also heated to 65° C, forming a cloudy liquid.

When both phases have reached 65° C, the organic phase is added gradually to the aqueous phase while stirring, forming a hazy yellow liquid. After stirring for approximately one minute, the mixture is charged to the holding vessel of a Microfluidizer® from MICROFLUIDS® Corp. The sample is passed six times through this machine at 5000-6000 psi, during which time it turns into a milky white emulsion with a slight bluish tint. This emulsion is then placed into a single-neck flask and the 2-butanone is stripped off at 60° C and 25 mm Hg vacuum on a vacuum rotary evaporator. The final solids content is 20 %.

Example 18

Using the same procedure, the polyurethane-polyether of Example 5 is emulsified to produce a 20 % aqueous emulsion.

Example 19

The BZT-diol of Example 1 is also emulsified, using the same emulsifiers and process steps as described in Example 17. This emulsion serves as a control for the application examples described below.

Example 20

The following example demonstrates the superiority of the inventive polyurethane-bound BTZ UV-absorbers (UVAs) over the monomeric BTZ-diol UV-absorber.

The BTZ-UVA emulsions prepared according to Examples 17 and 18 are spray-applied to the surface of brown aniline leather to give an add-on of 1.17g actives/ft^2. The sprayed leather is subsequently dried at 70° C for ten minutes, put into exposure frames and then subjected to UV radiation in an Atlas xenon arc WEATHER-O-METER controlled irradiation exposure system for 48 hours. The results are shown in the following Table:

Sample Emulsion of:	UVA (% of solid)	Fade resistance
Example 19 (BTZ-diol control) 40 % actives/solids	100	little
Example 17 75 % actives/solids	75	much improved
Example 18 25 % actives/solids	25	much improved

Example 21

The following example shows the performance of the inventive BTZ-UV-absorbing polyurethanes in comparison to other low-MW UV-absorbers designed for aqueous applications.

The products are spray-applied to the same leather as above for an add-on of 0.54g/ft^2 actives, put into exposure frames and exposed to various kilo-joules (KJ) of radiation in the WEATHER-O-METER. The results are measured on a gray-scale according to AATCC Test Method 16-1990. In this test a rating of 5 denotes no noticeable fading; a rating of 1 the greatest degree of color change due to fading. The results are given in the following table.

Product	Gray-Scale values after irradiation 25 KJ	75 KJ	95 KJ	150 KJ
CIBAFAST-W, a monomeric, ssufonated benzotriazole type UV-absorber (water soluble)	2-3	2	1-2	-
a monomeric watersoluble HALS UV absorber	2	1-2	1	-
Polymer emulsion of example 17	4-5; 5	3-4	3	2-3
untreated control	-	1-2	-	1

Example 22

Synthesis of a UV-absorbing polyester.

First 50 g (0.104 moles) of the benzotriazole-diol of Example 1 and 13.03 g (0.132 moles) of succinic anhydride are placed in a 250 ml reaction flask equipped with a stirrer, nitrogen inlet tube, reflux condenser with water separator and temperature controller. Then 30 g of toluene are added and the mixture is heated to reflux. The progress of the reaction is monitored both by GC and by the amount of water collected. After 17 hours 120 g of toluene are added, resulting in a polyester solution of 30 % solids and containing the benzotriazole-diol of Example 1 and succinic anhydride in a mol ratio of 4:5.

On drying, the polymer forms a hard, clear, light brown film. The molecular weight, as determined by titration of carboxylic end groups, is 3850.

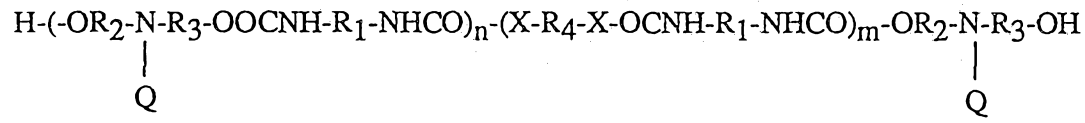
Example 23

The polyester product of Example 22 is emulsified according to Example 17 and spray-applied to the surface of brown aniline leather to give an add-on of 1.17g actives/ft^2. The sprayed leather is subsequently dried at 70° C for ten minutes, put into exposure frames and then subjected to UV radiation in an Atlas xenon arc WEATHER-O-METER controlled irradiation exposure system for 48 hours. Excellent resistance to fading is observed.

~~WHAT IS CLAIMED IS:~~

The claims defining the invention are as follows:

1. A polyurethane of 1,000 to 15,000 molecular weight of the formula I



(I)

wherein

n is a number from 2 to 20,

m is zero to 5,

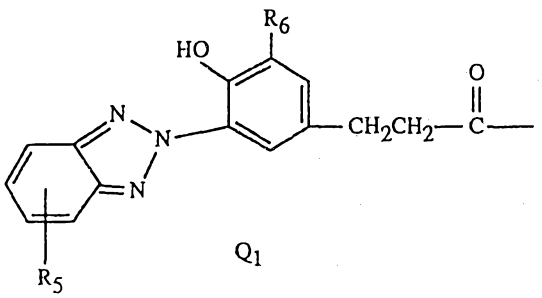
R_1 is the diradical residue of an aliphatic, cycloaliphatic or aromatic diisocyanate

R_2 and R_3 independently of each other are C_2-C_6alkylene,

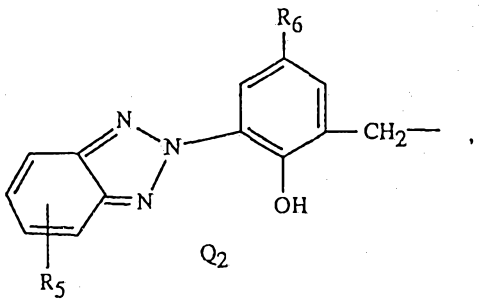
R_4 is the diradical residue of a diol or diamine of 40 to 5000 molecular weight,

X is oxygen or -NH- and

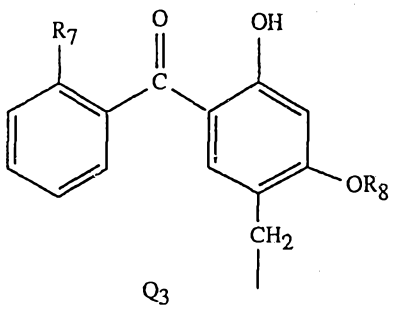
Q is a radical of the formula



Q_1

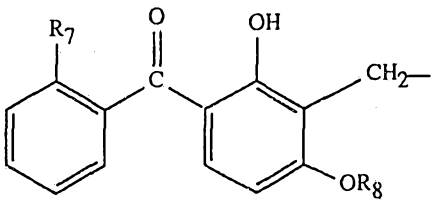


Q_2



Q_3

or



Q_4

in which

R_5 is hydrogen, chlorine or C_1-C_4alkyl,

R_6 is C_1-C_8alkyl,

R_7 is hydrogen or hydroxyl and

R_8 is hydrogen or C_1-C_8alkyl,

with the proviso that the sum of m + n is such that the resulting polymer has an average molecular weight of 1,000 to 15,000.

2. A polyurethane of the formula I according to claim 1, wherein

R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate, bis-(4-isocyanatocyclohexenyl)methane, ethylene diisocyanate, 1,2-diisocyanato-propane, 3-diisocyanatopropane, 1,2-diisocyanato-cyclohexane, 1,3-diisocyanato-cyclohexane, 1,4-diisocyanatobenzene, bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatophenyl)methane, 2,6- and 2,4-toluene diisocyanate, 3,3-dichloro-4,4'-diisocyanatobiphenyl, tris(4-isocyanatophenyl)methane, 1,5-diisocyanato-naphthalene, hydrogenated toluene diisocyanate, 1,3,5-tris(6- isocyanatohexyl)-biuret, 2,2'-diisocyanatodiethyl fumarate, 1,5-diisocyanato-1-carboxypentane, 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- and 2,3-diisocyanatonaphthalene, 2,4- and 2,7-di-isocyanato-1-methylnaphthalene, 4,4'-diisocyanatobiphenyl, 4,4'-diisocyanato-3,3'-diisocyanato-6(7)-methylnaphthalene; 4,4'-diisocyanato-2,2'-dimethyl biphenyl, bis-(4-isocyanatophenyl)ethane and bis(4-isocyanatophenyl)ether.

3. A polyurethane of the formula I according to claim 1 or 2, wherein m is zero.

4. A polyurethane of the formula I according to one of the claims 1 to 3, wherein

n is 2 to 10,

R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-di-isocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanato-cyclohexenyl)methane,

R_2 and R_3 are ethylene,

Q is Q_1,

R_5 is hyrogen and

R_6 is tertiary butyl.

5. A polyurethane of the formula I according to one of the claims 1 to 3, wherein

n is 2 to 10,

R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanatocyclohexenyl)methane,

R_2 and R_3 are ethylene,

Q is Q_2,

R_5 is hyrogen and

R_6 is tertiary butyl.

6. A polyurethane of the formula I according to one of claims 1 to 3, wherein

n is 2 to 10,

R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanatocyclohexenyl)methane,

R_2 and R_3 are ethylene,

Q is Q_3 or Q_4,

R_7 is hydrogen and

R_8 is methyl.

7. A polyurethane of the formula I according to claim 1, wherein

m is 1 or more and

R_4 is the diradical residue of a poly-(C_2-C_4alkyleneoxide), a poly-(dimethylsiloxane)-α,ω-dialkylene of 500 to 3000 molecular weight or a tertiary nitrogen-containing diol residue of 40 to 500 molecular weight.

8. A polyurethane of the formula I according to claim 7, wherein

n is 2 to 5,

R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanatocyclohexenyl)methane,

R_2 and R_3 are ethylene,

Q is Q_1,

R_4 is a poly-(tetramethyleneoxide) or a tertiary nitrogen-containing diol residue of 40 to 500 molecular weight,

R_5 is hyrogen and

R_6 is tert-butyl.

9. A polyurethane of the formula I according to claim 7, wherein

n is 2 to 5,

R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-di-isocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanato-cyclohexenyl)methane,

R_2 and R_3 are ethylene,

Q is Q_2,

R_4 is a poly-(tetramethyleneoxide) or a tertiary nitrogen-containing diol residue of 40 to 500 molecular weight,

R_5 is hyrogen and

R_6 is tert-butyl.

10. A polyurethane of the formula I according to claim 7, wherein

n is 2 to 5,

R_1 is the diradical residue of a diisocyanate selected from the group consisting of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, hexane-1,6-di-isocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and bis-(4-isocyanato-cyclohexenyl)methane,

R_2 and R_3 are ethylene,

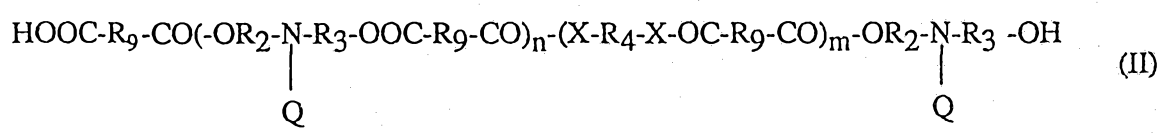
Q is Q_3 or Q_4,

R_4 is a poly-(tetramethyleneoxide) or a tertiary nitrogen-containing diol residue of 40 to 500 molecular weight,

R_7 is hydrogen and

R_8 is methyl.

11. A polyester of 1,000 to 15,000 molecular weight of the formula II



(II)

wherein

n is a number from 2 to 20,

m is zero to 5,

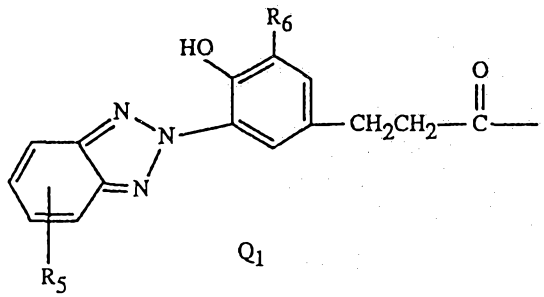
R_9 is the diradical residue of an aliphatic, cycloaliphatic or aromatic di- or tetracarboxylic acid with structure HOOC-R_9 -COOH,

R_2 and R_3 independently of each other are C_2-C_6alkylene,

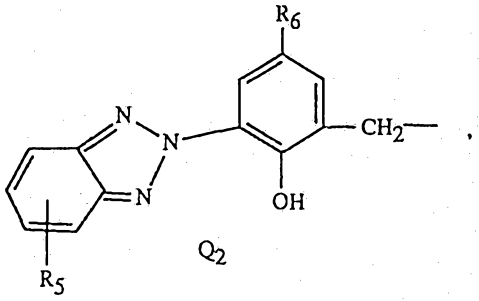
R_4 is the diradical residue of a diol or diamine of 40 to 5000 molecular weight,

X is oxygen or -NH- and

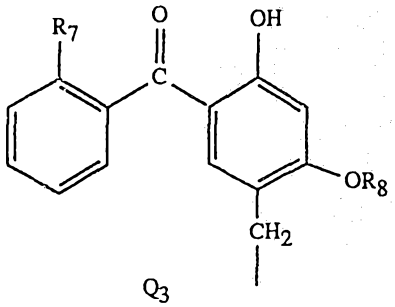
Q is a radical of the formula



Q_1 ,

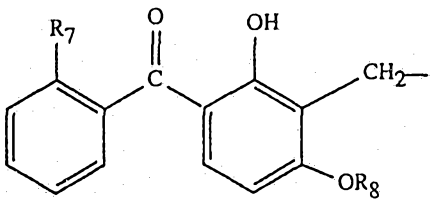


Q_2 ,



Q_3

or



Q_4

in which

R_5 is hydrogen, chlorine or C_1-C_4alkyl,

R_6 is C_1-C_8alkyl,

R_7 is hydrogen or hydroxyl and

R_8 is hydrogen or C_1-C_8alkyl,

with the proviso that the sum of m + n is such that the resulting polymer has an average molecular weight of 1,000 to 15,000.

12. A polyester of the formula II according to claim 11, wherein

R_9 is the diradical residue of a dicarboxylic acid selected from the group consisting of succinic, maleic, itaconic, phthalic, glutaric, adipic, isophthalic and terephtalic acids.

13. A polyester of the formula II according to claim 11, wherein

R_9 is the diradical residue of benzophenone-tetracarboxylic acid dianhydride or promellitic dianhydride and m is zero.

14. A polyester of the formula II according to claim 12, wherein R_9 is the diradical residue of succinic, maleic or adipic acid and m is zero.

15. A composition for protecting a substrate from degradation by UV radiation, which comprises a polyurethane of the formula I according to claim 1 dissolved or suspended in a liquid.

16. A method of protecting a substrate from degradation by UV radiation, which comprises applying to at least one surface of said substrate a composition according to claim 15.

17. A method according to claim 16, wherein the substrate is leather, paper, raw wood or a textile material.

18. A composition for protecting a substrate from degradation by UV radiation, which comprises a polyester of the formula II according to claim 11 dissolved or suspended in a liquid.

19. A method of protecting a substrate from degradation by UV radiation, which comprises applying to at least one surface of said substrate a composition according to claim 18.

20. A method according to claim 19, wherein the substrate is leather, paper, raw wood or a textile material.

21. A polyurethane of 1,000 to 15,000 molecular weight substantially as hereinbefore described with reference to any one of the Examples.

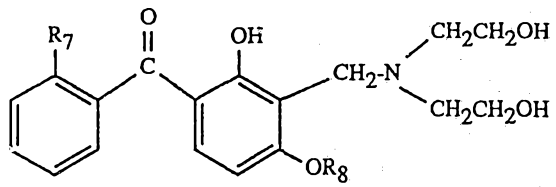
22. A polyester of 1,000 to 15,000 molecular weight substantially as hereinbefore described with reference to any one of the Examples.

23. A benzotriazol-2-yl-6-{[bis(2-hydroxyethyl)-amino]-methyl}-phenol derivative substantially as hereinbefore described with reference to any one of the Examples.

24. A {5-[bis-(2-hydroxyethylamino)-methyl]-hydroxyphenyl}-phenylmethanone derivative substantially as hereinbefore described with reference to any one of the Examples.

Dated 4 February, 1997
Ciba-Geigy AG
Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

AUSTRALIAN PATENT OFFICE



(IIId)

in which

R_7 is hydrogen or hydroxyl and

R_8 is hydrogen or C_1-C_8alkyl.

17. A compound of the formula IIIc or IIId according to claim 16, wherein

R_7 is hydrogen and

R_8 is methyl.

18. A composition for protecting a substrate from degradation by UV radiation, which comprises a polyurethane of the formula I according to claim 1 dissolved or suspended in a liquid.

19. A method of protecting a substrate from degradation by UV radiation, which comprises applying to at least one surface of said substrate a composition according to claim 18.

20. A method according to claim 19, wherein the substrate is leather, paper, raw wood or a textile material.

21. A composition for protecting a substrate from degradation by UV radiation, which comprises a polyester of the formula II according to claim 11 dissolved or suspended in a liquid.

22. A method of protecting a substrate from degradation by UV radiation, which comprises applying to at least one surface of said substrate a composition according to claim 21.

23. A method according to claim 22, wherein the substrate is leather, paper, raw wood or

a textile material.

24. A polyurethane of 1,000 to 15,000 molecular weight substantially as hereinbefore described with reference to any one of the Examples.

25. A polyester of 1,000 to 15,000 molecular weight substantially as hereinbefore described with reference to any one of the Examples.

26. A benzotriazol-2-yl-6-{[bis(2-hydroxyethyl)-amino]-methyl}-phenol derivative substantially as hereinbefore described with reference to any one of the Examples.

27. A {5-[bis-(2-hydroxyethylamino)-methyl]-hydroxyphenyl}-phenylmethanone derivative substantially as hereinbefore described with reference to any one of the Examples.

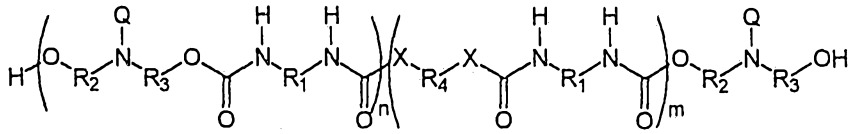
Dated 27 May, 1994
Ciba-Geigy AG

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

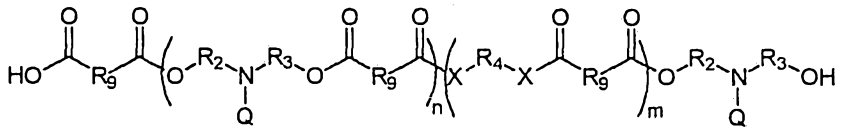
UV-Absorbing Polyurethanes and Polyesters

Abstract

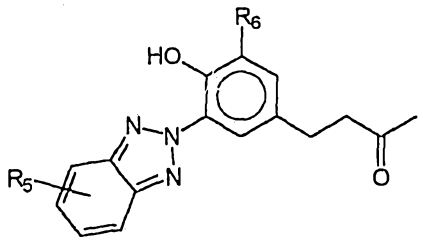
Polyurethanes and polyesters of the formulae:



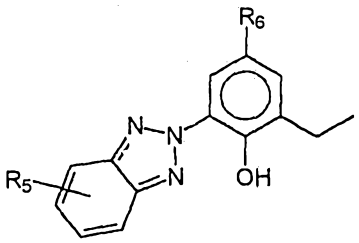
;



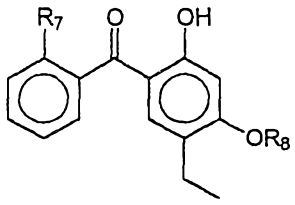
wherein n is a number from 2 to 20, m is zero to 5, R_1 is the diradical residue of an aliphatic, cycloaliphatic or aromatic diisocyanate, R_2 and R_3 independently of each other are alkylene, R_4 is the diradical residue of a diol or diamine of 40 to 5000 molecular weight, R_9 is the diradical residue of an aliphatic, cycloaliphatic or aromatic di- or terracarboxylic acid with the structure HOOC-R_9-COOH, X is O or NH and Q is a radical of the formula



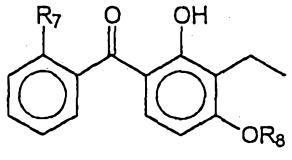
,



,



or



, in which R_5 is H, Cl or alkyl, R_6 is alkyl, R_7 is H or OH and R_8 is H or alkyl, with the proviso that the sum of m + n is such that the resulting polymer has an average molecular weight of 1000 to 15 000; are described which are the reaction products of an aromatic, aliphatic or cycloaliphatic diisocyanate, or of a diacid or diacid derivative respectively, with a diol containing a pendent UV-absorbing moiety, optionally also with one or more other diols or diamines. These UV-absorbing polycondensates can be applied to the surfaces of substrates by exhaustion methods or by spraying and act to protect polymers and dyes from degradation by UV radiation. They are therefore useful, either alone or in combination with other coating materials, for the treatment of wood, paper, textiles, leather or other surfaces which are exposed to degrading radiation.