Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2210059 C 2006/09/12
(11)(21) 2 210 059
(12) BREVET CANADIEN
CANADIAN PATENT
(13) C

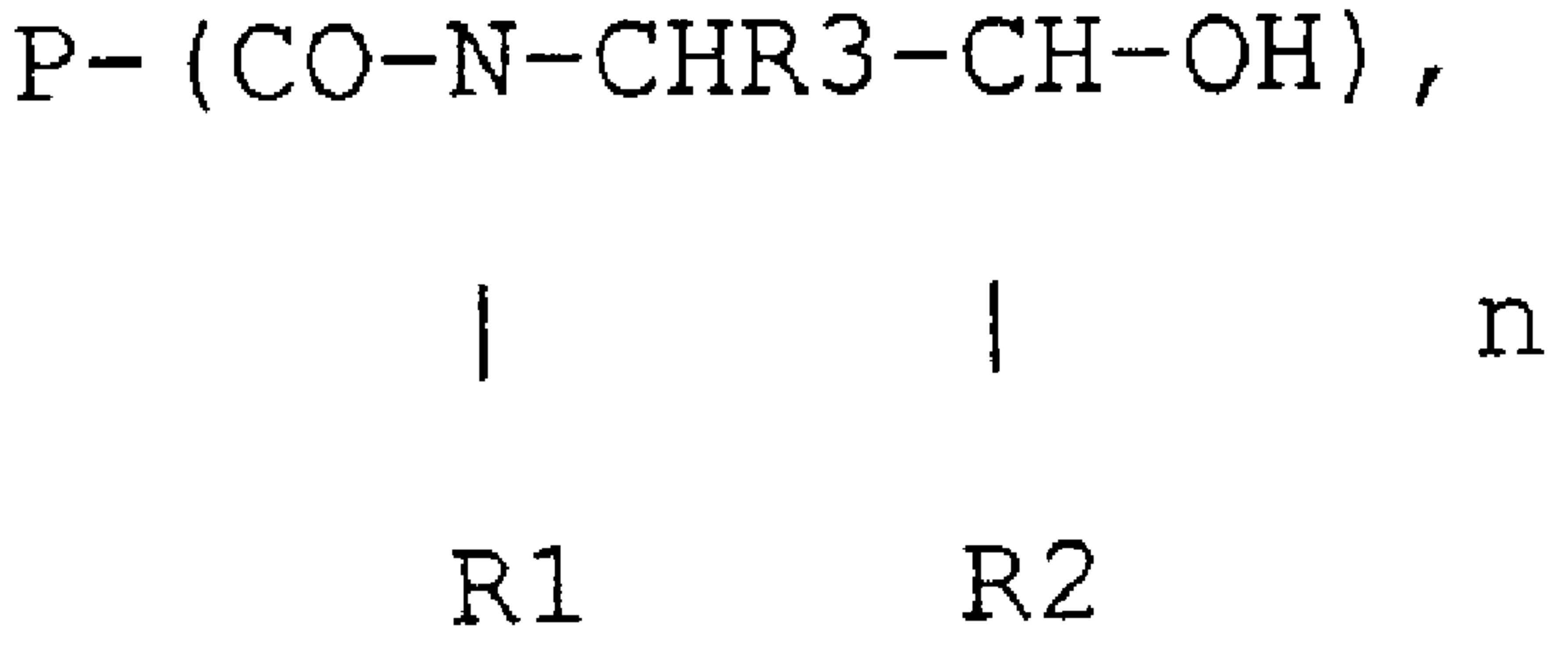
(22) **Date de dépôt/Filing Date**: 1997/07/08
(41) **Mise à la disp. pub./Open to Public Insp.**: 1998/01/12
(45) **Date de délivrance/Issue Date**: 2006/09/12
(30) **Priorités/Priorities**: 1996/07/12 (DE196 28 262.4); 1997/02/03 (DE197 03 952.9)

(51) **Cl.Int./Int.Cl.** *C08G 63/91* (2006.01), *C08G 63/685* (2006.01), *C09D 167/00* (2006.01)
(72) **Inventeurs/Inventors**:
KAPLAN, ANDREAS, CH;
GISLER, RENE, CH;
KINKELIN, EBERHARD, CH
(73) **Propriétaire/Owner**:
EMS-INVENTA AG, CH
(74) **Agent**: MCFADDEN, FINCHAM

(54) Titre : COPOLYMERES SEMI-CRISTALLISES ET/OU AMORPHES A BASE DE GROUPEMENTS β -HYDROXYALKYLAMIDE, METHODE DE FABRICATION DE CEUX-CI ET L'UTILISATIONDE L'ESTER

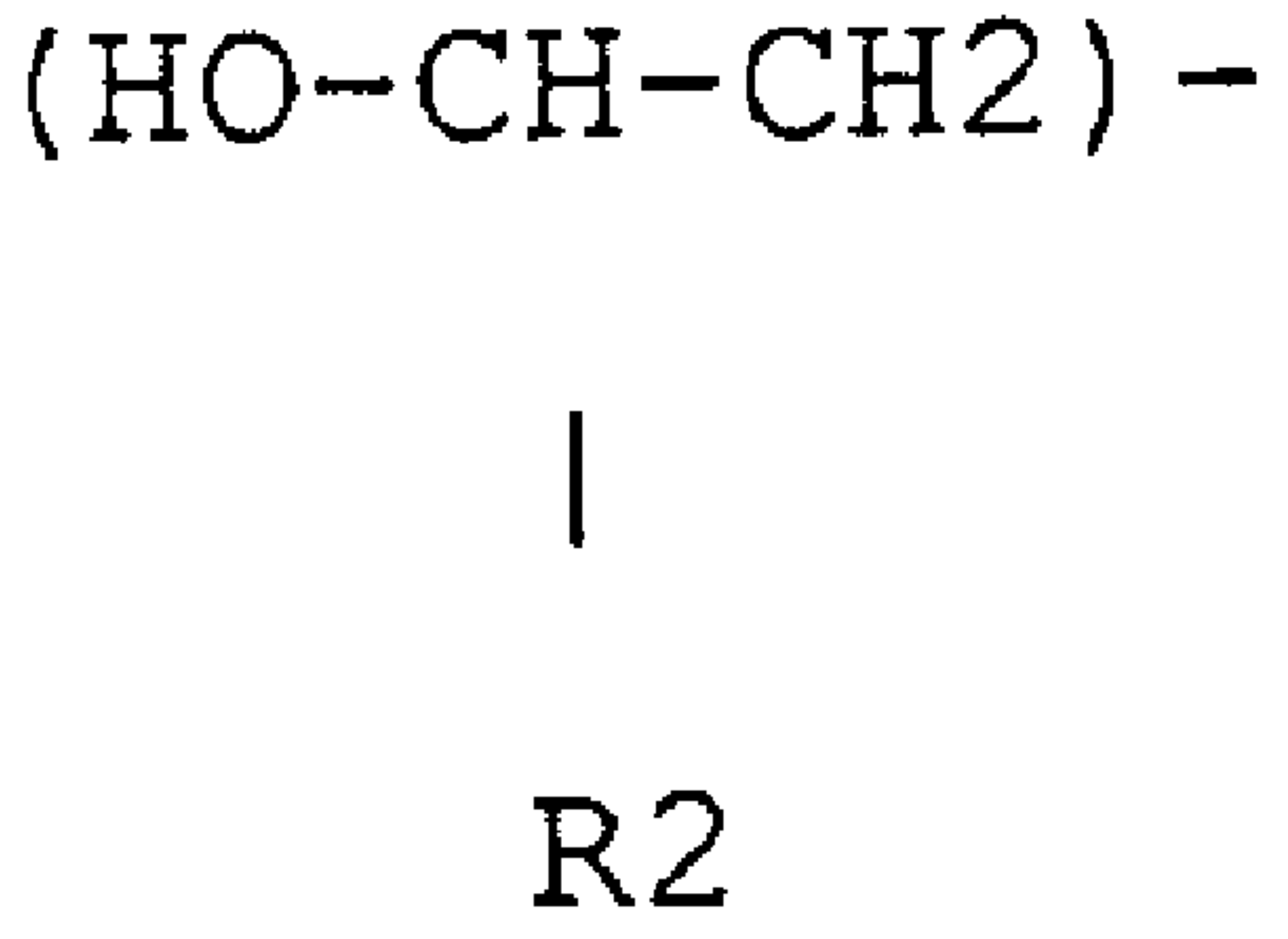
(54) Title: AMORPHOUS AND/OR SEMICRYSTALLINE COPOLYESTERS CONTAINING β-HYDROXYALKYLAMIDE GROUPS, METHOD FOR THEIR MANUFACTURE, AND UTILIZATION OF THE ESTERS

(I)



$$P\text{-}(CO\text{-}\underset{R1}{N}\text{-}CHR3\text{-}\underset{R2}{CH}\text{-}OH)_n$$

(II)



$$(HO\text{-}\underset{R2}{CH}\text{-}CH2)\text{-}$$

(57) **Abrégé/Abstract**:

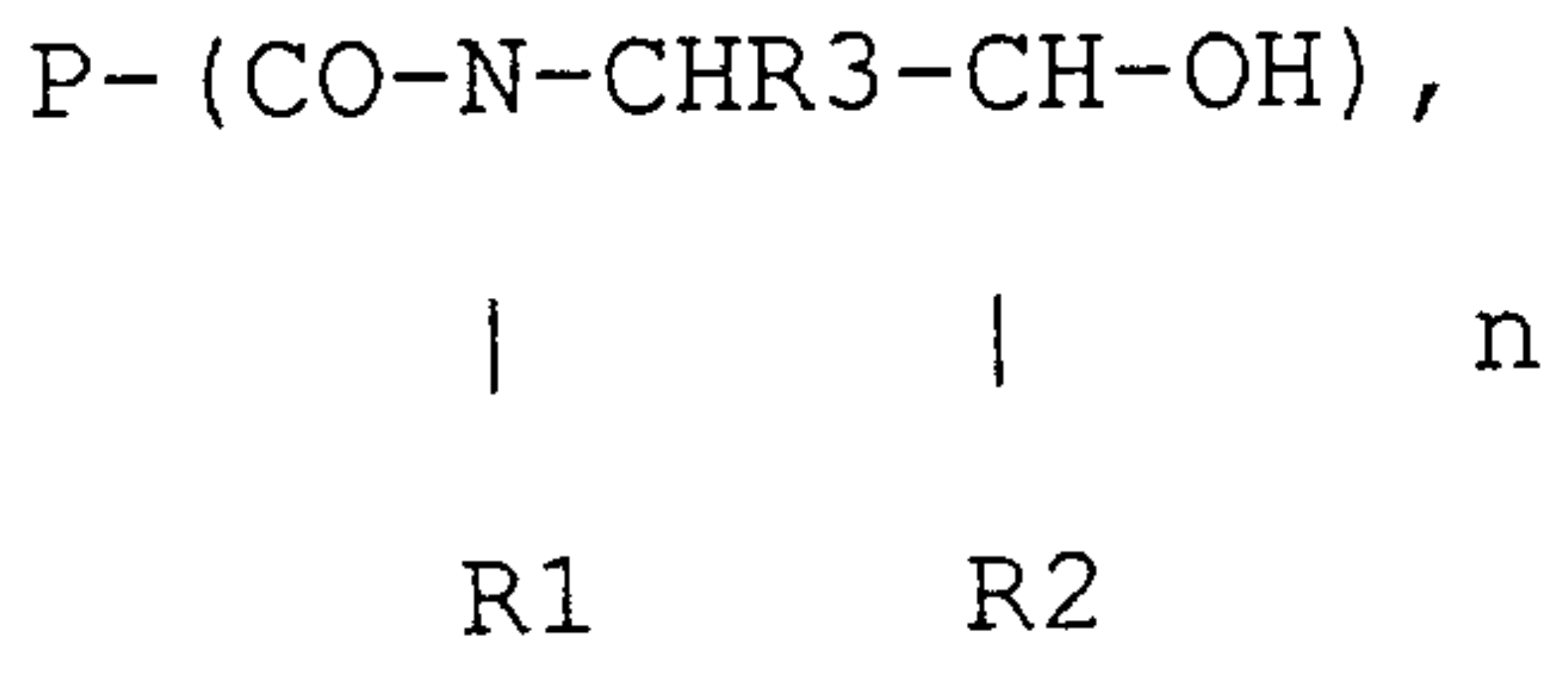
Amorphous and/or semicrystalline copolyesters containing β-hydroxyalkylamide groups according to formula (I). (see formula I) wherein P = polymer chain of the polyester R1 = alkyl residues with 1-5 C-atoms or hydrogen or (see formula II) R2 = alkyl residues with 1-5 C-atoms or hydrogen, R3 = alkyl residues and 1-5 C-atoms or hydrogen, and n ≥ 2, with a molecular weight (Mn) of 300 to 15'000 and a hydroxyl value of 10 to 400 [mg KOH/g].

Abstract

The invention relates to

Amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups according to formula (I).

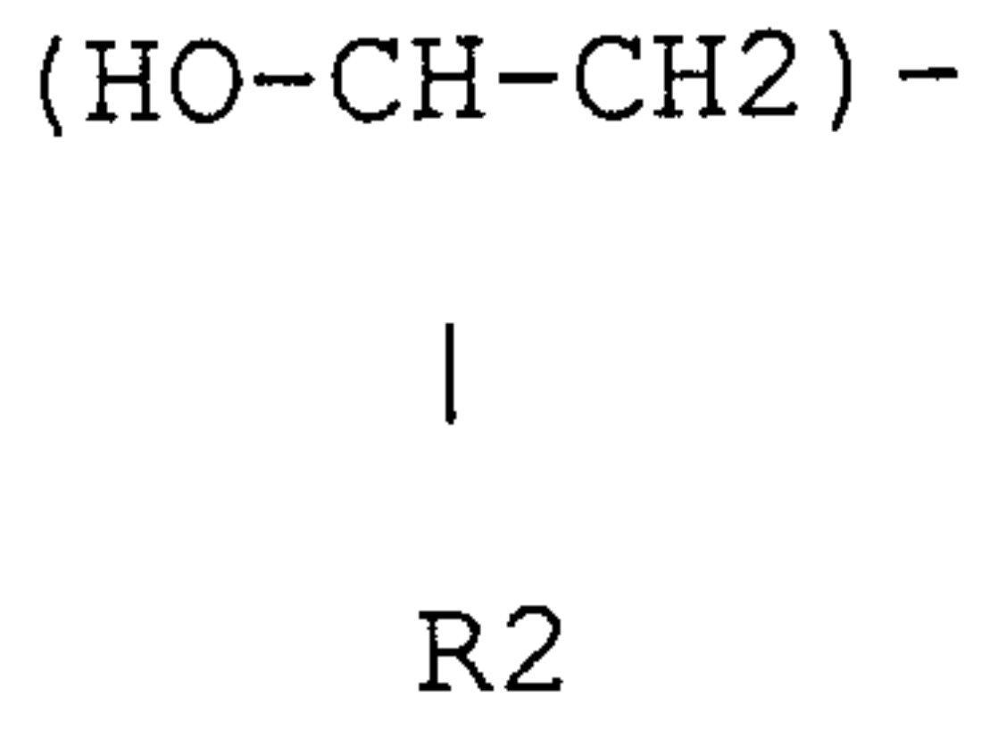
(I)



$$P\text{-}(CO\text{-}\underset{R1}{N}\text{-}CHR3\text{-}\underset{R2}{CH}\text{-}OH)_n,$$

wherein P = polymer chain of the polyester

R1 = alkyl residues with 1-5 C-atoms or hydrogen or



$$(HO\text{-}\underset{R2}{CH}\text{-}CH2)\text{-}$$

R2 = alkyl residues with 1-5 C-atoms or hydrogen,

R3 = alkyl residues and 1-5 C-atoms or hydrogen, and

$n \geq 2$,

with a molecular weight (Mn) of 300 to 15'000 and a hydroxyl value of 10 to 400 [mg KOH/g].

Amorphous and/or Semicrystalline Copolyesters containing ß-hydroxyalkylamide Groups, Method for their Manufacture, and Utilisation of the Esters.

The present invention relates to amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups, a method for manufacturing them and their use as cross-linkers in powder lacquers as well as in lacquers containing solvents and water-dilutable lacquers.

The document US 4, 076, 917 describes ß-hydroxyalkylamides as cross-linkers for carboxyl-functional polyacrylates in lacquers containing solvents and aqueous emulsions, as well as powder lacquers. The monomeric ß-hydroxyalkylamides described therein are obtained from the alkyl esters of saturated or unsaturated dicarboxylic acids by conversion with amino alcohols.

The document US 4, 801, 680 described powder lacquers containing as binders ß-hydroxyalkylamides and carboxyl-functional copolyesters. The monomoeric ß-hydroxyalkylamides described therein are likewise obtained from the alkyl esters of saturated or unsaturated dicarboxylic acids by conversion with amino alcohols.

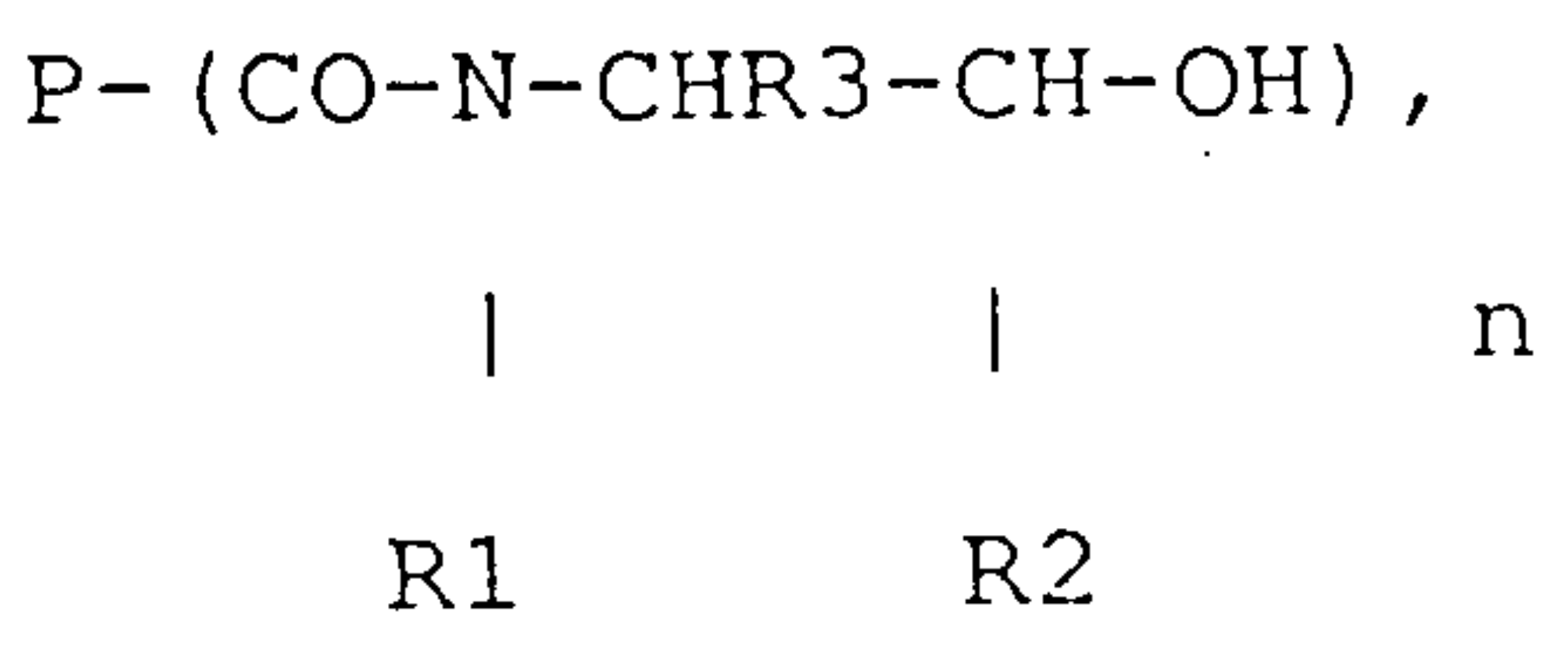
The document US 4,101,606 describes β-hydroxyalkylamide polymers as cross-linkers for polymers with a carboxyl or anhydride function in solvent-containing lacquers and aqueous emulsions as well as powder lacquers. These β-hydroxyalkylamide polymers are polyacrylates with β-hydroxyalkylamide groups, which are obtained by radical copolymerisation from β-hydroxyalkylamides with a vinyl group and further unsaturated compounds.

Amorphous and/or semicrystalline copolymers with β-hydroxyalkylamide groups were not previously known.

Proceeding from this point it is the object of the present invention to propose suitable polyesters containing β-hydroxyalkylamide groups, and a method for their manufacture.

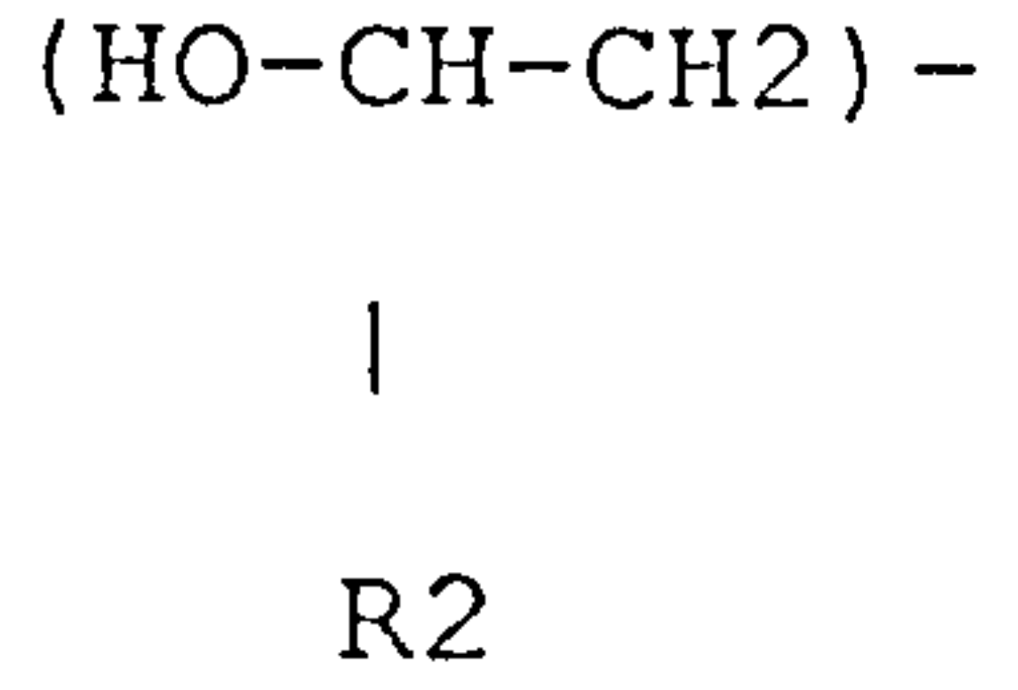
In accordance with one embodiment of the present invention there is provided amorphous and/or semicrystalline copolyesters containing β-hydroxyalkylamide groups according to formula (I)

(I)



$$P\text{-}(CO\text{-}\underset{R1}{N}\text{-}CHR3\text{-}\underset{R2}{CH}\text{-}OH)_n,$$

wherein P = polymer chain of the polyester, R1 = alkyl residues with 1-5 C-atoms or hydrogen or

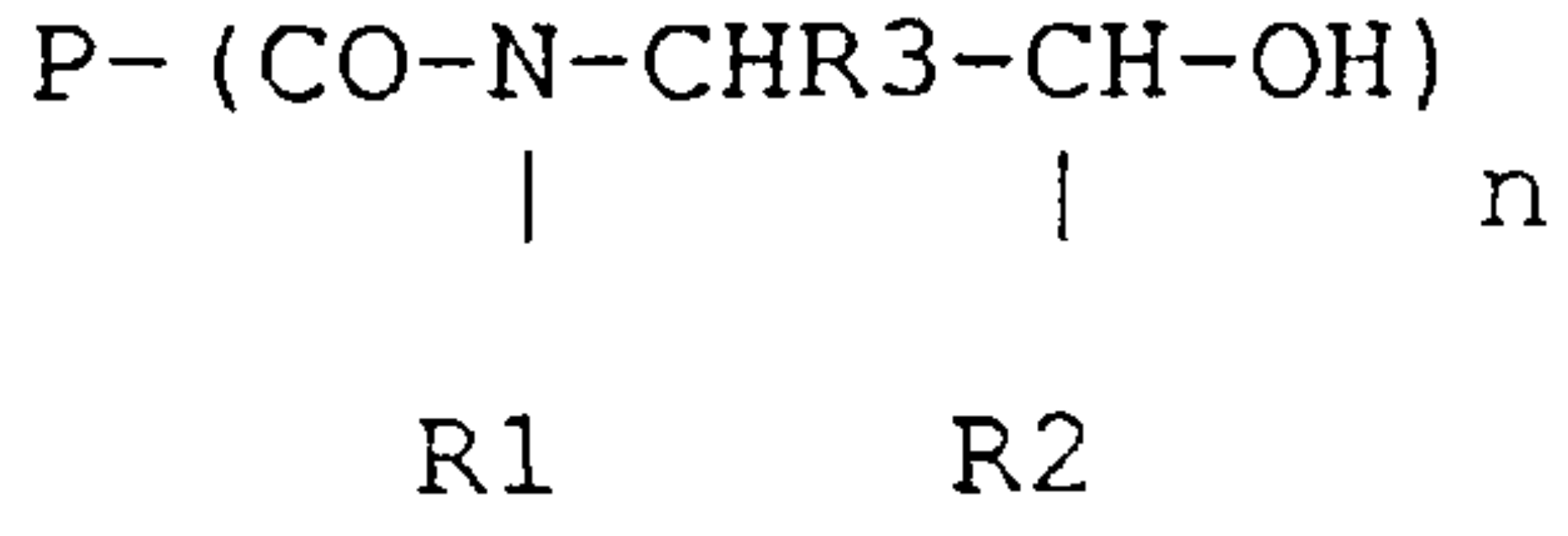


$$(\underset{\substack{|\\ R2}}{HO-CH}-CH2)-$$

R2 = alkyl residues with 1-5 C-atoms or hydrogen, R3 = alkyl residues and 1-5 C-atoms or hydrogen, and $n \geq 2$, with a molecular weight (Mn) of 300 to 15,000 and a hydroxyl value of 10 to 400 [mg KOH/g].

In accordance with another embodiment of the present invention there is provided a method of manufacturing amorphous and/or semicrystalline coplyesters containing β-hydroxyalkylamide groups, as disclosed herein above, characterized in that, in a first stage, a hydroxyl-functional amorphous and/or semicrystalline copolyester is converted with a dialkyl ester of a polycarboxylic acid in the presence of ester interchange catalyst to an amorphous and/or semicrystaline copolyester containing alkylester groups, and in a second stage the amorphous and/or semicrystalline copolyester containing alkylester groups is converted with an amino alcohol to the corresponding amorphous and/or semicrystalline copolyesters containing β-hydroxyalkylamide groups.

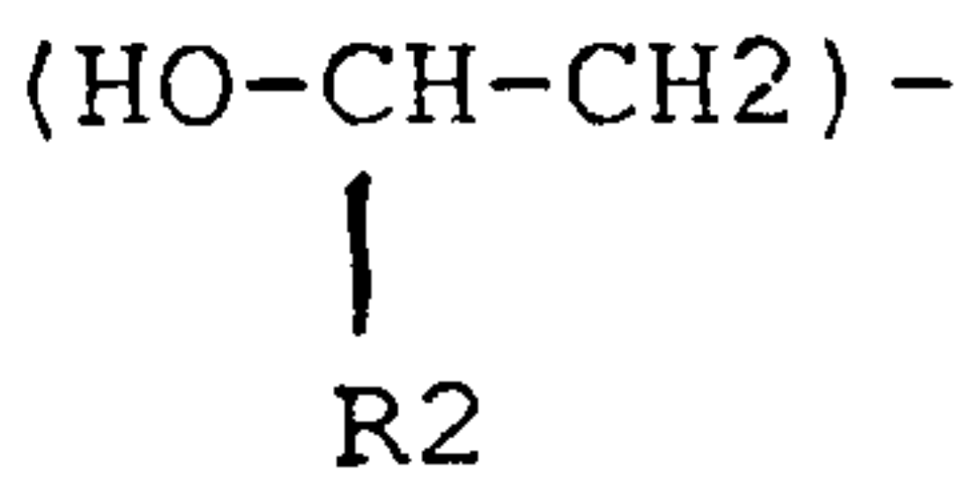
The amorphous and/or semicrystalline copolyesters containing β-hydroxyalkylamide groups correspond to Formula (I).

(I) 

$$P\text{-}(CO\text{-}\underset{R1}{N}\text{-}CHR3\text{-}\underset{R2}{CH}\text{-}OH)_n$$

P being the polymer chain of the polyester:

R1 alkyl residues with 1-5 C-Atoms or hydrogen or



$$(HO\text{-}\underset{R2}{CH}\text{-}CH2)\text{-}$$

R2 = alkyl residues with 1-5 C-atoms or hydrogen

R3 = alkyl residues with 1-5 C-atoms or hydrogen, and

n ≥ 2, preferably 2-100,

with a molecular weight (Mn) of 300 to 15'000 and a hydroxyl value of 10 to 400 [mg KOH/g].

Surprisingly, it became apparent that amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups are eminently suitable as cross-linkers for carboxyl- and/or anhydride-functional compounds, as well as those containing isocyanate, in powder lacquers and in lacquers containing solvents, and water-dilutable lacquers.

The amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups according to the invention are obtained either by conversion of carboxyl-functional amorphous and/or semicrystalline copolyesters with amino alcohols in the melt, or in solvents at temperatures of 80°C to 260°C, and if necessary in the presence of suitable catalysts, or preferably by the conversion of amorphous and/or semicrystalline copolyesters containing alkylester groups with amino alcohols, conversion being carried out either in the melt or in suitable solvents at temperatures from 80°C to 260°C, if necessary in the presence of suitable catalysts. Preferred alkylester groups are methylester groups. The following are mentioned by way of example as catalysts: sodium or potassium methylate, potassium tertiary butylate etc.; quaternary ammonium alcoholates such for example as tetraammonium methylate etc.; alkali metals; alkali hydroxides such for example as sodium or potassium hydroxide and ammonium hydroxide.

The following are named by way of example as amino alcohols : 2-aminoethanol, 2-methylaminoethanol, 2 ethylaminoethanol,2-n-propylaminoethanol, 2,2' iminodiethanol, 2-aminopropanol,2,2'-iminodiisopropanol, 2-aminocyolohexanol, 2-aminocyclopentanol, 2-aminomethyl 2-methyl-ethanol 2-n-butylaminoethanol, 2-methylamino-1,2 dimethylethanol, 2-amino-2-methyl-1-propanol, 2-amino-2 methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-hydroxymethyl-1,3-propanediol and 1-amino-2 propanol.

The amorphous and/or semicrystalline copolyesters containing alkylester groups are obtained either by the known ester-interchange methods from the alkylesters of di- or polyfunctional carboxylic acids with di- or polyfunctional alcohols in the melt or in solvents at temperatures of 80°C to 260°C in the presence of suitable catalysts, such for example as titanium tetrabutylate, or by a conversion, analogous to polymers, of hydroxyl-functional amorphous and/or semicrustalline copolyesters with the alkylesters of di- or polycarboxylic acids in the melt or in suitable solvents at temperatures of 80°C to 260°C in the presence of suitable catalysts.

Preferred alkylesters of polycarboxylic acids are dimethyl terephthalate and dimethyl adipate. The usual acidic or basic ester-interchange catalysts, such for example as titanium tetrabutylate, are suitable as catalysts.

The amorphous and/or semicrystalline hydroxy-functional copolyesters can be produced according to the condensation method known for polyesters (esterification and/or ester interchange) according to prior art. Suitable catalysts, such for example as dibutyl tin oxide or titanium tetrabutylate can also if necessary be used.

Suitable amorphous hydroxy-functional copolyster resins have a hydroxyl value of 10 - 200 [mgh KOH/g] and a glass transition temperature of >10°C. amorphous hydroxy-functional copolyesters contain as acidic components mainly aromatic multi-basic carboxylic acids such for example as terephthalic acid, isophthalic acid, phthalic acid, pyromellitic acid, trimellitic acid, 3,6-dichlorophthalic acid, tetrachlorophthalic acid and, as far as available, their anhydride, chloride or ester. The usually contain at least 50 Mol-% terephthalic acid and/or isophthalic acid, preferably 80 Mol-%. The remainder of the acids (difference from 100 Mol-%) consists of aliphatic and/or cycloaliphatic multi-basic acids such for example as 1,4-cyclohexanedicarboxylic acid, tetrahydrophthalic acid, hexahydroendomethylene terephthalic acid, hexachlorophthalic acid, azelaic acid, sebacic acid, decandicarboxylic acid, adipic acid, dodecandicarboxylic acid, succinic acid, maleic acid or dimeric fatty acids. Hydroxycarboxylic acids and/or lactones such for example as 12-hydroxystearic acid, Epsilon-Caprolacton or hydroxypivalic acid ester of neopentyl glucol, can likewise be used. Monocarboxylic acids, such for example as benzoic acid, tertiary butylbenzoic acid, hexahydrobenzoic acid and saturated aliphatic monocarboxylic acids are also used in small quantities.

The following aliphatic diols are named by way of example such for example as ethylene glycol, 1,3-propanediol, 1,2 propanediol, 1,2 butanediol, 1,3-butanediol,1,4 butanediol, 2,2-dimethylpropanediol-1,3 (neopentyl glycol),2,5-hexandiol, 1,6-hexandiol, 2,2-[bis-(4 hydroxycyclohexyl)]propane, 1,4 dimethyloloyclohexane, diethylene glycol,dipropylene glycol and 2,2-bis-[4-(2-hydroxy)]phenylpropane.

Polyols are used in small quantities, e.g. glycerol, hexanetriol, pentaeryltritol, sorbitol,trimethylolethane, trimethylolpropane and tris(2-hydroxy)isocyanurate. Epoxy compounds can also be used instead of diols or polyols. The proportion of neopentyl glycol and/or propylene glycol in the alcohol component preferably comes to at least 50 Mol-% relative to total acids.

Suitable semicrystalline polyesters have a hydroxyl value of 10 - 400 [mg KOH/g] and a precisely-defined DSC melting point. The semicrystalline polyesters are condensation products from aliphatic polyols, preferably, aliphatic diols and aliphatic and/or cycloaliphatic and/or aromatic polybasic carboxylic acids, preferably dibasic acids. The following are named by way of example as aliphatic polyols: ethylene glycol(1,2-ethanediol), propylene glycol(1,3 propanediol), butylene glycol(1,4 butanediol), 1,6 hexanediol, neopentylglycol, cyclohexanedimethanol,trimethylolpropane etc. Preferred are aliphatic diols, e.g. ethylene glycol, butylene glycol or 1,6-hexanediol.

Suitable polybasic carboxylic acids are aliphatic carboxylic acids, preferably C4-C20 dicarboxylic acids such for example as adipic acid, azelaic acid, sebacic acid, dodecandicarboxylic acid, succinic acid, undecandicarboxylic acid, and aromatic dicarboxylic acids such for example as terephthalic acid, isophtalic acid, phthalic acid and their hydrogenation products such for example as 1,4-cyclohexanedicarboxylic acid. Aliphatic dicarboxylic acids with 6 to 12 carbon atoms are preferred. Naturally, mixtures of various polyols and polybasic carboxylic acids can be used.

As hardening agents for these amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamides in thermohardening lacquers, there may be used aliphatic polybasic acids, preferably dibasic acids such for example as adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, malonic acid, succinic acid, glutaric acid, 1,12-dodecandiacid, etc. The anhydrides of these acids can likewise be used, e.g. glutaric acid anhydride, succinic acid anhydride, and the polyanhydrides of these dicarboxylic acids. These polyanhydrides are obtained by intermolecular condensation of the named aliphatic dibasic dicarboxylic acids.

Examples are adipic acid(poly)anhydride, azelaic acid(poly)anhydride, sebacic acid(poly)anhydride, dodecandiacid(poly)anhydride etc. The polyanhydrides have a molecular weight (weight average in relation to polystyrol standard) of 1000 - 5000. The polyanhydrides can also be modified with polyol.

The polyanhydrides can also be used in mixture with the aliphatic dibasic dicarboxylic acids as hardening agents, or in mixture with hydroxycarboxylic acids which have melting points between 40 and 150°C, e.g. 12-hydroxystearic acid, 2- or 3- or 10-hydroxyoctadecanic acid, 2-hydroxy-myristinic acid.

Cycloaliphatic dicarboxylic acids such for example as 1,4-cyclohexanedicarboxylic acid or its polyanhydrides can be used as hardeners.

Suitable hardeners are also amorphous and semicrystalline copolyesters.

Both the amorphous and the semicrystalline copolyesters can be produced according to the condensation method known for polyesters (esterification and/or ester interchange) according to prior art. Suitable catalysts such for example as dibutyl tin oxide or titanium tetrabutylate can if necessary also be used.

Suitable amorphous carboxyl-functional copolyester resins have an acidic value of 10 - 200 [mg KOH/g]and a glass transition temperature of >10°C. Amorphous carboxyl-functional copolyesters contain as acid components mainly aromatic polybasic carboxylic acids such for example as terephthalic acid, isophthalic acid, phtalic acid, pyromellitic acid, trimellitic acid, 3,6-dichlorophthalic acid, tetrachlorophthalic acid and, as far as available, their anhydride, choride or ester.They usually contain at least 50 Mol-% terephthalic acid and/or isophthalic acid, preferably 80 Mol-%. The remainder of the acids (difference from 100 Mol-%) consists of aliphatic and/or cycloaliphatic polybasic acids such for example as 1,4-cyclohexanedicarboxylic acid, tetrahydrophthalic acid, hexahydroendomethylenterephthalic acid, hexachlorophthalic acid, azelaic acid, sebacic acid, decandicarboxylic acid, adipic acid, dodecandicarboxylic acid, succinic acid, maleic acid or dimeric fatty acids. Hydroxycarboxylic acidsand/or lactones such for example as 12-hydroxystearic acid, Epsilon-Caprolacton or hydroxypivalic acid esters of neopentylglycol, can also be used.

Monocarboxylic acids such for example as benzoic acid, tertiary butylbenzoic acid, hexahydrobenzoic acid and saturated aliphatic monocarboxylic acids can also be used in small quantities.

The following are mentioned by way of example as suitable alcohol components: ethylene glycol, 1,3-propanediol, 1,2 propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,2 dimethylpropanediol-1,3(neopentylglycol), 2,5 hexanediol,1,6-hexanediol, 2,2-[bis-(4 hydroxycyclohexyl)]propane, 1,4 dimethylolcyclohexane,diethylene glycol, dipropylene glycol and 2,2-bis-[4-(2-hydroxy)]phenylpropane. Polyols are also used in small quantities,e.g. glycerol, hexanetriol,pentaeryltritol, sorbitol, trimethylolethane, trimethylolpropane and tris(2-hydroxy)isocyanurate. Epoxy compounds can also be used instead of diols or polyols. The proportion of neopentyl glycol and/or propylene glycol in the alcohol component preferably comes to at least 50 Mol-% relative to total acids.

Suitable semicrystalline polyesters have an acidic value of 10 - 400 [mg KOH/g] and a precisely-defined DSC melting point. The semicrystalline polyesters are condensation products from aliphatic polyols, preferably aliphatic diols,and aliphatic and/or cycloaliphatic and/or aromatic polybasic carboxylic acids, preferably dibasic acids. The following are mentioned by way of example as aliphatic polyols: ethylene glycol(1,2-ethanediol), propylene glycol(1,3propanediol), butylene glycol(1,4-butanediol), 1,6 hexanediol, neopentylglycol, cyclohexanedimethanol, trimethylolpropane etc. preferred are aliphatic diols, e.g.ethylene glycol, butylene glycol or 1,6-hexanediol.

Suitable polybasic carboxylic acids are aliphatic dicarboxylic acids, preferably C4-C20 dicarboxylic acids, such for example as adipic acid, azelaic acid, sebacic acid, dodecandicarboxylic acid, succinic acid, undecandicarboxylic acid and aromatic dicarboxylic acids such for example as terephthalic acid, isophthalic acid, phthalic acid and their hydrogenation products such for example as 1,4-cyclohexanedicarboxylic acid. Preferred are aliphatic dicarboxylic acids with 6 to 12 carbon atoms. Mixtures of various polyols and polybasic carboxylic acids can of course also be used.

Suitable carboxyl-functional acrylate polymers have an acidic value of 10 - 300 [mg KOH/g], produced by copolymerisation of a monomer mixture consisting of:

a) 0 to 70 parts by weight methyl(meth) acrylate,
b) 0 to 60 parts by weight (cyclo)alkyl esters of acrylic and/or methacrylic acid with 2 to 8 carbon atoms in the alkyl or cycloalkyl residue,
c) 0 to 90 parts by weight vinyl aromatics
d) 0 to 60 parts by weight of olefinic unsaturated carboxylic acids,

the sum of the weight proportions of the components a) to d) coming to 100.

The b) monomers are preferably (cyclo) alkyl esters of acrylic or methacrylic acid with 2 to 18 carbon atoms in the(cyclo) alkyl residue. Examples of suitable or preferably suitable b) monomers are ethyl(methyl)acrylate, n propyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate, isobutyl(meth)acrylate, tert.-butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, cyclohexylmethacrylate, neopentylmethacrylate, isobornylmethacrylate, 3,3,5-trimethylcyclohexylmethacrylate und stearylmethacrylate.

Styrol, vinyl toluol and α-ethylstyrol are considered as monomers.

Examples of d) are acrylic and methacrylic acid, which are also preferably used and also crotonic acid, itaconic acid, fumaric acid, maleic acid and citraconic acid.

The copolymerisates can be produced by copolymerisation of the a) to d) monomers named by way of example according to conventional radical polymerisation methods, such for example as solution, emulsion, pearl or mass polymerisation. The monomers are copolymerised at temperatures of 60 to 160°C, preferably 80 to 150°C, in the presence of radical formers and if necessary molecular weight chain-transfer agents.

The carboxyl-functional acrylate copolymerisates are produced in inert solvents. Suitable solvents are for example aromatics such as benzol, toluol, xylol; esters, such as ethylacetate, butylacetate, hexylacetate, , heptylacetate, methylglycolacetate, ethylglycolacetate, methoxypropylacetate; ethers, such as tetrahydrofuran, dioxan, diethyleneglycoldimethylether; ketones, such as acetone, methylethylketone, methylisobutylketone, methyl-n amylketone, methylisoamylketone or any mixtures of such solvents.

Manufacture of the copolymerisates can be carried out continuously or discontinuously. Conventionally, a monomer mixture and the initiator are metered uniformly and continuously into the polymerisation reactor, and at the same time the corresponding quantity of polymerisate is continuously removed. Thus chemically almost homogeneous copolymers can be produced. Chemically almost homogeneous copolymers can also be produced by running the reaction mixture at constant speed into a stirred-tank reactor, without removing the polymerisate.

It is also possible initially to place a proportion of the monomers, for example in solvents of the named type, and to add the remaining monomers and auxiliary agents separately or in common into this preliminary container at reaction temperature.

Polymerisation generally takes place at atmospheric pressure, but can also be carried out at pressure of up to 25 bar. The initiators are added in quantities of 0.5 to 15% by weight relative to the total quantity of monomers.

Suitable initiators are conventional radical starters such for example as aliphatic azo compounds such as azodiisobutyric acid nitrile, azo-bis-2-methylvaleronitrile,1,1′-azobis-1-cyclohexanenitrile and 2,2′-azo-bis-isobutyric acid alkyl ester; symmetrical diacyl peroxides such for example as acetyl-, propionyl- or butyryl peroxide, with bromo-, nitro-, methyl- or methoxy group-substituted benzoyl peroxides, lauryl peroxides; symmetrical peroxydicarbonates, e.g. tert.-butylperbenzoate; hydroperoxides such for example as tert.-butylhydroxyperoxide, cumenehydroxyperoxide; dialkyl peroxides such as dicumylperoxide, tert.-butylcumylperoxid or Di-tert.-butylperoxide.

In order to regulate the molecular weight of the copolymerisates, conventional chain-transfer agents can be used in production. Named by way of example are mercaptopropionic acid, tert.-dodecylmercaptane, n-dodecylmercaptane or diisopropylxanthogene disulphide. The regulators can be added in quantities from 0.1 to 10% by weight relative to the total quantity of monomers.

The solutions of copolymerisates resulting during copolymerisation can then be passed on to the evaporation of degassing stage without further processing; in these stages the solvent is for example removed in an evaporating extruder or spray drier at about 120 to 160°C and in a vacuum of from 100 to 300 mbar, and the copolymerisates to be used according to the invention are obtained.

Mixtures of various suitable hardeners can also be used.

The equivalence ratio of ß-hydroxyalkylamide to carboxylic acid equivalents lies in the range from 0.6 to 1.6:1.

Naturally the selection of hardener is not restricted to carboxyl- and anhydride-functional compounds. Possible hardeners are all compounds which react with the hydroxyl group of the amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups, such for example as compounds containing isocyanate. Examples of compounds containing isocyanates are isophorondiisocyanate and its derivatives.

For production of powder lacquers, the conventional pigments and/or fillers and/or additives may be used.

These are additives from the group of accelerators, flow and degassing agents, heat- UV- and/or HALS stabilisers and/or triboadditives and necessary delustrants such for example as waxes.

The production of powder lacquers is preferably effected in the melt by common extrusion of all components of the formulation at temperatures between 60 to 140°C. The extrudate is then cooled, ground and screened to a granular size less than 90 µm. Basically, other methods are suitable for producing powder lacquers, such for example as mixing the components of the formulation in solution with subsequent precipitation or distillative removal of the solvents.

Application of the powder lacquers according to the invention is carried out according to the method conventional for powder lacquers, e.g. by means of electrostatic spray devices (Corona or tribo), or according to the fluidised-bed principle.

For use as lacquers containing solvents, amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups, the appropriate hardeners and the conventional pigments and additives are dissolved in suitable solvents. Production is carried out according to the method normal for lacquers containing solvents.

Solvents contain aromatics such for example as toluol, xylol etc; aliphatics such e.g. as heptane, octane etc; water, dimethyl formamide, dimethyl sulphoxide, and also halogen-containing solvents, ether, esters and alcohols, depending on the solubility of the ingredients of the formulation.

Water-dilutable lacquers are produced from salts of the carboxyl-functional hardeners, e.g. amino salts such as dimethylaminoethanol, trimethylamine, triethylamine, diethanolamine, methylethanolamine or ammonium salts etc, if necessary with other suitable hardeners and the amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups, according to the usual methods with the conventional pigments and additives.

Examples of production and properties of the amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups according to the invention are given in the following.

Production of the copolyesters containing ß-hydroxyalkylamide groups

Example 1
501.8 g (4.82 Mol) of neopentyl glycol are preliminarily placed in a 2-esterification reactor provided with temperature sensor, stirrer, reflux column and distillation bridge, and melted at 140°C in a nitrogen atmosphere which is maintained during the entire reaction. 533.3 g (3.21 Mol) of isophthalic acid, 138.2 g (0.80 Mol) of cyclohexane dicarboxylic acid and 0.6 g of esterification catalyst are added to the stirred mixture. After staged increase in the internal temperature up to 235°C, the reaction is continued until no further distillate appears. Condensation is carried out under vacuum of 20 mbar until a melt viscosity of about 15 Pa*s at 160°C is attained. After blooming with nitrogen, 0.6 g ester-interchange catalyst and 186.39 g (1.07 Mol) dimethyl adipate are added. The reaction is continued under vacuum of 100 mbar until no further methanol

appears. After renewed blooming with nitrogen 80.37 g (1.07 Mol) of 1-amino-2-propanol are added. Under vacuum of 100 mbar, the reaction is continued until no further methanol appears.

The polyester obtained has an acidic value of < 2 mg KOH/g, a hydroxyl value of 60 mg KOH/g and an ICI melt viscosity at 160°C of 14 Pa*s.

The molecular weight calculated as a numerical average from the terminal group concentrations, comes to about 1700.

Example 2

533.1 g (4.51 Mol) of hexanediol are first placed in a test apparatus analogous to that in Example 1, and melted in a nitrogen atmosphere maintained during the entire reaction at 140°C. 629.3 g (2.73 Mol) of dodecandiacid and 0.6 g of esterification catalyst are added to the stirred mixture.
After staged increase in the internal temperature up to 235°C, the reaction is continued until no further distillate appears.

After blooming with nitrogen, 0.6 g ester-interchange catalyst and 620.15 g (3.56 Mol) dimethyl adipate are added.

The reaction is continued under vacuum of 100 mbar until no further methanol appears. After renewed blooming with nitrogen, 217.45 g (3.56 Mol) of 2-aminoethanol are added. The reaction is continued under vacuum of 100 mbar until no further methanol appears. The polyester obtained has an acidic value of < 2 mg KOH/g, a hydroxyl value of 199 mg KOH/g and an ICI melt viscosity at 160°C of 2 Pa*s.

The molecular weight calculated as a numerical average from the terminal group concentrations, comes to about 550.

Production of a Carboxyl-functional Copolyester

Example 3

400.3 g (3.84 Mol) of neopentyl glycol and 19.2 g (0.31 Mol)are preliminarily placed in a 2 1-esterification reactor provided with temperature sensor, stirrer, reflux column and distillation bridge, and melted at 140°C in a nitrogen atmosphere which is maintained during the entire reaction. 557.4 g (3.36 Mol) of terephthalic acid, 58.7 g (0.35 Mol) of isophthalic acid and 0.6 g of esterification catalyst are added to the stirred mixture. After staged increase in the internal temperature, the reaction is continued until no further distillate appears. Then 88.0 g (0.53 Mol) of isophthalic acid and 25.8 g (0.18 Mol) of adipic acid are added and esterised until the desired acidic value range of 30 to 36 mg KOH/g is reached. A portion of this second stage can be carried out at reduced pressure (< 100 mbar).

The polyester obtained has an acidic value of 33 mg KOH/g and an ICI melt viscosity at 160°C of 40 Pa*s.

The molecular weight calculated as a numerical average from the terminal group concentrations, comes to about 2800.

Production of a Thermohardening Lacquer

Example 4

346.5 g of the copolyester containing ß-hydroxyalkylamide groups from Example 1, 643.5 g of the carboxyl-functional copolyester from Example 3, 8 g Resiflow™ PV 88 (flow agent on polyacrylate base, commercial product of Worleè-Chemie GmbH) and 2 g benzoin are mixed dry in a Henschel mixer at 700 rpm for 30 sec., and then extruded on a Buss-Co kneader (PLK 46) at a jacket temperature of 100°C, with cooled worm conveyor and a worm rotary speed of 150 rpm. The extrudate is cooled, ground and screened to less than 90 µm.

The powder lacquers are applied electrostatically (Corona or Tribo) to aluminium plates (Q-panel AL-36 505 H 14/08 [0.8 mm]), and hardened at a firing temperature of 200°C and a firing time of 15 min. The layer thickness is 60 µm.

Table 1 shows the technical properties of the lacquer.

Example 5

Hardening Component

copolyester containing ß-hydroxyalkylamide groups from Example 2	75 g
benzoin	2 g
dimethyl sulphoxide	100 g

Resin Component

carboxyl-functional copolyester from Example 3	425 g
Resiflow PV 88 (flow agent on polyacrylate base, comm. Product of Worleè-Chemie GmbH)	8 g
Propylene glycol monomethyl ether	200 g
xylol	190 g

The hardening components and the resin component are dissolved separately at 60°C in a 3-litre stirring vessel, and mixed shortly before application.

Then a film of 200 μm is applied by a film-application apparatus to aluminium plates (Q-panel AL-36 5005 H 14/08 [0.8 mm]), and hardened at a firing temperature of 200°C and a firing time of 15 min. The layer thickness is 55 μm.

Table 1 shows the technical properties of the lacquer.

Example 6

Hardening Component

copolyester containing ß-hydroxyalkylamide groups from Example 2	75 g
benzoin	2 g
dimethyl formamide	23 g
water	100 g

Resin Component

carboxyl-functional copolyester from Example 3	425 g
2-methylaminoethanol	19 g
Resiflow PV 88 (Flow-control agent on polyacrylate base, commercial product of Worleè-Chemie GmbH)	8 g

Butyl Cellosolve	48 g
Water	200 g

The hardening components and the resin component are dissolved separately at 60°C in a 3-litre stirring vessel, and mixed shortly before application.

Then a film of 200 µm is applied by a film-application apparatus to aluminium plates (Q-panel AL-36 5005 H 14/08 [0.8 mm]), and hardened at a firing temperature of 200°C and a firing time of 15 min. The layer thickness is 55 µm.

Table 1 shows the technical properties of the lacquer.

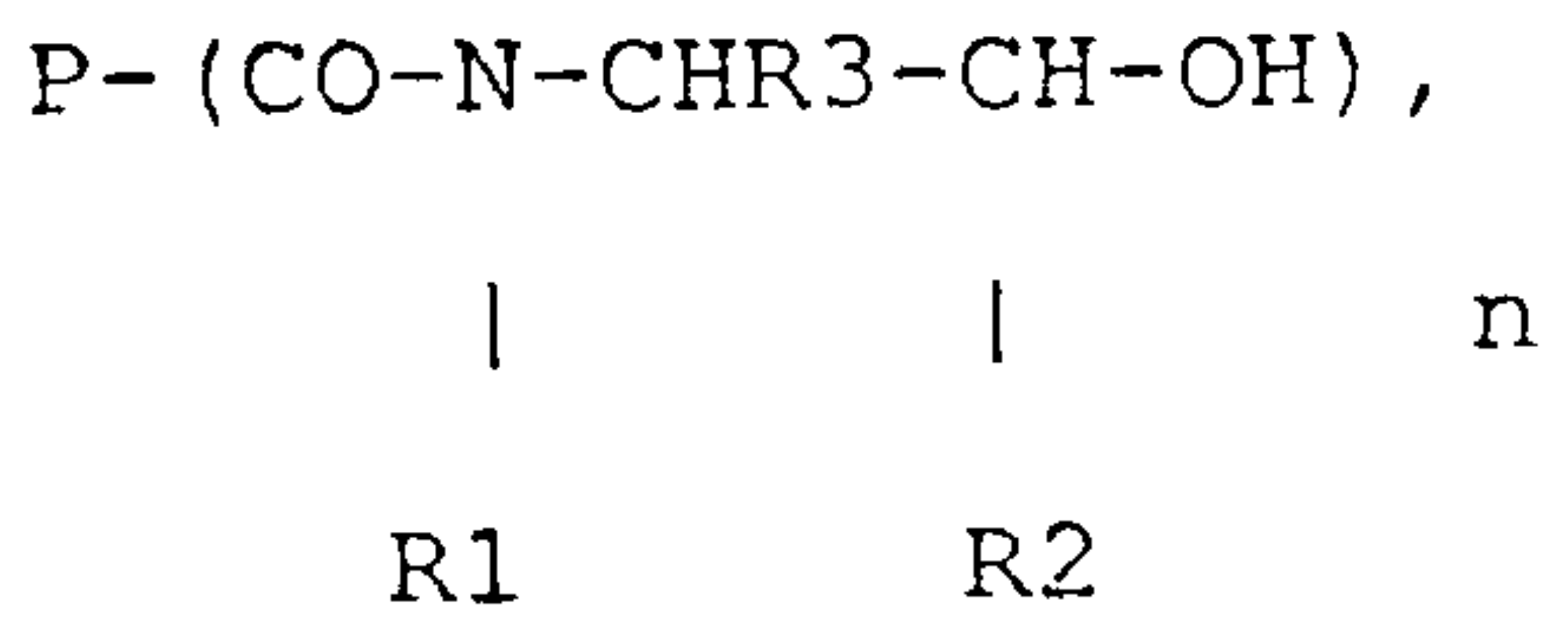
Table 1

	Ex.4	Ex.5	Ex. 6
Brilliance (60° DIN 67530)	105	104	103
Flow	very good	very good	very good
Cupping index (DIN 53156)	10	10	10
Grating section (DIN 52151)	0	0	0
Impact (ASTM D 2794, rear side)	> 160	> 160	>160

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups according to formula (I).

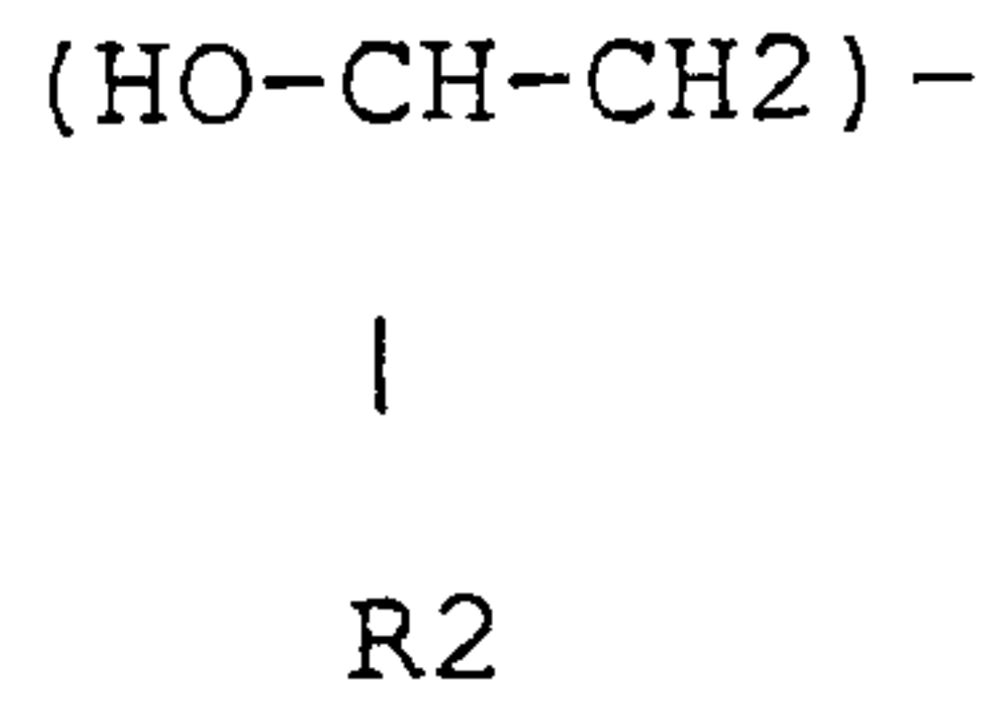
(I)



$$P\text{-}(CO\text{-}\underset{R1}{N}\text{-}CHR3\text{-}\underset{R2}{CH}\text{-}OH)_n,$$

wherein P = polymer chain of the polyester

R1 = alkyl residues with 1-5 C-atoms or hydrogen or



$$(HO\text{-}\underset{R2}{CH}\text{-}CH2)\text{-}$$

R2 = alkyl residues with 1-5 C-atoms or hydrogen,

R3 = alkyl residues and 1-5 C-atoms or hydrogen, and

$n \geq 2$,

with a molecular weight (Mn) of 300 to 15'000 and a hydroxyl value of 10 to 400 [mg KOH/g].

2. Method of manufacturing amorphous and/or semicrystalline copolyesters containing ß-hydroxyalkylamide groups according to claim 1,

characterised in that, in a first stage, a hydroxyl-functional amorphous and/or semicrystalline copolyester is converted with a dialkyl ester of a polycarboxylic acid in the presence of ester interchange catalyst to an amorphous and/or semicrystalline copolyester containing alkylester groups, and in a second stage the amorphous and/or semicrystalline copolyester containing alkylester groups is converted with an amino alcohol to the corresponding amorphous and/or semicrystalline copolyesters containing β-hydroxyalkylamide groups.

3. Method according to claim 2, characterised in that the hydroxyl value of the amorphous hydroxy-functional copolyester lies between 10 and 200 [mg KOH/g], and the glass transition temperature is > 10°C.

4. Method according to claim 2, characterised in that the amino alcohols are selected from the group 2-aminoethanol, 2-methylaminoethanol, 2 ethylaminoethanol, 2-n-propylaminoethanol, 2,2' iminodiethanol, 2-aminopropanol, 2,2'-iminodiisopropanol, 2-aminocyclohexanol, 2-aminocyclopentanol, 2-aminomethyl-2-methylethanol, 2-n-butylaminoethanol, 2-methylamino-1,2 dimethylethanol, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-hydroxy-methyl-

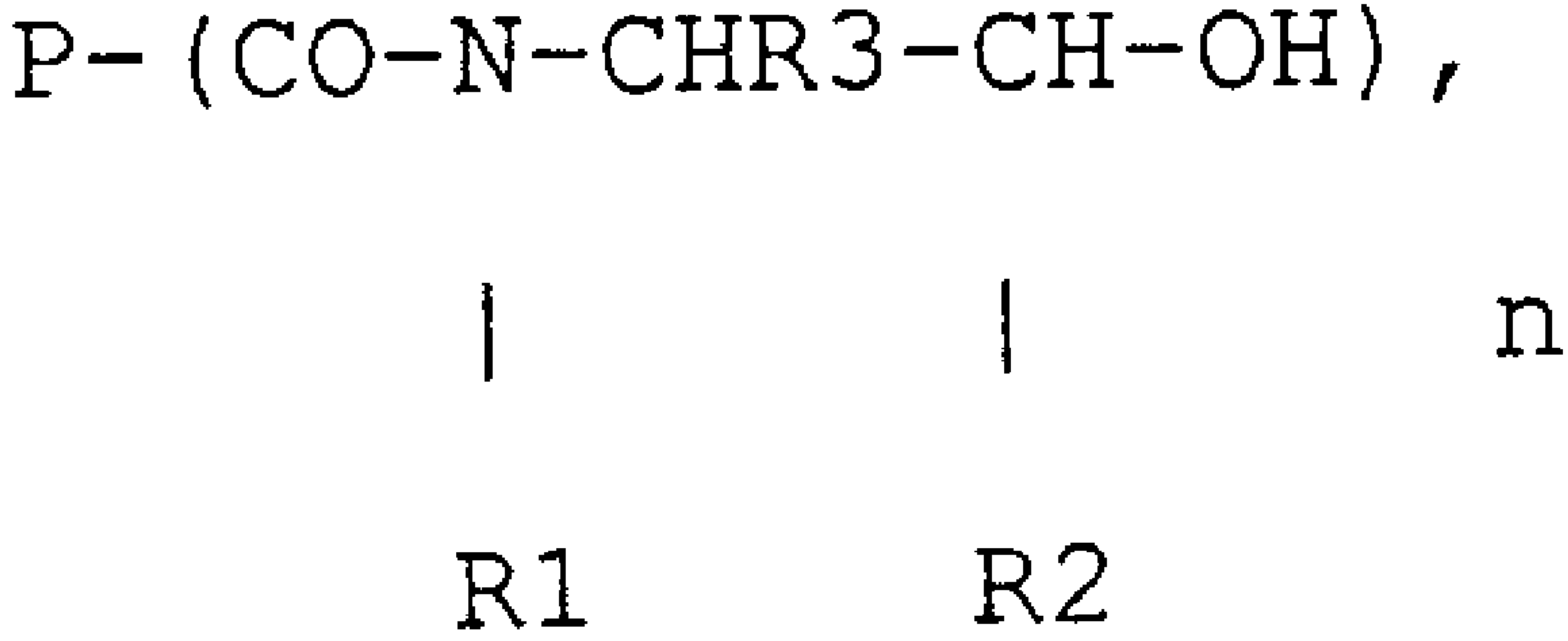
1,3-propanediol and 1-amino-2 propanol.

5. Method according to claim 2, characterised in that conversion of the amorphous and/or semicrystalline copolyester containing alkylester groups is carried out with an amino alcohol in the presence of catalysts selected from the group sodium or potassium methylate, potassium tertiary butylate; quaternary ammonium alcoholates; alkali metals, alkali hydroxides, and ammonium hydroxides.

6. Method according to claim 2, characterised in that the hydroxyl-functional amorphous and/or semicrystalline copolyesters are converted with dimethyladipate and/or dimethylterephthalate into the corresponding amorphous and/or semicrystalline copolyesters containing methylester groups.

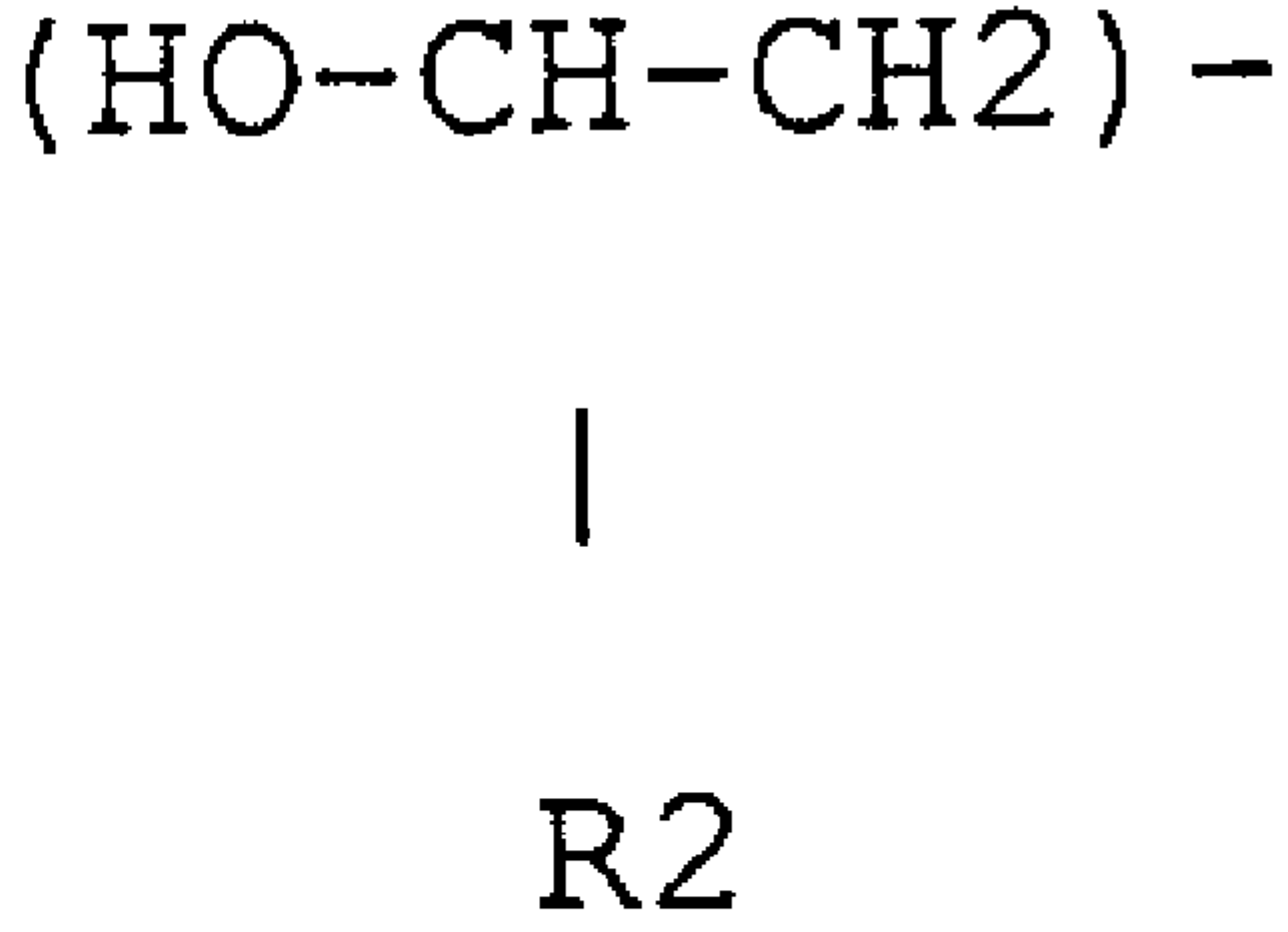
7. Utilisation of amorphous and/or semicrystalline copolyesters containing β-hydroxyalkylamide groups according to claim 1 as cross-linkers for carboxyl- or anhydride-functional compounds, containing isocyanate, in powder lacquers, lacquers containing solvents, and water-dilutable lacquers.

(I)



$$P-(CO-\underset{R1}{N}-CHR3-\underset{R2}{CH}-OH)_{n},$$

(II)



$$(HO-\underset{R2}{CH}-CH2)-$$